Coordination Chemistry Reviews, 98 (1990) 123–250
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

2. COBALT

Catherine E. Housecroft

CONTENTS

INTRODUCTION

This survey of cobalt coordination chemistry follows, approximately, the format of the previous article [1], and covers the literature for 1984. It is based on a data search of Volumes 100 and 101 of Chemical Abstracts, although *Journal of the American Chemical Society, Inorganic Chemistry,* and *Journal of the Chemical*

0010-8545/90/$44.80

Society (Dalton Transactions, and Chemical Communications) have been searched independently for the period from January to the end of December 1984. Due to unforeseen circumstances, a review covering the 1985 literature has already appeared [2]!

The present review does not cover multinuclear cobalt cluster compounds, cobaltaboranes nor cobaltacarboranes, nor does it attempt to explore organometallic compounds involving cobalt.

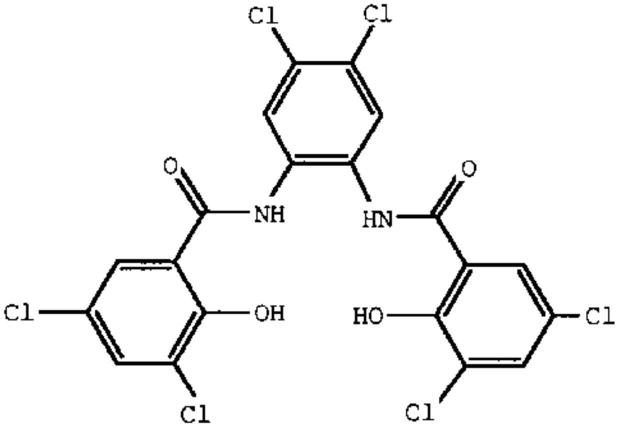
Some pertinent review articles to which the reader may wish to refer deal with substitution reactions in inert metal complexes of coordination number ≥6 (122 references) [3], the preparations of Co(III) complexes by chemical modification methods (21 references) [4], and the use of h.p.l.c. for the analysis of cobalt(II) and cobalt(III) complexes, using ion pair reversed phase silica or alumina columns [5]. Other reviews, specific to individual sections below, will be referred to in context.

2.1 COBALT(IV)

The results of a study of the cobalt(II) catalysed reduction of $[Ru(bipy)_3]^{3+}$ in aqueous solution comply with the following rate equation.

$$\rho = k[Ru(III)]^2[Co(II)]/[Ru(II)][H^+]^2$$

The involvement of a Co(IV) intermediate during oxygen formation is implied [6].



(1)

Multianionic chelates have been used to stablise cobalt in a high oxidation state; for the ligand, H_4L, (1), reaction with $[Co(O_2CMe)_2]$ in thf/EtOH, followed by treatment with excess NaOH and 4-^{t}butyl pyridine, py', leads to the formation of the complex $Na[CoL(py')_2]$ in 95% yield. Oxidation of this complex gives the neutral $[CoL(py')_2]$, and the electrochemistry of this latter redox reaction has been discussed [7].

2.2 *COBALT(III)*

2.2.1 *Complexes with pseudohalide ligands*

Mononuclear cobalt(III) cyano complexes have been reviewed (111 references) [8].

The preparation and characterisation of the complex $Ti[Co(CN)_6]$ have been reported; magnetic and spectral results are complimented by X-ray diffraction powder pattern data which reveal a f.c.c. crystalline form for the complex which contains a 3D lattice of octahedral CoC_6 and TiN_6 units. Differences between the Ti^{3+} and Na^+ salts are described [9].

The pentacyanocobalt complex anion reacts with molecular hydrogen to give $[Co(CN)_5H]^{3-}$; the kinetics of this reaction have been studied [10]. Related to this, the catalytic activity of $[Co(CN)_5]^{3-}$ has been the focus of attention, and has been found to inhibited in the presence of either dmf or dmso [11]. This trianion may be formed by the reduction of sodium or potassium cyanocobalt complexes in γ-irradiated aqueous solution [12].

The complex anion, $[Co(CN)_5X]^{n-}$, (*e.g.* X = Cl, n = 3), reacts in a carbon monoxide saturated CH_2Cl_2 solution to form $[Co(CN)_5(CO)]^{2-}$ which shows a characteristic infra red ν_{CO} mode at 2108 cm^{-1} [13]. The solid state reaction of $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) with $[Co(NH_3)_5(H_2O)]^{3+}$ gives $[(CN)_3M\text{-}NC\text{-}Co(NH_3)_5]_2[M(CN)_4]$; differences in kinetic parameters for M = Pt versus Pd or Ni have been discussed [14].

The cyano ligand in the complex *trans*-$[Co(en)_2(SO_3)(CN)]$ has been isotopically exchanged for $^{14}CN^-$, and the activation parameters for the process have been reported; $\Delta H^\ddagger = -18.3$ kcal mol^{-1} and $\Delta S^\ddagger = -23.9$ cal K^{-1} mol^{-1}. Mechanistic discussions illustrate the labilising effect of the $SO_3{}^{2-}$ group [15]. For the related complex anion, *trans*-$[Co(H_2O)(SO_3)(CN)_4]^{3-}$, the kinetics of competitive substitutions by the ligands NH_3, CH_3NH_3, or CN^- have been described; substitutions are found to be generally dissociative, but I_d pathways also play a rôle [16].

2.2.2 *Complexes with oxygen donor ligands*

2.2.2.1 *Carbonate, phosphate, sulphate, chromate, and related ligands*

In this section are collected together those ligands which one would consider as inorganic acid derivatives.

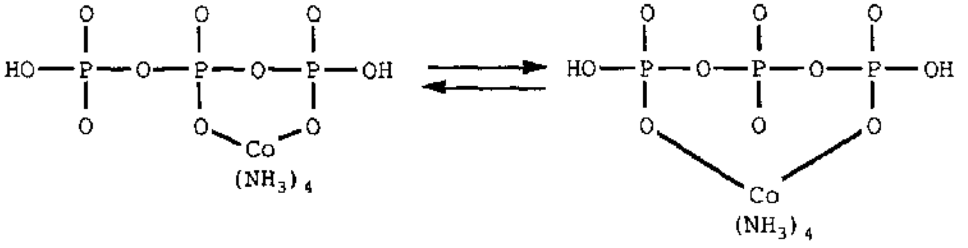
The acid catalysed aquation of some cobalt(III) carbonato species has been reported; rapid scan spectrophotometry was used to follow the decarboxylation of the complexes $[Co(NH_3)_5(OCO_2)]^+$, *cis*-$[Co(edda)(CO_3)]^-$ and $[Co(nta)(CO_3)]^{2-}$, and to monitor the spectral properties of intermediate species in solution [17]. In a related piece of work by the same authors, volumes of activation for ring opening in the aforementioned anionic complexes have been determined; values of $\Delta V^\ddagger$ for the spontaneous process are found to be ≈10 cm^3 mol^{-1} more negative than for the acid catalysed ring opening, whereas for the cationic complexes, both spontaneous and catalysed activation volumes are the same. These results are discussed in mechanistic terms [18].

The reaction between $[Co_2(SO_4)_3]$ and H_2O_2 in aqueous solution, and in the presence of competing reagents to accept the intermediate radicals, has been studied; factors influencing the mechanism are discussed [19].

Stability constants for the outer sphere sulphite complexes, $\{[Co(NH_3)_3(NO_2)_3](S_2O_3)_n\}^{2n-}$, have been determined in water/acetone solution [20]. Each of the ions $S_2O_5{}^{2-}$, $HSO_3{}^-$ and $SO_3{}^{2-}$ reacts in buffered (pH 4-7) solution with *cis*-$[Co(en)(H_2O)_2]^{3+}$ to give an O-bonded sulphito complex. The kinetics of SO_2 uptake by the same complex have been studied, and results indicate the degree to which reverse SO_2 elimination is important [21]. The reaction between $[Co(NH_3)_5Cl]Cl_2$ and trifluorosulphonic acid leads to the complex $[Co(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_2$ with elimination of HCl; the preparation of the related *cis*-$[Co(en)_2(OSO_2CF_3)_2][CF_3SO_3]$ is also reported [22].

The complex $[Co(NH_3)_5(PO_4)]$ has been prepared and used to model ML_4(nucleotide) complexes. Structural characterisation of

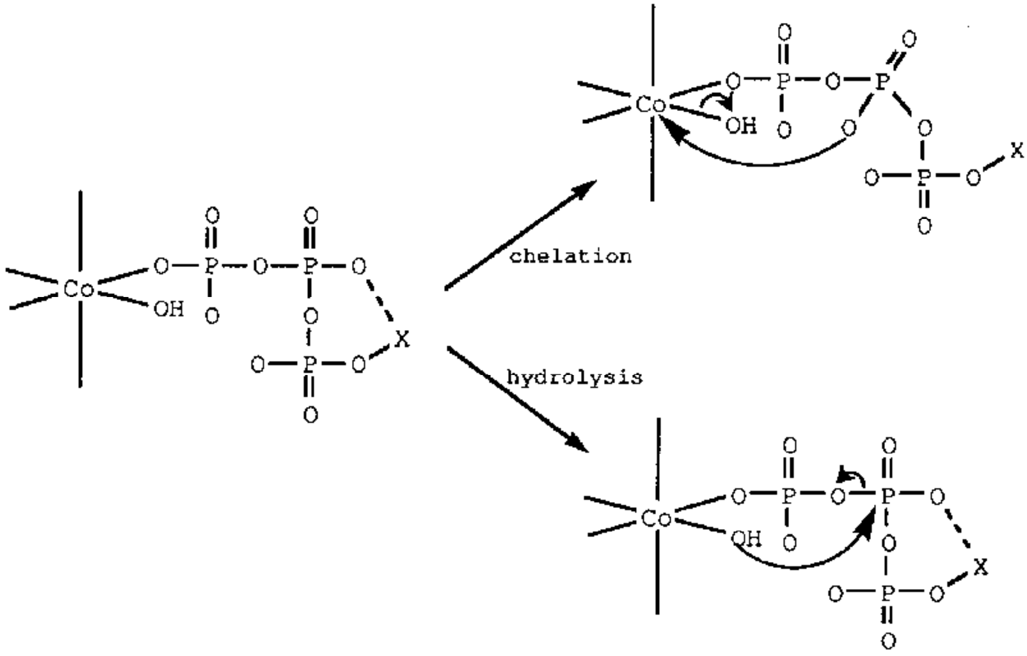
$[Co(NH_3)_5(PO_4)]$ shows a slightly distorted octahedral cobalt(III) centre with Co-O = 1.945(1)Å, and Co-N ranging from 1.952(2) to 1,971(2)Å; ^{31}P n.m.r. spectroscopic studies indicate that the phosphate ligand remains coordinated in solution, and emphasise the significant shift difference between monodentate $PO_4{}^{3-}$ (observed here) and bidentate phosphate ligands [23]. The kinetics of the base hydrolysis of the dinuclear complex $[(en)_2Co(\mu\text{-}RPO_3)_2Co(en)_2]$, (R = Ph, $4\text{-}NO_2\text{-}C_6H_4$), has been followed by using ^{31}P n.m.r. spectroscopy; hydrolysis of the bridging phosphate group is shown to be *intra*molecular [24]. Chelation of the phosphate ligand, H_2L, $H_2O_3PCH_2PO_3H_2$, to a cobalt(III) centre has been structurally exemplified in the complex $[Co(NH_3)_4L]Cl$; pertinent distances are Co-O = 1.942(4) and 1.949(4)Å, $Co\text{-}N_{equatorial}$= 1.925(4) and 1.926(4)Å, $Co\text{-}N_{axial}$= 1.956(4) and 1.957(4)Å. Interest in this complex stems from its application as a model compound for certain enzyme inhibitions [25]. Hydrolysis of the compounds β,γ- and α,γ-$[Co(NH_3)_4(H_2P_3O_{10})]$ has been studied by using ^{31}P n.m.r. and UV-visible spectroscopy; rate constants of 3×10^{-6} and 6.5×10^{-6} s^{-1} have been determined respectively. Isomerisation for the complex involves the following equilibrium, for which K = 0.07 (40°C, pH = 6.5) [26]:



β,γ-isomer α,γ-isomer

The same authors have reported n.m.r. spectroscopic and X-ray diffraction data for β- and γ-$[Co(NH_3)_5(P_3O_{10}H_2)]$, and have proposed mechanisms for phosphate hydrolysis in the anion, β-$[Co(NH_3)_5(P_3O_{10})]^{2-}$ [27]. Competition between the chelation and hydrolysis of polyphosphate ligands has also been investigated, and the pH dependence of the system examined. The two competing pathways are shown in Scheme 1. The substituent, X, plays a vital rôle in determining whether the chelation or hydrolysis pathway is favoured; if X is electron withdrawing, the polyphosphate loses some of its nucleophilic characteristics, and hydrolysis predominates [28].

The chromate ligand in the complex cation, $[HCo(NH_3)_5(CrO_4)]^{2+}$, has been the subject of an ^{18}O exchange (from $H_2{}^{18}O$) study; exchange as a function of pH and complex concentration has been investigated, and a mechanism proposed [29].



Scheme 1

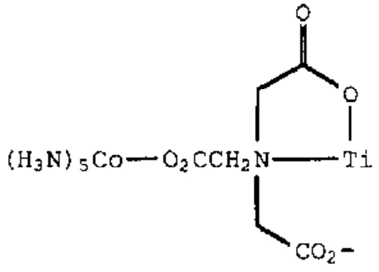
Cleavage of the $P_2O_7{}^{4-}$ ion from $[Co(en)_2(P_2O_7)]^-$ by $[Co(1,3\text{-}pn)_2(OH)(H_2O)]^{2+}$ has been observed, and monitored by using ^{31}P n.m.r. spectroscopy [29a].

2.2.2.2 Carboxylate ligands

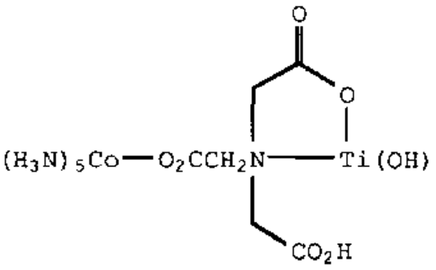
The kinetics and mechanism of the iodine oxidation of coordinated formate ion in the complex $[Co(HCO_2)(NH_3)_5][ClO_4]_2$ have been described; the reaction is first order with respect to each of the substrate and oxidant [30]. The kinetics of the reduction by $[Fe(CN)_6)]^{4-}$ ion of $[Co(NH_3)_5(CO_2R)]^{2+}$, (R = various), have been studied in the presence of H_2edta^{2-} and ascorbic acid; the former sequesters free cobalt(II) as it forms, and the latter rapidly reduces the product Fe^{3+} to Fe^{2+}, thus rendering the net concentration of iron(II) ion constant. An inverse relationship between rate constant for electron transfer, and the pK_a of the ligating RCO_2H has been evidenced [31]. A comparison of the reductions by Cr(II) or by Eu(II) ions of cobalt(III) complexes involving *N*-substituted isonicotinic acid ligands supports differences in mechanism for the two reducing agents; the transmission of spin density from activated ring to cobalt(III) centre occurs by a through-bond mechanisn for Cr(II) systems and by a through-space mechanism for Eu(II) species [32].

The reduction by vanadium(V) ions of $[Co(NH_3)_5L]^{2+}$, where HL is an α-hydroxyacid, takes place either by a one electron, or a two electron reaction pathway; the reaction rate is proportional to the concentration of the intermediate [V(V)-Co(III)] complex, which may be observed spectrophotometrically [33].

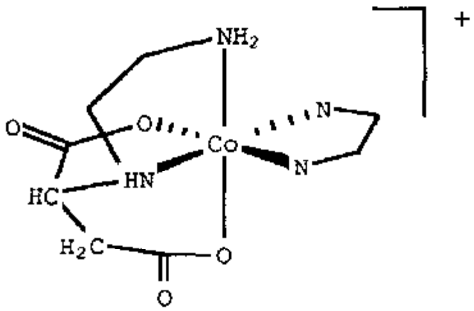
The kinetics of the reaction between the complex cation, $[Co(NH_3)_5(H_2L)]^{2+}$, ($H_3L = N(CH_2COOH)_3$), and Ti(III) ions in aqueous solution have been investigated using rapid scan spectroscopy; electron transfer via a stepwise mechanism is proposed, and the binuclear intermediate, having one of the structures (**2**) or (**3**), is evidenced [34].



(**2**)



(**3**)



(**4**)

The complex cation Λ-$[Co(en)_2L]^+$, where H_2L is maleic acid, undergoes parallel base catalysed reactions in aqueous solution to give either the essentially stereospecific product, (**4**), or else the *cis*- and *trans*-$[Co(en)_2(OH)L]$ complexes; the *fac*-isomer (**4**) is found to the thermodynamically favoured over the *mer*-isomer to the extent of being formed in >96% yield [35].

The complex $Li[Co(dipic)_2].2H_2O$ has been prepared by the oxidation of $[Co(dipic)_2]^{2-}$; the complex is proposed as a simple, 6-coordinate complex, but exhibits an extremely unusual redox chemistry [36].

Two papers from the same research group describe complexes of the type $[Co(NH_3)_5L]$, anchored to either an Au, Cu, or Hg surface; L is either a thioalkylcarboxylate ligand, [37], or a thiophenecarboxylate ligand, [38]. For the thioalkylcarboxylate ligands, the coordinating carboxylate moiety is separated from the thio-group, (i.e. from the site of adsorption to the surface), by carbon chains of differing length and bulk; results appertaining to intramolecular electron transfer via electron tunnelling are presented [37]. Complexes containing the thiophenecarboxylate ligands are the subject of one electron electroreductions, and the kinetics of these processes are reported; the energetics of the organic bridged electron transfers at the Au, Cu, or Hg surfaces vary significantly with the extent to which the redox centre is electronically coupled to the electrode [38].

2.2.2.3 Oxalate ligands

As with other small ligands which occur in numerous complexes, there are always classification problems. Although oxalato containing compounds are discussed in other sections in this review, the chemistry of those complexes chosen to appear in this section centres about the oxalate ion itself.

A series of cobalt(III) complexes exhibiting mixed ligands, but in which the oxalate ligand is the common link, has been prepared; the anions $[Co(ox)_{3-x}L_x]^{3-}$ where L = CO_3^{2-} or $CH_2(CO_2)_2^{2-}$ and x = 1 or 2, and $[Co(CO_3)_x(ox)_y(en)_{3-x-y}]^{n-}$ where x,y = 1,2, have been characterised [39].

The hydrolysis in aqueous solution, (pH $\leq$ 4.5), of the complex $[\{Co(ox)_2\}_2(\mu\text{-}OH)_2]$ has been studied; the kinetics of the reaction adhere to the simple rate law:

$$\mathrm{dln}[\{Co(ox)_2\}_2(\mu\text{-}OH)_2] = k_{obs}\ dt$$

and a mechanism involving a bridged dinuclear intermediate, which undergoes inner sphere coordinate substitution, is proposed [40]. Related to this is a discussion of the kinetics and mechanism of the redox reaction between $[Co(ox)_2(OH)(H_2O)]^{2-}$ and iodide ion; the reaction has been observed over a temperature range from 20° to 35.5°C, and again shows first order kinetics with respect to the starting complex [41].

The photochemistry of penta- and tetra-amminocobalt(III) oxalato complexes in aqueous solution has been investigated as a function of the wavelength of irradiation, as well as of pH [42].

A variety of hydrophilic ligands, including oxalate ion, has been used in a study of the solubilities of cobalt(III) salts in methanol-water mixtures; observed trends in the transfer potentials, (H_2O into MeOH), are discussed in terms of electrostatics and the hydrophilicity and hydrophobicity, (exemplified by the ligand en), of the ligands [43,44].

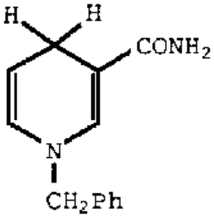
The reaction of cobalt(III) oxalate with *L*-ascorbic acid, H_2L, in the presence of a Cu(II) catalyst has been investigated as a function of copper ion concentration; results confirm the following rate equation [45]:

$$\rho = k[HL^-][Co(III)][Cu(II)].$$

2.2.2.4 β-Diketonate ligands

Diffusion coefficients for the binary acac complex, $[Co(acac)_3]$, in H_2O, ROH (R = Me, Et, Pr, Bu), MeC(O)R (R = Me, Et), C_6H_5R (R = H, Me), MeCN, thf and CCl_4 have been measured at infinite dilution; the Stokes-Einstein coefficient is found to be larger in water than in organic solvents, and is also temperature dependent [46]. Thermodynamic parameters for the formation of outer sphere complexes of sulphate ion with $[Co(acac)_3]$, $[Co(en)(acac)_2]^+$, and $[Co(en)_2(acac)]^{2+}$ have been determined [47].

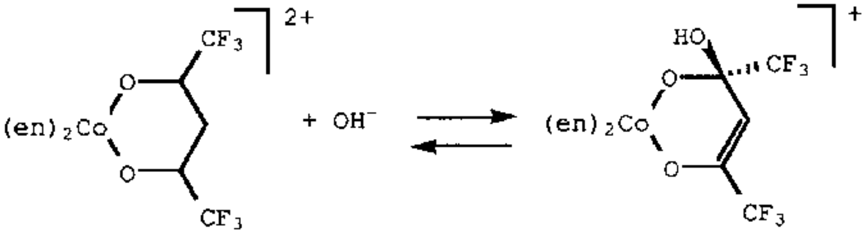
The reduction of $[Co(acac)_3]$ by HL, (**5**), under conditions of micellar accelerated photoirradiation ($\lambda > 310$ nm) has been shown to produce Co(II) ions in greater than 50% yield [48].



(5)

Room temperature conductance measurements for the complexes $[CoL_2(en)]ClO_4$ in which L is acac, 3-bromo-acac, or 3-nitro-acac, have illustrated a trend in the degree of ionic character in the order acac > 3-bromo-acac > 3-nitro-acac, and a counter trend in ionic mobility of the chelate cations along the same series; hydrogen bonding between the diamine ligand N-H protons and the ClO_4^- ions plays an important rôle in determining these observed trends [49]. The cation $[Co(acac)_2(en)]^+$ has also been the focus of reduction studies; a comparison between rates of inner and outer sphere pathways for the Cr(II) reduction of $[Co(acac)_2(en)]^+$ in the presence of chloride ion, and a determination of activation parameters have been reported [50]. In an accompanying paper, solvent effects, over the temperature range 25° to 45°C, and mechanistic details for the Cr(II) reduction of $[Co(acac)_3]$ have been discussed [51].

A detailed kinetic study using stopped flow and temperature jump techniques has looked at the reaction:



For the forward hydrolysis process and the back acidolysis reaction, rate constants of ≈3 x 10^{-6} and 1 x 10^{8} M^{-1} s^{-1} respectively have been determined [52].

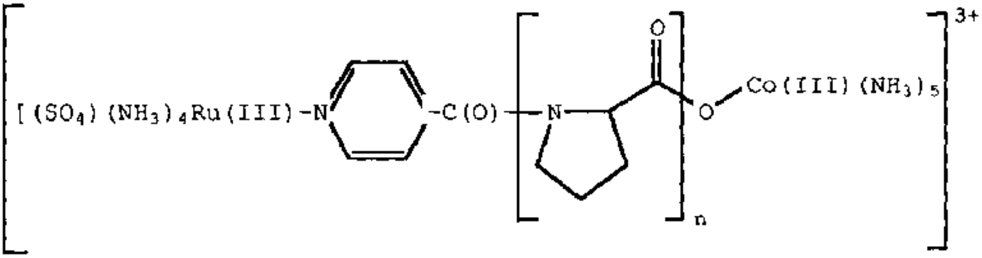
2.2.2.5 Amino acids and related ligands

The complexes Λ-*C*$_1$-*cis(N)*-, Δ-*C*$_1$-*cis(N)*-, Λ-*C*$_2$-*cis(N)*-, and Δ-*C*$_2$-*cis(N)*-K[CoL$_2$(CO$_3$)], (HL = proH), have been prepared, separated by ion exchange chromatography, and characterised from CD and electronic spectral data; Δ-*C*$_1$-*cis(N)*-K[CoL$_2$(CO$_3$)] is the compound which is formed in highest yield, and it is argued that the *C*$_1$-*cis*-structure possesses a greater inherent stability than the *C*$_2$-*cis*- configuration [53].

The metal centres Co(III) and Ru(III) have been coupled *via* amino acid residues of differing chain lengths in the complex shown in (**6**). Reduction of the complex to a Co(III)---Ru(II) species is followed by slow, intramolecular electron transfer; the rate of electron transfer as a function of peptide bridge chain length is presented in Table 1 [54].

Table 1: Rate constants for intramolecular Co(III)---Ru(II) electron transfer in the reduced form of (**6**)

n	k_1/s^{-1}
0	1.2×10^{-2}
1	1.04×10^{-4}
2	0.64×10^{-5}
3	5.6×10^{-5}
4	1.4×10^{-4}

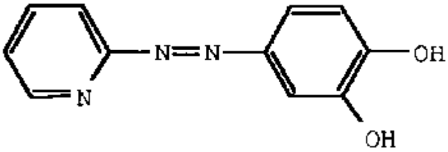


(**6**)

2.2.2.6 Phenols

This rather sparsely exemplified section begins with a report of the prepartion of the complex [CoL(H_2O)Cl], (H_2L = 2,5-$(HO)_2C_6H_3C(R)=N(CH_2)_6N=C(R)-C_6H_3(OH)_2$-2,5, R = Me, Et, Ph); the complexes are characterised as being octahedral on the grounds of their physicochemical and spectral properties [55].

The reduction of the complex formed between cobalt(III) ions and HL, **(7)**, has been studied spectrophotometrically (λ = 560 nm) under pseudo-first order conditions; mechanistic proposals are put forward [56].



(7)

2.2.3 Complexes with oxygen-nitrogen donor ligands

2.2.3.1 Ethylenediaminetetraacetic acid and related ligands

Complexes containing edta and related ligands always figure significantly in coordination chemistry, and this year has, naturally, been no exception. An account of the optical activity of cobalt(III), chromium(III) and rhodium(III) complexes possessing edta^{4-}, edda^{2-}, pdda^{2-} (propylenenediaminediacetic acid), and some related quinquedentate ligands has been presented; absorption and CD spectral data are tabulated (195 references) [57].

Apparent molar volumes for K[Co(edta)] and analogous Cr(III) and lanthanide(III) complexes have been determined and compared; the larger molar volumes noted for cobalt(III) and chromium(III) with respect to the lanthanide metal complexes are attributed to stronger hydration and greater water ordering in the case of Ln^{3+} ions [58]. An investigation of the reduction of some cobalt(III) complexes including $[Co(edta)]^-$ by $[V(pic)_3]^-$, (pic = py-2-CO_2H), indicates second order kinetics (25°C and 0.5M ionic strength); results are discussed in terms of Marcus theory [59].

The crystal structure of the spontaneously resolved complex $\Lambda(R,R)$-$\Delta(G,R)$-[Co(edtaH)(H_2O)].$3H_2O$ has been determined; uncoordinated carboxylic residues are found to be involved in intermolecular hydrogen bonding. There are two independent molecules, and pertinent bond lengths for this complex are listed in Table 2 [60].

The complex anion $[Co(edta)Cl]^{2-}$ has been prepared; interest lies in the ability of the dangling carboxylate group of the edta ligand to couple to amino groups, specifically to that in *p*-aminobenzamidine. The coupling renders the complex an effective inhibitor of trypsin activity [61].

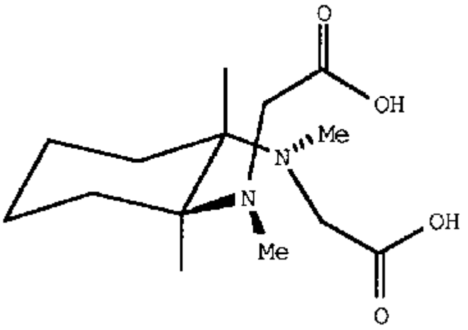
Table 2: Bond Lengths in $\Lambda(R,R)$-$\Delta(G,R)$-[Co(edtaH)(H_2O)].$3H_2O$ /Å

	Molecule A	Molecule B
Co-N	1.937(6)	1.925(6)
	1.986(6)	1.978(5)
$Co-O_{edta}$	1.913(6)	1.908(6)
	1.896(5)	1.865(5)
	1.881(5)	1.879(6)
$Co-O_{water}$	1.927(5)	1.929(5)

The preparation of the complex anions $[Co(SCN)(edta)]^{2-}$ and $[Co(SCN)L']^-$, (H_3L' = *N*-hydroxyethylethylenediaminetriacetic acid), has been reported; the complexes exhibit linkage isomerism with respect to the thiocyanate ligand, and the relative stabilities of the *N*- and *S*-bonded isomers in solution are discussed [62]. The stepwise reaction of $CoCO_3$ with racemic, *R*- and *S*-1,2-H_4pdta, followed by the addition of H_2O_2 and MOH (M = K, Rb, Cs) leads to the formation of M[CoL]; the optically active isomers of $[CoL]^-$ have been characterised by ORD and CD spectroscopy [63].

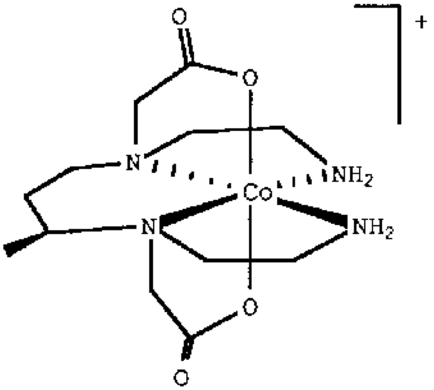
Structural characterisations of [Co(edda)(en)]ClO_4 and [Co(edda')(en)]ClO_4 (H_2edda' = *N,N*-ethylenediaminediacetic acid) show that the nitrogen donors lie in the equatorial plane of the octahedral ligand set in *each* complex [64]. The asymmetrical

H_2edda' ligand appears again in the complexes *cis*-K[Co(edda')(CO_3)].H_2O, *cis*- and *trans*-K[Co(edda')L] (H_2L = H_2mal or H_2ox), and *cis*- and *trans*-[Co(edda')(1,3-pn)]Cl; syntheses of the H_2edda' ligand and its complexes are described, and use is made of ion exchange chromatography to separate the *cis*- and *trans*-isomers [65]. Related to H_2edda is the cyclohexane- derived ligand, H_2chxnda, (**8**); structural characterisation of *S*-*cis*-[Co(*N,N'*-Me_2-*R,R*-chxda)(en)][ClO_4] shows the N-donors of both ligands lying in the equatorial plane, Co-N_{en} = 1.995(8), 1.973(11)Å and Co-N_{chxda} = 1.972(7), 1.990(6)Å [66].



(**8**)

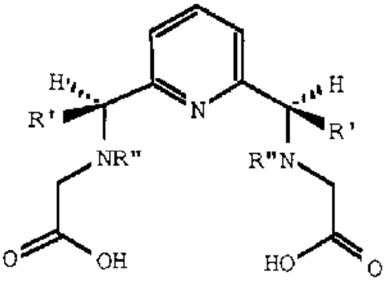
Photolysis of the complex anion $[CoL]^-$, in which H_4L is the edta related ligand $(HO_2CCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2CO_2H)_2$, leads to carboxylation of the ligand if irradiation is in the LMCT region (λ_{max} = 264 nm); mechanistic details are implied [67]. Variations on the edta theme continue with the complex $[CoL]^+$ which is the first example of a structurally characterised complex, (**9**),



(**9**)

containing the ligand mddda^{2-}; again we see the N-donors lying in the equatorial plane of the octahedral ligand set. Metal-ligand bond lengths are Co-N$_{1°\ \mathrm{amine}}$ = 1.944(4), 1.934(4)Å, Co-N$_{3°\ \mathrm{amine}}$ = 1.968(4), 2.008(4)Å, Co-O = 1.895(3), 1.884(3)Å. A detailed ^{13}C n.m.r. spectroscopic study is also presented for this complex [68].

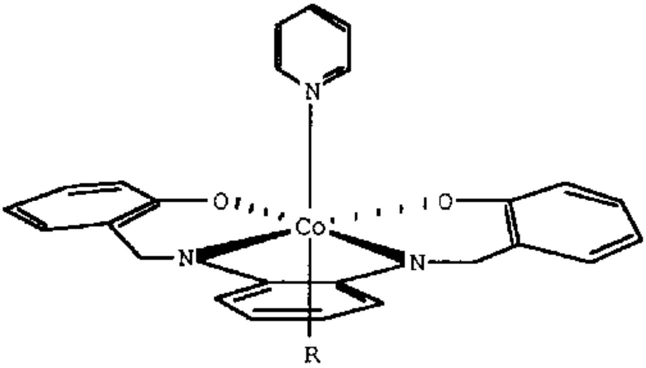
The final variant in this section is the pentadentate ligand, H_2L, **(10)**. The preparation of H_2L and its complexation to Co(III) have been investigated; particular attention is paid to the stereoselectivity of this novel ligand [69].



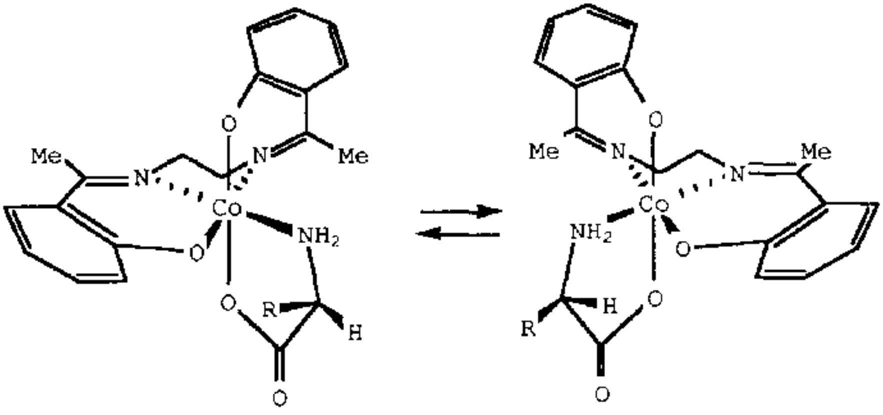
(10)

2.2.3.2 Imine ligands

Models for vitamin B_{12} have included complex **(11)**. X-ray characterisation of **(11)** shows the Co(III) ion in a distorted octahedral environment; bond parameters within the inner coordination sphere are equivalent for R = Et and CH_2CN, within experimental error, and the Schiff base ligand is planar to within ±0.02 Å and ±0.05Å for R = Et and CH_2CN respectively [70].



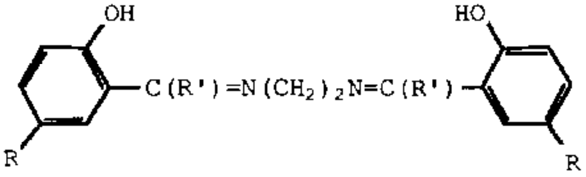
(11) R = Et or CH_2CN



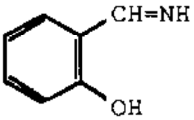
Δ_L-β_2-isomer ⇔ Λ_L-β_2-isomer

(12)

The kinetics and mechanism of the isomerism between the Δ_L-β_2- and Λ_L-β_2-diastereomers of [Co(III)L], **(12)**, has been a subject of investigation; the isomerism is catalysed by H^+, and exhibits a significant solvent dependency, the rate being increased in the presence of a strongly H-bonding solvent [71]. The oxidation of [CoL], H_2L, **(13)**, by iodine gives the cobalt(III) complex [CoLI]; spectroscopic characterisation of [CoLI] suggests a monomeric, non-electrolyic complex, and L^{2-} is proposed to be tetradentate, coordinating *via* the N- and deprotonated O-atoms [72]. The complexes $[CoL(NH_3)_4]X_2.nH_2O$ and $[CoL_2(NH_3)_2]X.nH_2O$ (HL = **(14)**, X = Cl, NO_3, ClO_4, picrate) have been prepared by the reaction of hydrated $CoCl_2$, 25% aqueous NH_3, 30% H_2O_2, and salicylaldehyde; three isomers of the latter complex have been separated by chromatography, and analysis of their ^{13}C and ^1H n.m.r. spectral data has led to assignments of configuration [73].



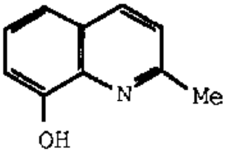
(13) R = Me; Cl and R' = Me; Et

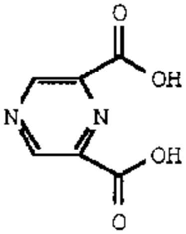


(14)

2.2.3.3 *Heterocyclic ligands*

Three octahedral isomers of the complex cation $[CoL_2(en)]^+$ (L = **(15)**) are possible; ^{13}C and ^1H n.m.r. spectroscopic data have illustrated that the two N-donors are *trans*, and the two O-donor atoms are *cis* to each other. The complex ion $[CoL_2(en)]^{2+}$ has been reported in the same work [74].





(15) **(16)**

The binuclear complex ions $[(H_3N)_5Ru^{II}\text{-L-}Co^{III}(dien)]^{3+}$ and $[(NC)_5Fe^{II}\text{-L-}Co^{III}L']^{2-}$, (L' includes dien, $(NH_3)_3$, dpt), possess a bridging ligand derived from H_2L, **(16)**; the ligand exhibits an O-N-O tridentate coordination mode. Rate constants for intramolecular electron transfer between metal centres in these complexes have been reported [75].

Table 3: Comparison of ionisations in some heterocyclic ligand complexes

Complex ion	pK_{a1}	pK_{a2}
cis-$[Co(en)_2(H_2O)(ImidH)]^{3+}$	5.85	10.5
cis-$[Co(en)_2(H_2O)(N\text{-}MeImid)]^{3+}$	5.95	-
cis-$[Co(en)_2(H_2O)(4\text{-}MeImid)]^{3+}$	5.95	10.8
$[Co(en)(H_2O)(HisH)]^{2+}$	6.20	10.8

A series of cobalt(III) complexes involving imidazole and histidine ligands has been prepared, and pK_a values for the complexes have been determined; results are summarised in Table 3, with pK_{a1} referring to ionisation from H_2O, and pK_{a2} referring to heterocyclic N-H ionisation. Structural characterisation of [Co(hisH)(en)Cl]Cl illustrates hisH behaving as a tridentate ligand, with Co-N = 1.946(3), 1.938(3), and 1.921(2)Å [76].

2.2.3.4 Amino acid ligands

The preparation of the cobalt(III) complexes $[Co(NH_3)_2L_2]Cl$ in which HL is an amino acid, glyH, *S*-alaH, or *S*-valH has been reported; disproportionation of these complexes, versus further ligand substitution to give $[CoL_3]$, is discussed [77]. Oxidation of an α-amino acidato complex to give a 2-imino-carboxylate compound has been discussed; it is the first example of this type of preparative route [78].

2.2.3.5 Miscellaneous ligands

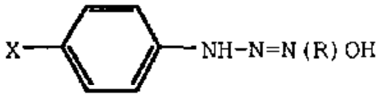
Several other N-O donor ligands remain. The simplest is the nitrite anion. Linkage isomerism for NO_2^- has been exemplified by using ^1H n.m.r. spectroscopy to observe the species formed in aqueous solutions of $[Co(NO_2)_6]^{3-}$, with the complex anions $[Co(NO_2)_4(ONO)_2]^{3-}$, $[Co(NO_2)_4(ONO)(H_2O)]^{2-}$ and $[Co(NO_2)_4(H_2O)]^-$ all being detected; the effects of adding excess nitrite ion, and of changing the pH have been discussed [79].

Complexation by the sulphinate ligand $H_2NCH_2CH_2SO_2^-$ leads to the formation of Λ-$[Co(H_2NCH_2CH_2SO_2)(en)_2][ClO_4]_2$. Separation of the two diastereomers has been achieved, and their characterisation by UV-visible, n.m.r., and CD spectroscopy has allowed absolute configurational assignments [80]. The analogous selenato ligand chelates to the Co^{3+} ion *via* an N-O mode; structural characterisation of the red complex dication $(-)_{500}$-$[Co(H_2NCH_2CH_2SeO_2)(en)_2]^{2+}$, is complimented by electronic and CD spectral studies. Pertinent distances for the latter complex cation are: $Co-N_{selenato}$ = 1.988(5), $Co-O_{selenato}$ = 1.922(4), $Co-N_{en}$ in the range 1.950(5) to 1.972(5)Å), [81].

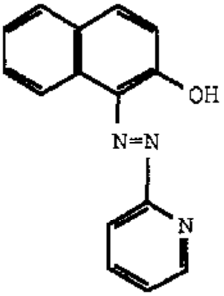
The preparation, and spectroscopic and X-ray powder diffraction characterisation of the complexes $[CoL_2(H_2O)_2]$ and $[CoL_3]$, in which HL is PhC(O)NHC(S)NHC(O)NHPh, have been described;

the complexes have been tested for their anti-fungal activity, and interest in the complexes obviously lies with this potential application [82].

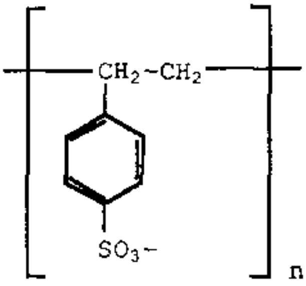
Cobalt(III) complexes with ligands containing azo-groups have included $[CoL_3]$, in which HL is (**17**); facile ligand redistribution occurs for ligands, L^-, in which the substituents R and X are varied. In view of the stereochemically rigid, low spin nature of this cobalt(III) complex, the novelty of this redistribution should be noted [83]. A second azo-complexthat has received attention is $[CoL_2]^+$, (HL = (**18**)). The interaction of this complex cation with the PSS^- chain, (**19**), has been described; once bound to the PSS^- moiety, a racemic mixture of $[CoL_2]^+$ appears as a stereoregular aggregate due to inter-cation interactions [84].



(**17**) R = Et, Ph; X = OMe, Me, H, Cl, CO_2Et, NO_2



(**18**)

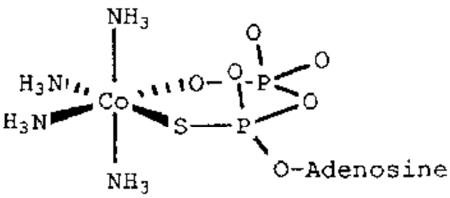


(**19**)

2.2.4 *Complexes with oxygen-sulphur donor ligands*

Since there are so few entries in this section, no subsections have been designed.

The ability of adenosine 5'-*O*-(1-thiodiphosphate) to act as an S-O chelate as well as an O-O chelate to cobalt(III), has been demonstrated; ^{31}P n.m.r. spectroscopy has been used to probe the coordination modes of this ligand, one example of which is shown in (**20**) [85].



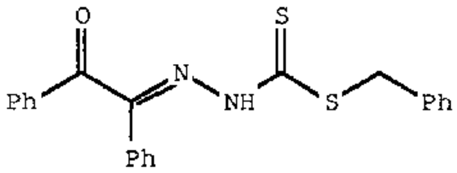
(20)

Two related pieces of work have investigated complexes of the type $[Co(tren)L]^+$, where H_nL has the general formula $RSCHMeCO_2H$ [86,87]. For R = Me, the ion $(-)_{589}$-$[Co(tren)L]^{2+}$ has been crystallographically characterised; pertinent bond lengths are Co-S = 2.239(1) and Co-O = 1.902(3) Å [86]. The same cation has been prepared, along with $(+)_{589}$-$[Co(tren)(SCHMeCO_2]^+$, and $(+)_{589}$-$[Co(tren)(O_2SCHMeCO_2)]^+$; racemisation of the latter species in aqueous solution has been investigated as a function of pH, ionic strength, and temperature [87].

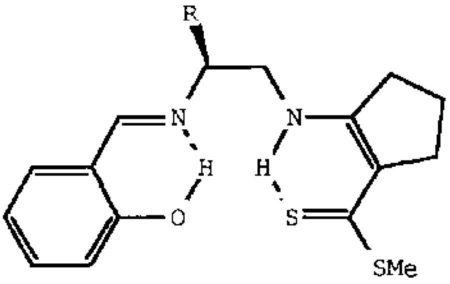
2.2.5 *Complexes with oxygen-sulphur-nitrogen donor ligands*

The cobalt(III) complex cation Δ-*trans(O)-mer(N)-R(S)*-$[Co(\text{L-aehc})(gly)]^+$ (Haehc = $H_2NCH(CO_2H)CH_2CH_2SCH_2CH_2NH_2$) has been crystallographically characterised; the observed octahedral cobalt(III) centre is consistent with electronic spectral data, and bond lengths for the inner coordination sphere are $Co\text{-}O_{gly}$ = 1.897, $Co\text{-}N_{gly}$ = 1.954, $Co\text{-}O_{aehc}$ = 1.891, $Co\text{-}N_{aehc}$ = 1.964 and 1.956, $Co\text{-}S_{aehc}$ = 2.247 Å [88]. A related piece of work reports the absolute configurational assignment and crystallographic characterisation of $(+)_{560}$-*cis.cis.cis*-$[Co(\text{DL-epb})]^+$, in which H_2epb is the ligand $H_2NCH(CO_2H)CMe_2SCH_2CH_2SCMe_2CH(CO_2H)NH_2$; the cobalt to sulphur distances of 2.189 and 2.221Å are noticably shorter than corresponding bond lengths in related thioether complexes [89]. The same authors have looked at complexes containing the cations $[CoL_2]^+$ and $[CoL']^+$ in which L^- is a terdentate ligand, ($HL = RSCH_2CH(NH_2)CO_2H$; R = Et, Bz) and L'^- is sexidentate, ($HL' = R'(CH_2)_nR'$; $R' = MeSCH_2CH(CO_2H)NH$, or $SCH_2CH(NH_2)CO_2H$; n = 2,3); chromatographic separation of, and spectroscopic characterisation of, isomers of these complexes are presented [90].

The reaction of furfural or benzil with *S*-benzyldithiocarbazate has led to new Schiff bases; cobalt(III) complexes of the two new ligands have been prepared and characterised, and for the benzil derivative, (HL = (**21**)), O-N-S ligation is proposed [91].



(21)



(22) R = H; Me

The synthesis and complexation of the new ligand, H_2L, (**22**), have been described; spectroscopic details for the cobalt (III) species $[CoL(H_2O)_2]X$, ($X = Cl, ClO_4$) are given, and assignments for ν_{Co-N}, ν_{Co-S}, and ν_{Co-O} i.r. modes are made. For Co(II), a comparison is made between the electronic spectra of the complexes [CoL] and [Co(salen)] [92].

A further complex which involves an S-O-N donor set in conjunction with N-donors is described later in this review [178].

2.2.6 *Complexes with sulphur donor ligands*

2.2.6.1 *Dithiocarboxylate ligands*

Cobalt(III) complexes involving S-donor ligands are most commonly exemplified by dithiocarboxylate species. A report of the preparation and physicochemical characterisation of [CoL_3], (HL = p-EtO-$C_6H_4NHCS_2H$) also contains a discussion of the thermal behaviour of this complex; $\Delta H_{decomp.}$ has been determined [93]. Related to this is [CoL_3] in which HL is $(C_6H_{11})_2NCS_2H$ [94], or p-HO-C_6H_4-CS_2H [95]; syntheses, and characterisation by spectral, and magnetic moment data, have been described. Structural characterisation of, again, [CoL_3], this time with HL being a heterocyclic dithiocarboxylate ligand, shows the Co(III) ion to be in a distorted octahedral environment, with Co-$S_{average}$ = 2.26Å [96].

The reaction of $Co(ClO_4)_2$ with R_2dtc (R = Me, Et, Bz; R_2 = MePh, pyrrolidine, Me-piperazine) leads to [$Co(R_2dtc)_3$]; further reaction, (for R_2 = Et_2 or MePh), with $Cu(BF_4)_2$ in acetone leads to the dinuclear complex, [$Co_2(R_2dtc)_5$][BF_4], the formation of which appears to be driven by the high affinity of Cu(II) for the dtc ligand [97].

2.2.6.2 Other S-donor ligands

One interesting complex, [$CpCo(CS_3)(CN^tBu)$], is worthy of a mention in this section. This and related complexes may be prepared either from the reaction of $CpCoLI_2$ (L = PR_3 or organoisocyanide) with Na_2CS_3, or by heating CS_2 with CpCoL(CO) or $CpCo(CO)_2$. Structural characterisation of [$CpCo(CS_3)(CN^tBu)$] shows that the CS_3^{2-} ligand is bidentate, with Co-S = 2.235(3) and 2.252(3)Å [98].

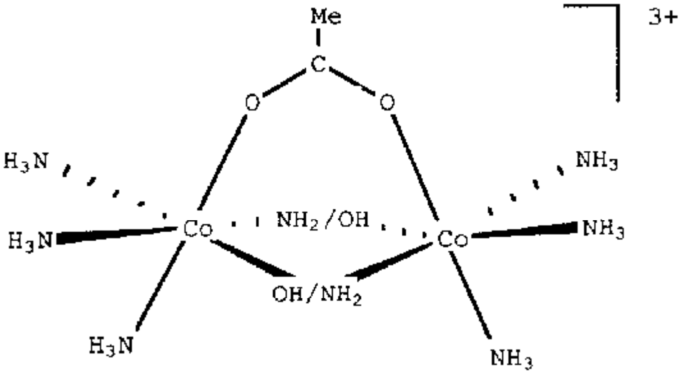
2.2.7 Complexes with nitrogen donor ligands

2.2.7.1 Ammine complexes

Complexes containing coordinated NH_3 are numerous. Often, the chemistry described for the complex as a whole involves a ligand other than ammonia, and hence, as usual, categorisation is difficult. The criteria used here for inclusion of a complex in this ammine section are either that NH_3 is the predominant ligand, or that the chemistry described centres upon NH_3.

The structure of the dinuclear complex cation [$Co_2(MeCO_2)(NH_2)(NH_3)_6(OH)$]$^{3+}$, (**23**), has been reported; the bridging sites are disordered, with fractional occupancies for the

OH^- and NH_2^- ligands. For coordinated ammine, bond lengths are $Co-N_{axial}$ = 1.964(8) and 1.950(8)Å, and $Co-N_{equ.}$ = 1.985(6) and 1.972(6)Å [99]. An X-ray investigation of $[Co(NH_3)_4Cl(H_2O)]Cl_2$, prepared *via* the acid hydrolysis of $[Co(NH_3)_4(HP_2O_7)]$ or $[Co(NH_3)_4(PO_4)]$, shows hydrogen bonding between the ligated water H atoms and the Cl^- counterions with H----Cl of 3.087(6) and 3.123(6)Å; the average Co-N bond length is 1.914(6)Å [100].



(23)

Preparation and substitution chemistry of the cations *cis*-$[Co(NH_3)_4(dmf)_2]^{3+}$ and *cis*-$[Co(NH_3)_4(O_3SCF_3)_2]^+$ have been described [101]. A Raman spectroscopic study of $[Co(NH_3)_6X_3]$ for X = Cl, Br and I, ($40 \leq T \leq 310K$), has assigned stretching vibrations, thereby resolving previously anomalous data [102]. Isomers of $[Co(NH_3)_4(NO_2)_2]^+$ have been the subject of polarographic investigations; variations in reduction waves as a function of pH have been reported [103]. Ion-pairing effects for $[Co(NH_3)]^{3+}$, and for the related $[Co(en)_3]^{3+}$, have been studied by ^{13}C n.m.r. spectroscopy; mechanisms for relaxations have been discussed [104]. The sonolysis of $[Co(NH_3)_5(N_3)]Cl_2$ leads to the formation of the radicals $N_3^\bullet$, $H^\bullet$, and $HO^\bullet$, illustrated by spin trapping experiments; it is proposed that reaction is initiated by fission of H_2O, formation of NH_4^+, and combination of $HO^\bullet$ and N_3^- to form $N_3^\bullet$ [105].

Several thermal studies involving ammine complexes have been reported. The thermal decomposition of crystalline $[Co(NH_3)_6]Cl_3$ over the temperature range 170-220°C has been studied by using electron microscopy; the morphology of the products depends upon the conditions of the thermal reaction [106]. The same thermal decomposition has application in thermal imaging [107]. Details of the use of mass spectrometry to follow the thermal decomposition of $[Co(NH_3)_6]Cl_3$ have been described; the composition of the gaseous products depends upon reaction conditions, but NH_3 and Cl_2 are the major products [108]. The thermal stabilities of the complexes $[Co(NH_3)_{6-n}X_n]$ for X = Cl, Br, I, NO_3 and ClO_4 in the solid state have been compared [109].

Photoaquation of $[Co(NH_3)_5Br]^{2+}$ (λ = 254 nm) proceeds with a 25±10% quantum yield; a comparison is made with the efficiency of photoredox reactions [110].

A measure of the *trans*-effect of coordinated sulphite on proton exchange in cobalt(III) ammines has been discussed; the rate of exchange is decreased in the presence of the *trans*-sulphite ion [111].

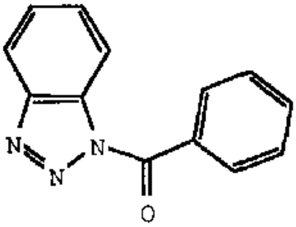
An investigation of the ammoniation of $[Co(NH_3)_5X][ClO_4]_2$, (X = N_3 or Cl), and of the isomerisation of $[Co(NH_3)_5(NO_2)][ClO_4]_2$ in liquid ammonia, illustrates a conjugate base mechanism operating over a pressure range 10-4000 bar; activation and thermodynamic parameters are determined [112]. The extent to which ion-pairing is important in the predissociation step of the base hydrolysis of $[Co(NH_3)_5X]^{n+}$ in the presence of competing ligands, Y^{m-}, (various X and Y), has been described; results illustrate that there is no relationship between the rate law and the distribution of products [113]. The kinetics and mechanisms of the reactions of *cis*- $[Co(NH_3)_4(H_2O)_2]^{3+}$ with NO_2^-, N_3^-, and sal^{2-} have been compared [114]. A study of the kinetics of the aquation of $[Co(NH_3)_5Br][ClO_4]_2$ in 10% ethanol and in the presence of various dicarboxylate ligands has illustrated the following empirical correlation between the ion-pair rate constant, the ion hydrolysis rate constant, and the dicarboxylic acid dissociation constant [115]:

$$k_{\text{ion pair}} / k_{\text{ion hydrolysis}} = 0.502(K_a)^{0.28}$$

Measurements of the volumes of activation for the base hydrolysis of $[Co(NH_3)_5X]^{(3-n)+}$, (X^{n-} = F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, Me_2SO), accompany an estimation of the partial molar volume of the 5-coordinate complex ion $[Co(NH_3)_4(NH_2)]^{2+}$; the authors find that the partial molar volume is independent of X^{n-}, thus supporting the validity of the S_N1CB mechanism [116]. The anation of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ with NCS^- at 40-60°C is stepwise through to *cis*-$[Co(NH_3)_4(NCS)_2]^+$; an I_d mechanism is proposed [117].

The complex $[Co(NH_3)_5(H_2O)][ClO_4]_3$ catalyses the hydrolysis of the heterocycle **(24)**; the rates of OH^- *vs*. complex catalysed hydrolyses are compared, with the latter being more efficient [118].

Aquation of $[Co(NH_3)_5(ox)]^+$ is catalysed by iron(III) ions, and adheres to a first order rate law; the formation of the intermediate species $[(NH_3)_5Co\text{-}OCOCO_2\text{-}Fe]^{4+}$ shows significant solvent dependence [119]. The reduction of $[Co(NH_3)_5X]^{2+}$, (X = F or HCO_2), by Cu(I) in dmso/H_2O solvent media is shown to proceed *via* an inner sphere mechanism; the chosen solvent system is advantageous because, in it, Cu(I) is relatively stable with respect to disproportionation [120]. The rate of electron self exchange for the couple $[Co(NH_3)_6]^{3+/2+}$ has been measured by observing the rate of exchange of ammonia between $[Co(NH_3)_6]^{3+}$ and $NH_3(aq)$, catalysed by cobalt(II) ions; the rate is found to be independent of pH, and the following rate law is confirmed [121]:



(24)

$$\rho = k_1[Co(NH_3)_6{}^{3+}][Co(NH_3)_6{}^{2+}].$$

Studies of the electrochemical reduction of some halide-bridge containing cobalt(III) complexes at platinum- or gold-aqueous interfaces, have shown that the metal surface is able to significantly influence the energetics of the reaction [122]. The products and kinetics of the reaction between $[(H_3N)_5Co\text{-}NCCH_2X]^{3+}$, (X = I, Cl), and $[Cr(H_2O)_6]^{2+}$ have been compared with those of the reaction of the uncomplexed nitrile with hydrated Cr(II) ions; the cobalt(III) complex gives >95% of the dinuclear species $[(H_3N)_5Co\text{-}NCCH_2\text{-}Cr(H_2O)_5]^{5+}$, whereas the free nitrile produces only 25% of $[Cr(H_2O)_5(CH_2CN)]^{2+}$ [123].

The base hydrolysis in ethanol/water or acetone/water of $[Co(NH_3)_5(OSO_2)]^+$ follows both alkali dependent and independent pathways; the overall rate constant is given by:

$$k_{obs} = k_1 + k_{OH}[OH^-]$$

where k_1, k_{OH}, and the corresponding activation parameters are found to depend markedly on solvent polarity [124]. Intramolecular hydrolysis occurs in $[(H_3N)_4(HO)Co(\mu\text{-}NH_2)Co(NH_3)_4MeCN]^{4+}$ to give a chelated acetamide [124a].

2.2.7.2 Amino ligands

As usual, there is a significant array of cobalt(III) complexes containing coordinated amines. The preparation of *cis*- and *trans*-$[Co(NH_3)_4(RNH_2)Cl]^{2+}$, (R = Me, Et, Pr, Bu), has been described, along with UV-visible spectroscopic studies; increasing alkyl chain length for the amine ligand produces an increase in the ligand field strength [125]. Values of $\Delta V^\ddagger$ for the aquation of $[Co(MeNH_2)_5Cl]^{2+}$ and *trans*-$[Co(MeNH_2)(NH_3)_4Cl]^{2+}$ (-2.3 and -4.6 cm^3 mol^{-1} respectively) have been compared with $\Delta V^\ddagger$ for the analogous reaction for $[Co(NH_3)_5Cl]^{2+}$ (-9.9 cm^3 mol^{-1}); variations in mechanism are discussed [126].

The complex cations $[(H_3N)_5CoL]^{3+}$, in which L is $H_2N(CH_2)_nOH$ (n = 2,3), $H_2N(CH_2)_2NHEt$, 3-HO$(CH_2)_n$-py (n = 1,3), or 4-MeOC(O)CH_2-py, have been prepared, and their acylation to isonicotinate derivatives studied; spectral properties of the final complexes are reported, as are several reduction reactions [127]. The oxidation of (-)-dopa, (dopa = 3,4-$(HO)_2$-C_6H_3-$CH_2CH(NH_2)CO_2H$), by the optically active complex $[Co(NH_3)(en)_2Cl]Br_2$ is reported to involve an intermediate with a large (-)rotation; this species is proposed as the 5-coordinate complex, *trans*-$[Co(en)_2(dopa)]$ [128].

Several related studies appertain to the tris-en complex, $[Co(en)_3]^{3+}$. Solubility products and free energies of solution in ethanolic media for $[Co(en)_3][Fe(CN)_6)]$ have been determined as a function of the concentration of chloride and bromide ion present; stability constants for the outer sphere complexes $[Co(en)_3]Cl^{2+}$ and $[Co(en)_3]Br^{2+}$ have also been calculated [129]. Complimentary studies involving $[Co(en)_3]^{3+}:2[RCO_2]^-$ outer sphere complexes illustrate a stability dependence upon R (Cl_3C > H > Me > Et) [130]. Some outer sphere complexes of $[Co(en)_3]^{3+}$ with monosaccharides [131], and with $S_2O_3^{2-}$ ions [132], have similarly been investigated. The electronic spectrum of aqueous $[Co(en)_3]Cl_3$ has been analysed in detail [133]. The preparation and characterisation by X-ray powder pattern and spectroscopic data of $[Co(en)_3]_4[MoO_2L_2]_3.7H_2O$, $[Co(en)_3]_4[\{MoO_2L\}_2O]_3.13H_2O$, and $[Co(en)_3][MoO_5(OH)(HL)_2].3H_2O$ in which H_3L = tartaric acid, have been reported [134].

Assignment of absolute configurations has been achieved for a range of cobalt(III) cationic complexes of the general formula $[Co(diamine)_2XY]^{n+}$ by investigating the interaction with the chiral shift reagent, $[Cr(ox)_3]^{3-}$; the diamines and ligands X and Y used in this study are summarised in Table 4 [135]. A detailed ^{13}C n.m.r. spectroscopic investigation of several cobalt(III) complexes, again of the general type $[Co(diamine)_2XY]^{n+}$ but here for the diamine = en, and for XY = $(CN)_2$, $(NO_2)_2$, phen, or ox, has made successful use of ^{15}N labelled diamine to assign all ^{13}C n.m.r. spectral resonances; comparisons with simulated spectra are made [136].

Table 4: Combinations of ligands in $[Co(diamine)_2XY]^{n+}$ [135]

X	Y	Diamine
CN	CN, Cl, Br, H_2O, NO_2	en
Cl	NH_3, $MeNH_2$, NCS, H_2O	en
NCS	H_2O	en
NO_2	H_2O	en
CN	CN	1,3-pn
Cl	NH_3	1,3-pn
Cl	$MeNH_2$	1,3-pn
	XY	**Diamine**
	gly	1,3-pn

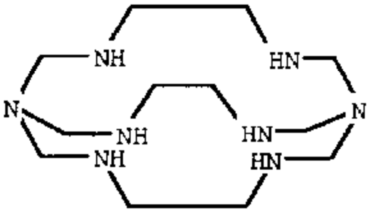
A study of the kinetics of the aquation of *cis*-$[Co(en)_2(NH_3)Br]^{2+}$ in aqueous and non-aqueous solvents in the presence of supporting electrolytes provides the basis for a discussion of the effects of co-solvents on the solvation spheres of reactants and of activated complexes [137]. Volumes of activation for the aquation of *trans*-$[Co(en)_2(NO_3)X]^+$ (X = Br, Cl) have been determined to be 0.3±0.2 (283K) and 0.7±0.6 (303K) cm^3

mol^{-1} [138].

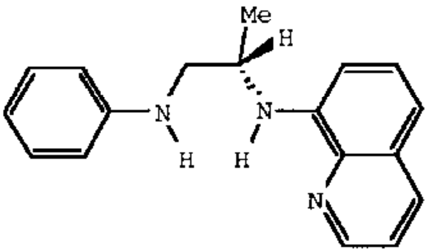
The reaction of $[(en)_2Co(\mu\text{-}OH)_2Co(en)_2]^{4+}$ with carbonate ion has been followed as a function of pH, temperature, and carbonate concentration; hydroxide bridge cleavage leads to $[Co(en)_2(CO_3)]^+$ as the ultimate product [139].

Details of the electronic spectra of the complexes *cis*- and *trans*-$[Co(en)_2Cl_2]^+$, *trans*-$[Co(en)_2(NO_2)_2]^+$, *cis*-$[Co(en)_2(NCS)Cl]^+$ and the related ammine complex, $[Co(NH_3)_5Cl]^{2+}$, illustrate that a 355 nm excitation results in the population of a ligand→metal charge transfer state [140]. Irradiation of $[Co(en)_2(N_3)_2]^+$, *trans*- and *cis*-$[Co(en)_2(NO_2)(H_2O)]^{2+}$, and other related species has been observed with λ = 254, 313, and 365 nm; the effects of viscosity, concentration, and pH on the photochemical reduction of these complexes have been presented [141].

Use has been made of h.p.l.c. to explore the kinetics of substitution in *trans*-$[Co(en)_2(S_2O_3)_2]^-$; nucleophilic substitution takes place *via* a simple dissociative mechanism, and a square pyramidal intermediate, $[Co(en)_2(S_2O_3)]^+$, is postulated [142]. The complex cations, *cis*- and *trans*-$[Co(en)_2(NCS)Cl]^+$, are oxidised by cerium(IV) ions and by peroxosulphate ions; the kinetics of these reactions have been studied and the effects of the supporting electrolytes have been shown to be significant [143]. The alkaline hydrolysis of *cis*-$[Co(en)_2(NH_3)L]^+$, (H_2L = 5-NO_2-salH_2), in the presence of $CH_3(CH_2)_{15}NMe_3Br$, or in a specific phase transfer catalytic medium, has been shown to be more efficient than hydrolysis of the said complex in an aqueous phase [144].



(25)



(26)

The aquation of $[Co(en)(dien)X]X_2$, (X = Cl, Br), catalysed by either Ag(I) or Tl(I) ions, has been followed by spectrophotometric techniques, over a range of temperatures and at constant pH and ionic strength; activation parameters have been determined, and mechanistic details discussed [145,146]. The oxidation of $[Co(sep)]^{2+}$, (sep = (**25**)), by *cis*-$[Co(en)_2LCl]^{2+}$, (L = cyclohexylaniline, aniline, or *p*-nitroaniline), has been explored; MLCT interactions are important, with electron transfer reactions becoming more adiabatic as the acceptor orbitals of the amine ligand, L, become lower in energy [147].

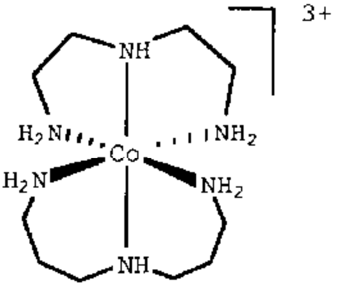
Four diastereomers of the complex $[Co(acac)L][ClO_4]$, (HL = (**26**)), co-crystallise; high resolution n.m.r. spectroscopy shows that all the diastereomers exist in solution as well, and gives no evidence for the redistribution of their coordination spheres in either neutral or acidic solutions [148]. The synthesis of the complex *unsym-fac-cis*-$[CoCl(dien)L]^{2+}$, ($L = H_2N(CH_2)_4NH_2$), has been reported; ^{13}C n.m.r. spectroscopy aids the elucidation of configuration of the ligand. Further, the aquation of this complex proceeds with a rate constant of 6.27×10^{-5} s^{-1} at 298K [149].

The preparation and characterisation of various rotaxane complexes have been described; the complexes have the general formula [2]-$[[(en)_2ClCo(\mu\text{-}L)CoCl(en)_2]X_4]$-[CDX], in which CDX = α-or β-cyclodextrin, and L = 1,10-, 1,12-, or 1,14-diaminoalkanes. Techniques applied for characterisation of the latter species are CD, electronic, and ^{13}C n.m.r. spectroscopy [150].

Structural characterisation of the cobalt(III) complex cation, *s-fac*-$[CoLL']^{3+}$, (**27**), supports the results of molecular mechanical calculations, (Table 5) [151].

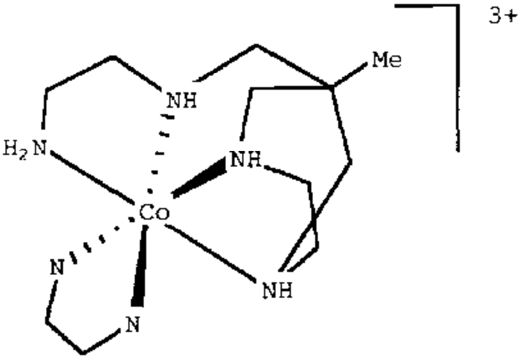
Table 5. Comparison of bond distances for complex (**27**) from the results of X-ray crystallography *vs*. molecular mechanics; $L = H_2N(CH_2)_2NH(CH_2)_2NH_2$; $L' = H_2N(CH_2)_3NH(CH_2)_3NH_2$ [151]

Ligand	Bond	X-ray /Å	Molecular mechanics /Å
L	Co–N(NH_2)	2.028(8)	1.978
		1.954(8)	1.984
	Co–N(NH)	1.997(8)	1.984
L'	Co–N(NH_2)	2.020(8)	1.986
		1.959(7)	1.968
	Co–N(NH)	2.010(8)	1.984



(27)

The complex cations $[Co(dpt)_2]^{3+}$ and $[Co(dpt)(NH_3)_3]^{3+}$ have been prepared and spectroscopically characterised; resolution of *trans*-λ-NH- and *trans*-δ-NH-*mer*-$[Co(dpt)_2]^{3+}$ has been achieved by use of column chromatography [152].

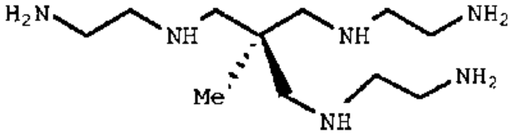


(28)

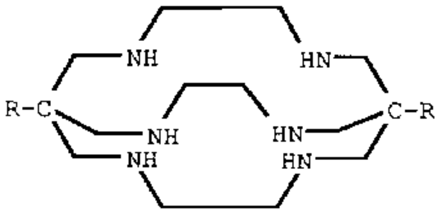
The aquation of α-*cis*-$[Co(NH_3)(ox)(trien)]^+$ has been studied; rate constants for the spontaneous aquation are compared with those for acid catalysed aquation, and it is reported that the trien ligand sterically hinders the aquation rate [153]. Several cobalt(III) complex cations, including α- and β-*cis*-$[Co(H_2O)_2(trien)]^{3+}$, and $[Co(H_2O)_2(tme)_2]^{3+}$, have been prepared, and tested for their ability to catalyse the hydrolysis of phosphorus esters [154]. The cobalt(III) complex, $[CoL(en)][ClO_4]$, **(28)**, contains a branched cyclic tetramine ligand, L; structural analysis gives bond distances of $Co-N_L$ =

1.997(3), 1.995(3), 1.979(3), and 2.000(3)Å, and Co-N_{en} = 1.966(3) and 1.996(3)Å [155]. The reaction of the tetramine containing complex, *trans*-$[CoLCl_2]Cl$ (L = $H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ or $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$) with sodium cyanide gives products, the stereochemistry of which, (*trans*- or *uns-cis*-), depends upon the reaction conditions; discussions of reaction pathways are complimented by molecular mechanics calculations [156]. The green, paramagnetic compounds, $[CoLL']Cl.NO_3.nH_2O$, (L = $H_2N(CH_2)_xNH(CH_2)_yNH(CH_2)_xNH_2$, x = 2,3,3, with y = 3,2,3, respectively; H_2L = 5-O_2N-salH_2), along with their orange, cobalt(II) analogues, have been prepared and isolated; characterisation includes details of ^1H and ^{13}C n.m.r. spectroscopic properties [157,158].

The complex cations $[CoL_3]^{3+}$ with L being en or sen, **(29)**, react with HCHO and CH_3NO_2 to give compounds containing cage ligands which are formally derivatives of sar, **(30)**; structural characterisation of one product, $[Co(dinitro\text{-}sar)]^{2+}$, (R = NO_2 in **(30)**), shows that the Co(III) ion is 6-coordinate, with Co-N distances lying in the range 1.946(7) to 2.016(7)Å [159].



(29)



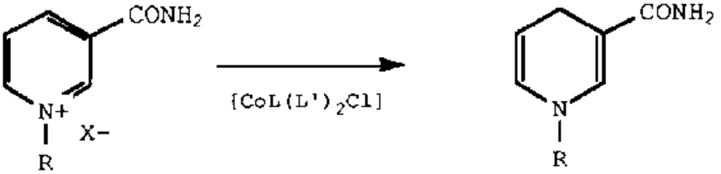
(30)

The base hydrolysis of *α-β-S*-$[Co(tetren)(salH)]^{2+}$ has been studied by using rapid scan spectrophotometry; initially, with λ_{max} = 480 nm), the formation of $[Co(tetren)(sal)]^+$ is observed [160].

2.2.7.3 *Oxime ligands*

A variety of complexes involving the dimethylglyoxime ligand has, as expected, been investigated. Cobalt(II) perchlorate reacts with dmgH_2 in acetone, in air, to give the oxidised product, *cis*-$[Co(dmgH_2)(dmgH)_2][ClO_4]$; all three ligands are shown, by X-ray analysis, to be bidentate [161]. The structure of the complex $[Co(Hdmg)_2Cl(NHMe_2)]$ has been elucidated; the two dioxime ligands reside in slightly different positions with respect to the cobalt(III) ion, and thus, there is some debate as to whether the complex cation should be formulated as $[Co(Hdmg)_2Cl(NHMe_2)]^+$ or $[Co(H_2dmg)(dmg)Cl(NHMe_2)]^+$ [162]. The reaction of $[LCo(dmgH)_2]$, ($L = PR_3$ or $P(OR)_3$), with Ph_3AsCl gives $[Co(Hdmg)_2ClL]$ and $[Co(Hdmg)_2Cl(Ph_2AsOH)]$; the latter has been structurally characterised, and pertinent bond lengths to the octahedral cobalt centre are: $Co\text{-}N_{dmgH}(av.) = 1.89(1)$, $Co\text{-}Cl = 2.252(2)$, and $Co\text{-}As = 2.322(1)$Å [163]. A report of the preparation and spectroscopic characterisation of *trans*-$[Co(Hdmg)_2X(L)]$, (X = Cl, Br, I, NCO, NCS, NCSe, NO_2; $L = R_2NC(=NH)NR_2$, R = H or Me), is accompanied by a discussion of thermal decomposition of these complexes; a dependence of the thermal stability upon the ligand X is noted, and comparisons between thermal and solution stabilities of the complexes are made [164,165].

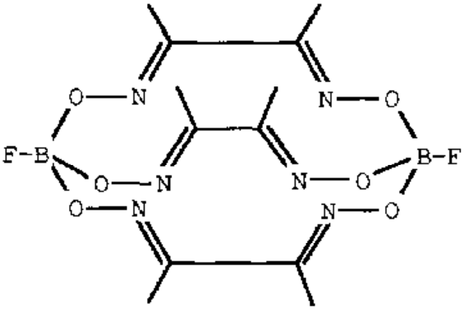
The octahedral complex, $[CoL(dmgH)_2Cl]$, (L = py, PPh_3, pip, SMe_2), and its diphenyldioxime analogue, (for L = py), is found to reduce pyridinium salts *via* the reaction shown in scheme 2. The reaction proceeds with a high regioselectivity, and it is proposed that a dihydropyridyl cobalt complex functions as the active intermediate [166]. The complex *trans*-$[Co(dmgH)_2(1\text{-}Me\text{-}imid)L]$, (L = adamantyl), is a B_{12} model compound exhibiting a novel Co-tertiary carbon bond of 2.154(5)Å [166a].



R = Pr, X = Br;   R = CH_2CH_2Ph, CH_2Ph, Ph,   X = Cl

Scheme 2

The thermolysis of $[Co(HL)_2py_2]I$, (where H_2L is the $dmgH_2$ related ligand MeC(=NOH)C(=NOH)R), *via* loss of a py ligand occurs endothermically in the solid state. Heats of reaction have been determined, and the kinetics of decomposition have been studied as a function of the substituent R; the Co-py bond is weakened if the group, R, is either electron donating or bulky [167]. Complexes of the type $[Co(dmgH_2)(SO_3)L][NH_4]$, (L = various O- or N-donors), have been prepared by using lead or mercury salts of mixed sulphito acids of cobalt(III); the results of thermal analysis of the products have been described [168].

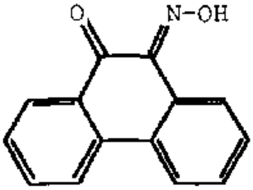


(31)

Outer and inner sphere electron transfers between $[CoL]^+$, (L = **(31)**), and ferrocene have been the subject of an investigation; the reaction shows a first order dependence on each reactant, and an analysis of the results in terms of Marcus theory is provided [169].

The catalytic activity of a range of cobalt(III) complexes containing the ligands, L^- where H_2L = HON=C(R')C(R)=NOH, (R = Me, 2-furyl; R' = H, Me, Et, Ac, CO_2Et, 2-furyl), has been explored, with respect to the reduction of vat dyes by *Rongalite C;* all the complexes are found to enhance reduction, with $dmgH_2$ being particularly active [170].

The syntheses, characterisation, and complexation with Co(III) of several azo-oximes have been reported; the free ligand, R-C(=NNHR')(NO), has R = 2-furyl or 2-thienyl, and R' = Ph or *o*-tolyl, and a contribution from the resonance form $R\text{-}C(=NN^-R')(N=O^+H)$ is evidenced from the observed i.r. ν_{NO} mode at 1008-1080 cm^{-1} [171].

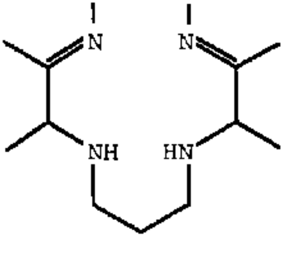


(32)

Six complexes of type [(*m*- or *p*-F-C_6H_4)CoL_m]$^{n+}$, where H_2L = dioxime or a Schiff base, have been studied within the confines of ^{19}F n.m.r. spectroscopy [172]. The red complex [CoL_3], HL = **(32)**, has been prepared and physicochemically characterised; ligand field parameters have been determined from the electronic spectrum, and a value for LFSE of 265 kJ mol^{-1} is reported [173].

A complex [Co(py)L_2] in which L is an α-hydroxylamino-oxime ligand has been reported [174]. The binary species [CoL_3], containing a ligand related to the latter, exhibits an e.s.r. spectrum which is dependent upon solution pH; this observation is attributed to non- dissociative ligand rearrangement [175].

The ligand, H_2L, **(33)**, complexes with cobalt(III) to give *trans*-[$CoCl_2$(HL)] which has been structurally characterised, ($Co-N_{imine}$ = 1.917(4), $Co-N_{oxime}$ = 1.887(4), Co-Cl(av.) = 2.239(1)Å); a comparison of this complex with the analogous rhodium species illustrates the effect that the size of the central metal ion may have on intramolecular hydrogen bonding [176]. An interesting crystallographic investigation shows that, upon exposure to X-rays at 293K, a crystal of *R*-[Co(py)(dmgH)$_2$(CHMeC(O)OMe)].nMeOH changes its cell dimensions without losing crystallinity; loss of MeOH, which results in a conformational change of the $-CO_2Me$ moiety, is evidenced [177]. The complex [CoL_3]Cl_3.3.5H_2O, (L = MeC{$CH_2N=NCH_2CH_2NH_2$}$_3$), is chiral, and racemises upon being heated in the solid state; structural and kinetic details have been described [178].



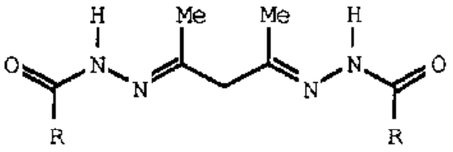
(33)

2.2.7.4 Hydazine, and hydrazide ligands

The preparation and physicochemical characterisation of the octahedral complex [Co(N_2H_4)$_2$(SO_4)].nH_2O have been reported [179].

Mixed ligand complexes of type [CoLXY].$2H_2O$ (in which HL is malonic acid dihydrazide, and X^{n-} and Y^{n-} are combinations of the ligands Cl^-, Br^-, NO_3^- and NCS^-), have been prepared and spectroscopically characterised; the effect that the dihydrazide ligand exhibits upon the coordinating ability of the metal centre with respect to ligands X^{n-} and Y^{n-} is investigated [180].

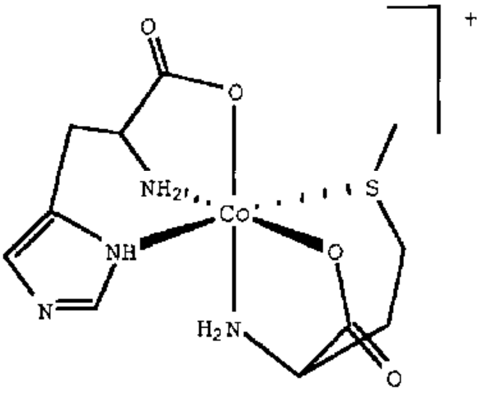
The ligand HL, (**34**), has been prepared *in situ* and then reacted with a source of cobalt(II); a cobalt(III) complex, [$CoLX_2$], results, and has been spectroscopically characterised. The coordination mode of L^- is dependent upon the substituent, R, in HL; for R = 2-pyridyl, coordination of L^- is through the py and azomethine-N atoms, whilst for R = 4-pyridyl, coordination of the ligand is *via* the azomethine-N atom and the amido-O atom [181].



(**34**) R = 2-pyridyl or 4-pyridyl

2.2.7.5 Amino acid ligands

Those amino acid complexes which are not readily classified elsewhere in this review are noted in this section.



(**35**)

As far as categorisation by ligand types, the complex [Co(L-his)(L-met)]$^+$ is probably worthy of several entries in this review! Three geometrical isomers of this complex have been isolated, namely the *trans-*(N_iS), *trans-*(N_iO), and *trans-*(N_iN) isomers, in which N_i denotes the imidizole nitrogen atom of the his$^-$ ligand. One isomer of $[Co(L\text{-his})(L\text{-met})]^+$ is shown in **(35)** [182].

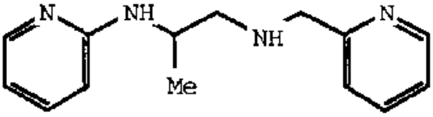
For the amino acids, HL = *(S)*-serH, *(S)*-thrH, *(S)*-valH and *(S)*-glutamic acid, the complex $[CoL(en)_2]Cl_2$ has been reported; the compound $[CoL(bipy)_2]Cl_2$ has been prepared for HL = *(S)*-serH only, $[CoL(phen)_2]Cl_2$ has been synthesised for HL = *(S)*-serH and *(S)*-valH, and Λ-$[CoL(en)_2]I_2$ has been isolated for HL = *(S)*-serH. Details of the CD spectroscopic properties of these complexes are described, as well as conformational characteristics of the amino acid chelates [183].

A variety of cobalt(III) complexes with α-amino acidato ligands have been the subject of an analysis which develops a relationship between the chelate ring torsion angles, and the pseudorotational coordinates; it is concluded that the pseudorotational parameters are useful for probing and categorising ligand conformation [184].

2.2.7.6 Heterocyclic ligands

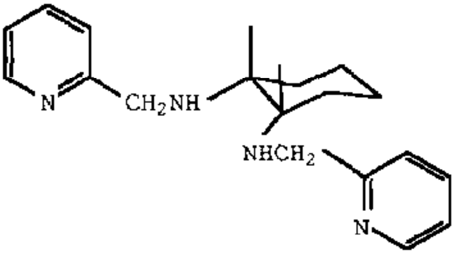
This section begins with pyridine-based ligands, works through bipyridine, and phenanthroline ligands, and culminates in a variety of more exotic heterocycles.

The extent to which solvent structure influences the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ has been investigated; the thermodynamics of solvolysis is discussed [185]. A related study looks at the solvolysis, and kinetics thereof, of *trans*-$[Co(4\text{-Me-py})_4Cl_2]^+$ in butanol-water mixtures; again, the thermodynamics of the process are detailed [186].



(36)

Some chemistry of the ligand picpn, **(36)**, has been discussed. Of the 40, theoretically possible, isomers of the complex $[Co(R\text{-picpn})L]^{2+}$, (HL = *R*- or *S*-alaH), five have been observed as products from a synthesis which begins with Λ-α-$[Co(picpn)Cl_2]^+$; high resolution ^1H n.m.r. spectroscopy is used to distinguish between the isomers [187]. The reaction of Λ-α-$[Co(picpn)Cl_2]^+$ with NO_2^- ion is reported to produce Λ-α-$[Co(picpn)(NO_2)_2]^+$, which undergoes stereospecific inversion to one of four possible Δ-β-isomers; treatment with HCl results in Δ-β-$[Co(picpn)Cl_2]^+$ [188]. The cation Λ-α-$[Co(R\text{-}picpn)Cl_2]^+$ reacts with $Na_2(ox)$ in a reaction which is accompanied by a total inversion of the absolute configuration with respect to the cobalt(III) centre [189]. The complex $[CoLCl_2][ClO_4].0.5H_2O$, (L = (**37**)), has been isolated as the Λ-β-diastereomer from the oxidation of cobalt(II) ions in HCl in the presence of the ligand, L; the new complex reacts with a range of ligands, retaining its configuration as it does so [190].



(**37**)

The rotational motion of the complexes $[Co(bipy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ in D_2O, as well as that of the analogous Ru(II) complexes, has been studied by using ^{13}C n.m.r. spectroscopy; relaxation time measurements indicate an isotropic motion for the ions. The rotational correlation times, τ, at infinite dilution, show a linear dependence upon η/T, where η is the viscosity of the solvent, and T is the absolute temperature [191].

Stability constants for outer sphere complexes of H_2edta^{2-} with $[Co(bipy)_3]^{3+}$, $[Co(phen)_3]^{3+}$, $[Co(en)_2(phen)]^{3+}$, $[Co(en)_3]^{3+}$, and $[Co(en)_2(bipy)]^{3+}$ have been measured; $K_{stab.}$ decreases as en is replaced by the heterocyclic ligand [192].

Assignments of the absolute configurations of the complexes $[CoL_2L']I_2.nH_2O$ in which L is bipy or phen, and L' is an amino acidato ligand, have been made; syntheses and optical resolution of the complexes have been described, along with their CD spectroscopic properties [193].

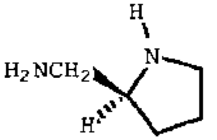
Quenching of the triplet excited state of some phthalocyanine complexes by the complex cations $[Co(bipy)_3]^{3+}$, $[Co(phen)_3]^{3+}$, and $[Co(terpy)_2]^{3+}$ has been investigated; a discussion of the kinetics of relevant electron transfer processes is presented [194].

The oxidation of $[CoL_3][ClO_4]_2$ by hydrogen peroxide to a cobalt(III) complex is successful for L = bipyrimidine, but fails for L = bipy or phen; a comparison of the electrochemistry of these complexes illustrates that the Co(II)/Co(III) couple has a potential which is significantly more positive for the bipyrimidine complex than for complexes with L = bipy or phen [195]. Details of the oxidation of a modified form of parsley plastocyanin, PCu(I)Cr(III), by $[Co(phen)_3]^{3+}$ have been presented, and the rate of reaction has been compared to that using $[Co(dipic)_2]^-$ as the oxidising agent [196].

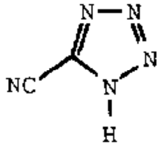
Diastereomers of the complex cation $[Co(S\text{- or }R\text{-}1,2\text{-pn})(phen)_2]^{3+}$ have been prepared and spectroscopically characterised; high stereoselectivity is noted, and the Λ-isomer of $[Co(S\text{-}1,2\text{-pn})(phen)_2]^{3+}$ is observed in preference to the Δ-isomer [197]. Preparation and isolation of diastereomers of $[CoL_3][tart]_3$, (L = Ph_2-phen), leads into a study of the application of this complex to stereospecific cleavage of DNA; incubation of *p-ColE1* DNA with $\Delta\text{-}[CoL_3]^{3+}$ produces cleavage of the DNA double helix, while repetition of the experiment using the Λ-diastereomer produces no such result [198].

Kinetic and mechanistic data for the acid-, base-, or Hg(II)-catalysed hydrolysis of *cis*-$[Co(en)_2(imidH)X]^{2+}$, ($X^- = N_3^-$ or NCS^-), illustrate that the coordinated $imid^-$ ligand labilises the Co-X bond ≈1000 times more than does the protonated imidH [199]. The complex cations $[Co(en)_2L(H_2O)]^{3+}$, for L = imidH, bzimidH, and imidMe, hydrolyse $4\text{-}O_2N\text{-}C_6H_4\text{-}OCOMe$ in the range pH 5.4 to 8.9; comparisons of the behaviours of the complexes as a function of the heterocyclic ligand, L, and of solution pH, are discussed [200]. Proton n.m.r. spectroscopic results for several cobalt(III) coordinated imidazoles have been reported; the study is complimented by determinations of pK_a values for the coordinated heterocycles [201].

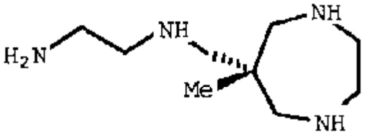
Two isomers of the complex *trans-(NO₂)*-$[Co(NO_2)_2L_2][ClO_4]$, (L = (**38**)), have been isolated by fractional crystallisation, and their structures assigned; starting from the nitro-derivatives, chloro-complexes have also been prepared, and concomitant changes in stereochemistry have been discussed [202].



(38)



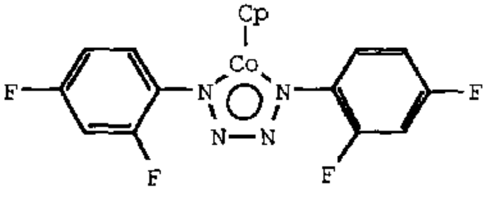
(39)



(40)

Attention is drawn to the explosive properties of the complex $[Co(NH_3)_5L][ClO_4]_3$, (L = (**39**)); the kinetics of the decomposition of this compound have been studied [203].

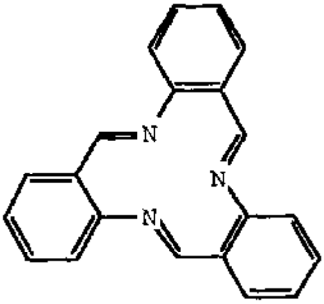
Reaction of *trans*-$[CoCl_2(py)_4]Cl$ with the ligands en, L, ((**40**)), and L', ($MeC(CH_2NHCH_2CH_2NH_2)_3$), leads to the formation of the complexes $[CoL']Cl_3$ and $[Co(en)L]Cl_3$; the latter has been structurally characterised as the ClO_4^- salt, and details of the absorption spectra are also presented [204]. A photochemical investigation of the cobalt(III) complex, CpCoL, (**41**), illustrates an interesting loss of dinitrogen, and rearrangement which involves aryl C-H bond fission, and C_{aryl}-N bond formation [205].



(41)

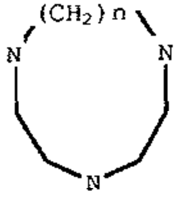
2.2.7.7 Macrocyclic ligands

For the ligand cyclam, studies of proton exchange and the base catalysed hydrolysis of its complexes *trans*-[$CoCl_2$(*RSSR*-L)] and *cis*-[$CoCl_2$(*RRRR*(*SSSS*)-L)] have been presented; the ratio of rate constants for solvolysis:reprotonation for the former complex is 0.79±0.15, whereas for the latter complex, proton exchange is faster than base hydrolysis [206]. The preparation and characterisation of the cobalt(III) complex cation $[CoL_2]^{3+}$, (L = (**42**)), have been reported, along with a discussion of outer sphere electron transfer reactions involving this, as well as related N-donor heterocyclic and macrocyclic ligand Co(III) complexes [207]. The complex $[Co(NH_3)_3L]^{3+}$, (L = (**43**)), and its analogue which contains the *R*-2-Me-derivative of L, have been investigated; the spectral properties of these complexes are compared with those of $[CoL_2]^{3+}$ and $[Co(NH_3)_6]^{3+}$ [208]. The green complex, *trans*-$[CoLCl_2][ClO_4]_2$, (L = (**44**)), is susceptible to axial ligand substitution; for the *cis*-complex, the coordinated ligand, L, is able to undergo a change in configuration [209].



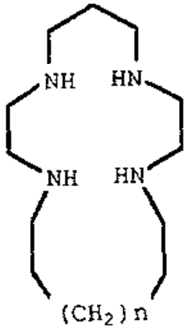
(**42**)

Structural characterisation of $[Co(CO_3)(Me_2\text{-cyclen})][ClO_4]$ and solution n.m.r. spectroscopic studies have been described; the cobalt(III) centre is octahedrally disposed, with the carbonate ion lying in the equatorial plane: Co-O = 1.910(6), 1.909(5)Å, Co-N = 1.915(6), 1.925(6), 2.007(5), 2.007(5)Å [210]. Two papers by the same authors describe the complex cations $[CoCl_2L]^+$ in which L is the *C-meso-* or *C-rac*-tetradentate cyclic ligand, (**45**) or (**46**) respectively; details of the configuration of the coordinated ligand, and the results of aquation studies, are presented [211,212]. A hexamethyl-derivative of (**45**), L, forms *trans*-[$CoCl_2L'$] *via* an oxidation route; during the reaction, one Me group of L is converted to a $-CH_2OH$ residue [212a] The preparation of the ligand, L, (**47**), and of some of its complexes, (*e.g.* $[CoLCl][ClO_4]_2$, $[CoL(CO_3)][ClO_4]$, $[CoL(O_2CCH)][ClO_4]$), have been described, along with some chemistry of the complexes [213]. A polyammonium macrocyclic ligand has been successfully employed in the control of photosubstitution reactions at Co(III) centres; the macrocycle encapsulates $[Co(CN)_6]^{3-}$, thereby hindering reaction [213a].



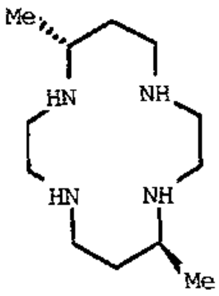
n = 1,2

(43)

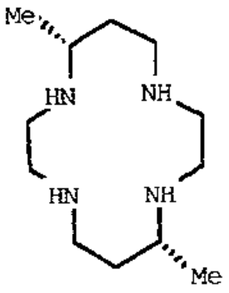


n = 1,2

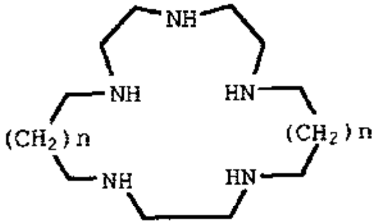
(44)



(45)



(46)



n = 1,2

(47)

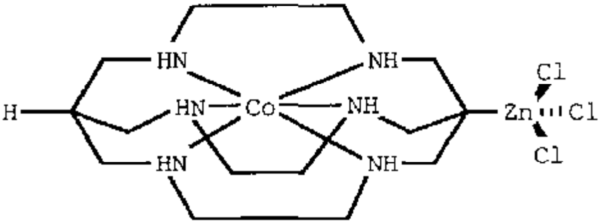
Cobalt(III) complexes containing porphyrin ligands are, of course, numerous in the literature. The thiolate reduction of $[Co(TPP)]^+$ gives $[Co(TPP)]^-$, X-ray structural characterisation of which illustrates significant back donation of charge from the metal ion to the porphyrin π-system, ($Co-N_{av.}$ = 1.942(3)Å) [214]. In ethanol, [Co(TPP)Cl] loses the axial chloride ligand, and accepts two axial EtOH molecules; studies of the optical and e.s.r. spectra of the one electron reduced form of [Co(TPP)Cl] are presented [215]. Related work discusses three paramagnetic species which are observed in single crystals of [Co(TPP)Cl]; the radical cation $[Co(TPP)]^{2+\bullet}$ is identified as one of the species present [216]. Changes in the MCD spectrum which accompany the photo-oxidation of $[Co(TPP)]^+$ to $[Co(TPP)]^{2+\bullet}$ have been described, and a reaction mechanism is proposed [217].

The syntheses and structures of two bis(mercapto)-cobalt(III) complexes which may act as model systems for the active site of cytochrome P-450 have been reported; in $[Co(SC_6HF_4)_2(TPP)]^-$, the Co-N distances are 1.978(4) and 1.976(4)Å, and Co-S = 2.346(3) and 2.330(4)Å, whilst in $[Co(SC_6H_2Cl_3)_2(TPP)]^-$, the porphyrin is distorted, with shortened Co-N distances, (average 1.973(4)Å) [218]. Application to the chemistry of cytochrome P-450 is again noted in a report of octaethylporphyrin, ($OEPH_2$), complexes of cobalt(III) [219]. The photolysis of [Co(OEP)(CN)], (and some related Co(II) compounds), has been investigated [220].

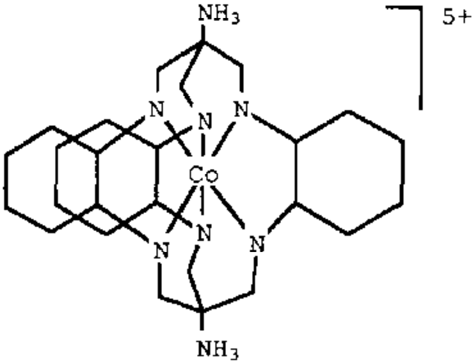
The catalytic properties of the complex cations $[Co(MTPP)]^+$, ($MTPPH_2$ = tetra(*p*-methyl)porphyrin), and $[Co(PTPP)]^+$, ($PTPPH_2$ = tetra(*p*-tolyl)porphyrin), in oxidation reactions have been investigated [221,222]. Factors influencing the catalytic activity of related complexes have been discussed [223].

At pH 4.0, the rate of substitution of axial py and NCS^- ligands attached to the porphyrin complex cation $[Co(M'TPP)]^+$, ($M'TPPH_2$ = tetra(*p*-methylammoniumphenyl)porphyrin), or $[Co(STPP)]^+$, ($STPPH_2$ = tetra(*p*-sulphonatophenyl)porphyrin), has been found to be proportional to the base strength of the parent free porphyrin [224]. The reaction of $[Co(TpyP)]^+$, ($TpyPH_2$ = *meso*-tetra(4-pyridyl)porphyrin), with a variety of amines, L, in 48% HBr gives complexes of type [Co(TpyP)Br(L)] in yields varying from 40 to 82% [225]. The kinetics of the complexation of cobalt(III) acetate with tetraphenyltetrabenzoporphine have been investigated; the phenyl substituents on the porphyrin moiety do not enhance the complexing ability of the ligand with respect to Co(III), although the reverse is true when the metal ion is either Zn(II) or Cd(II) [226]. Substitution of MeOH in [Co(PP)(MeO)(MeOH)] by py, 4-Me-py, or 4-CN-py follows a dissociative pathway [226a].

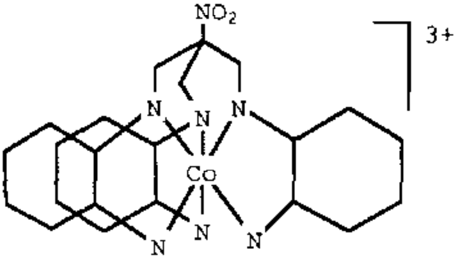
Sepulchrate complexes, (sep = (**25**)), of cobalt(III) have been reviewed, with an emphasis on the $[Co(sep)]^{3+/2+}$ redox couple [227]. The reduction of $[Co(chloro\text{-}sar)]^{3+}$, (sar = (**30**)), by zinc metal leads to insertion of the Zn atom into the C-Cl bond; ^1H and ^{13}C n.m.r. spectroscopic and electrochemical data are recorded for the product, (**48**), and a structural analysis reveals distances for Co-N bonds ranging from 1.971(4) to 1.988(4)Å. The Zn-C bond, (2.049(4)Å), in complex (**48**) is stablised by the electron withdrawing effect of the CoN_6 unit [228]. A new pentacyclic, metal ion cage system has been prepared; the cage complexes are configurationally and conformationally rigid. Complex (**49**), is prepared *via* a dinitro-derivative, but reaction conditions must be carefully controlled to prevent the formation of (**50**) as the final product; spectroscopic and electrochemical properties of the



(**48**)



(**49**)



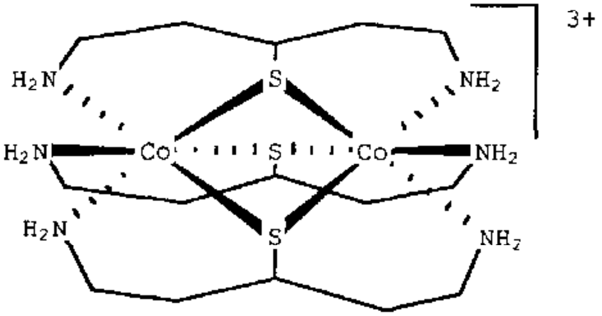
(**50**)

complexes are reported [229]. A discussion of the kinetics of quenching the excited state of some polypyridine ruthenium(II) complexes by $[Co(sep)_3]^{3+}$ has been presented; parallel reaction pathways are evidenced [230].

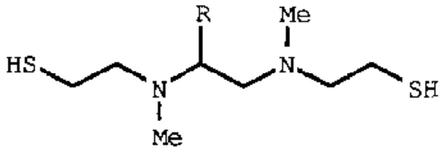
2.2.8 Complexes with nitrogen-sulphur donor ligands

2.2.8.1 Aminothiols and related ligands

The preparation and spectroscopic characterisation of the complexes $[CoL_3]$, (HL = $H_2N(CH_2)_2SH$, $Me_2N(CH_2)_2SH$, $Me_2N(CH_2)_3SH$), and $[Co_3L_6]X_3$, (HL = $H_2N(CH_2)_3SH$; X = Cl or Br), are reported [231]. An analysis of the CD spectra of $[Co(en)_2L]^{2+}$, $[Co(tren)L]^{2+}$, and $[Co(L')_2L]^{2+}$, (HL = $H_2NCH_2CH(Me)XH$ with X = S or Se; L'= *(R,R)*-1,2-$(H_2N)_2C_6H_{10}$)), accompanies preparative details [232]. The aminothiol ligand $H_2N(CH_2)_2CH(S^-)(CH_2)_2NH_2$ complexes with cobalt(III) ions to give a binuclear complex; the structure shown in **(51)** is proposed on the basis of spectroscopic data [233].



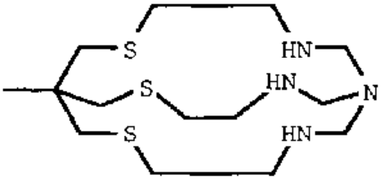
(**51**)



(**52**)

Several complex cations of the general formula $[CoLL']^+$ in which H_2L is the tetradentate S-N-N-S donor ligand, (**52**), and L' is a diamine, (en, 1,2-pn, or 1,2-$(H_2N)_2C_6H_{10}$), have been synthesised and characterised; both aminothiol ligands give the *cis*-α- and *cis*-β-isomers of $[CoLL']^+$ [234]. The preparation of a series of [2]-[[$(en)_2Co\{H_2N(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]Cl_6$]- [$\alpha$- or β-CDX]-rotaxanes has been reported to proceed with partial stereoselectivity; details of the spectroscopic properties of the complexes are presented [235].

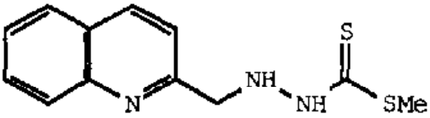
Cobalt(III) complexes containing some SN-ligands, (e.g. (**53**)), related to sep, (**25**), and sar, (**30**), have been prepared; the cavities of the mixed donor ligands are larger than those of their all N-donor counterparts. Some electrochemistry of the complexes is described [236].



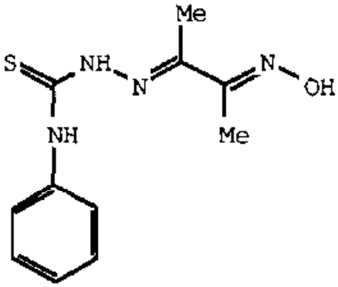
(**53**)

2.2.8.2 *Thioamides and related ligands*

The octahedral complex, $[Co(HL)_3]Cl_3$, in which HL = $H_2NNHC(S)OEt$, has been prepared and characterised spectroscopically and magnetically; the complex exhibits effective antifungal activity [237]. The dithiocarboxylate derived ligand, HL, (**54**), and its 3-quinoyl analogue, form the complexes $[CoL_2](NO_3)$ and $[CoL_2]_2[CoX_4]$, (X = Cl, Br, I, NCS, NCSe); spectroscopic and magnetic characterisation evidence a tridentate N-N-S-coordination mode for L^- [238]. Another N-N-S-donor is L^{2-} where H_2L is the thiosemicarbazone, (**55**); the reaction with Co(III) ions illustrates a pH dependence for the active denticity of the ligand [239].



(**54**)



(**55**)

2.2.9 Complexes with nitrogen-phosphorus donor ligands

The only entry for this section is $[CoL_2L']Br_3.2H_2O$, in which L is $H_2NCH_2CH_2PMe_2$ and L' is $Me_2PCH_2CH_2PMe_2$. The complex has been prepared, but of the three possible isomers, only one has been confirmed structurally; the cobalt atom is octahedrally sited, with each N-donor *trans* to P-donor. Pertinent bond lengths are $Co-P_L$ = 2.294(3), 2.245(4)Å, $Co-N_L$ = 2.047(10), 2.058(10)Å, and $Co-P_{L'}$ = 2.273(4), 2.295(3)Å [240].

2.2.10 Complexes with phosphorus donor ligands

Firstly, a cross reference [240] to the complex $[Co(Me_2PCH_2CH_2PMe_2)(H_2NCH_2CH_2PMe_2)_2L]Br_3.2H_2O$, described above, should be made.

The photophysical and photochemical properties of two cobalt(III) complexes containing the phosphite ligands, $(MeO)_2P(CH_2)_2P(OMe)_2$, (L), and $P(OCH_2)_3CMe$, (L'), have been described; values for λ_{max} of 620 nm and 700 nm were recorded respectively for the complexes $[CoL_3][ClO_4]_3$ and $[CoL'_6][ClO_4]_3$ [241].

2.3 COBALT(II)

2.3.1 Complexes with halide and pseudohalide ligands

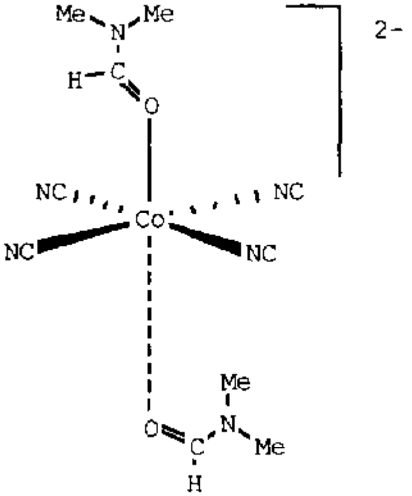
Comments on the structure of the $[CoCl_4]^{2-}$ ion in different environments have been made. In the cyclohexylammonium salt, the $[CoCl_4]^{2-}$ ion exhibits slight distortion from tetrahedral symmetry due to the cation-anion association which leads to chains following the directions of the crystallographic *b*- and *c*-axes [242]. The anions present in the blue 2-, 3-, or 4-acetylpyridinium complexes, $[LH]_2[CoCl_4]$, show little distortion from tetrahedral symmetry [243].

Cobalt(II) chloride solutions containing $Cl^-:Co^{2+}$ ions in a ratio 4:1, 6:1, or 7:1 have been investigated; a comparison of the complexes evidenced by X-ray analysis has been presented [244]. Formation constants for the complexes $[CoCl_n]^{2-n}$ (n = 1-4) have been determined from distribution coefficient data for solutions containing aqueous $CoCl_2$, $MgCl_2$ or $CaCl_2$, and H_2TBP [245]. The extraction of cobalt(II) chloride from HCl solutions by using Hyamine-1622 has been studied [246].

The preparation and characterisation of diaminium salts of cobalt(II) chlorides have been described; for n = 3, 5-10, $[H_3N(CH_2)_nNH_3][CoCl_4]$ is the formula proposed, but for n = 2, the complex product is formulated as $[enH_2]_2[CoCl_6]$ [247]. When dissolved in benzene, the complex $[(n\text{-}C_8H_{17})_3NH]_2[CoCl_4]$, gives rise to species $[(n\text{-}C_8H_{17})_3NH\cdots Cl\cdots HN(n\text{-}C_8H_{17})_3]^+$ [248].

Studies of the anions $[CoX_4]^{2-}$ for X^- being Cl^-, Br^-, or I^- have led to determinations of crystal field parameters [249]. X-ray diffraction studies of concentrated aqueous solutions of cobalt(II) bromide show the presence of $[CoBr(H_2O)_5]Br$, exhibiting an octahedral geometry as expected [250].

An unusual coordination environment has been evidenced around the cobalt(II) ion in $[PPN]_2[Co(CN)_4]$; the complex is formed by the reaction of $Co(CN)_2$ with 4 equivalents of [PPN]Cl in dmf, and, when spectroscopic and magnetic data failed to confirm the anticipated tetrahedral geometry, X-ray crystallographic data were collected. The structure shown in (**56**) was elucidated. The axial Co-O distances of 2.64 and 5.89Å are indicative of one bonding and one non-bonding interaction respectively, while the Co-CN distances of 1.869(15)Å through to 1.875(14)Å are unusually short [251]. Studies of the magnetic susceptibility of the complex $[Co(CN)_2].L$, (L = dmf, dmso, dma), over the temperature range 78



(**56**)

to 320K have been reported [252]. Mechanistic details of the reaction of aqueous $[Co(CN)_5]^{3-}$ with molecular hydrogen have been discussed, emphasising the effects of varying the ionic strength of the reaction medium [253].

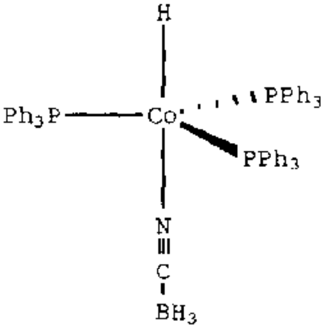
The preparation, and spectral and magnetic characterisation of the complexes $[HCo(NCS)_{3-m}X_m].nL$, (X = halide; m = 0, 1, 2; L = Et_2O, py, $PhNH_2$; n = 1.5, 2, 3, 3.5), illustrates pseudo-tetrahedral complex anions [254]. Structural characterisation of the substituted [18-crown-6] salt of $[Co(NCS)_4]^{2-}$ confirms a tetrahedral anion, with the crown ether cations hydrogen bonded to solvate acetone molecules [255]. A report of the preparation and spectroscopic characterisation of $[R_4N][Co(SCN)_3L]$, (R = Me, Et; L = 4-Me-py, 4-Et-py, 4-HO-py), and $[R_4N]_2[Co(SCN)_4L']$, (R = Me, Et; L' = bipy, phen), proposes tetrahedral and pentagonal complexes respectively [256]. By using UV-spectrophotometric data, stability constants for the complex ion, $[Co(SCN)_n]^{2-n}$ have been tabulated in dmso/acetone/water solvent systems [257].

The reaction of $[Co(NH_3)_5X]^{n+}$ with NaNCS, for X^{n-} being various simple ligands, gives, initially, a mixture of S- and N-bonded isomers which finally equilibrate; an accurate determination of the S:N capture ratio of 2.0±0.1 has been made, and the results compared with previously published data [258].

As part of a study of several first row transition metal perchlorates, the apparent molar volume and molar conductivity in dmf, (25°C), of $Co(ClO_4)_2$ has been measured [259]. Twenty four, pseudo-tetrahedral complexes of general formula $[CoL_2X_2]$, (X = Cl, Br, I, NCS; L = PPh_3, $OPPh_3$, $SPPh_3$), have been synthesised and spectroscopically characterised; analyses of the electronic spectra, including discussions of Racah parameters, are presented [260]. The effect of the leaving group upon the steric course of the base hydrolysis of the complex cations *cis*- and *trans*-$[Co(en)_2X]^{n+}$, (X = Br^-, Cl^-, $OSMe_2$, Me_2NCHO, N_3^-, HCO_2^-), has been investigated; a short lived intermediate in which X or X^- is held close to, but strictly dissociated from, the cobalt(II) centre is postulated [261].

Finally, the cobalt hydride species, $[HCo(H_3BCN)(PPh_3)_3]$, **(57)**, is a complex of special interest, and rather difficult to categorise within the confines of this review. The complex has been synthesised and structurally elucidated; the metal atom coordinates a hydride ligand in the axial site, (Co-H = 1.42Å; Co-N =

1.904(8)Å), and the equatorial phosphine ligands are observed to bend towards to hydride position, (Co-P = 2.291(3), 2.245(3), 2.234(3)Å) [262].



(57)

Finally, the synthesis, and magnetic and e.s.r. properties of the complex [$(^tBu_2NO)_2CoBr_2$] have been presented; on aging, a marked variation in $\mu_{eff.}$ is observed, due to the formation of a paramagnetic species [263].

2.3.2 Complexes with oxygen donor ligands

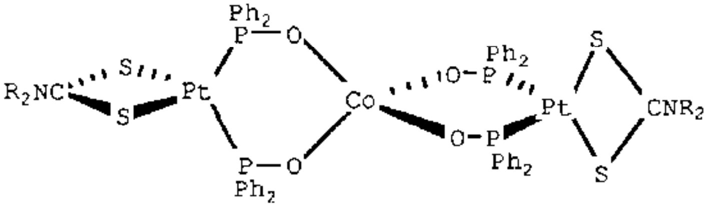
2.3.2.1 Selenite, phosphate, and related ligands

The thread running through this section is that of ligands derived from inorganic acids. The preparation, and physicochemical characterisation of some polymeric selenito cobalt(II) complexes have been reported; purple [$5CoSeO_3.Co(OH)_2$].$15H_2O$, magenta [$CoSeO_3.Co(OH)_2$].$17H_2O$, and pink [$5CoSeO_3.Co(OH)_2$].$19H_2O$ are all species in which the cobalt atom is high spin, and is in a distorted octahedral environment. Low magnetic moments are observed, and these are attributed to antiferromagnetic coupling [264]. The thermolysis of the complex [$Co(S_2O_6)$].$6H_2O$ leads to partial degradation, with simultaneous loss of water and sulphur dioxide resulting in stable cobalt(II) sulphates [265].

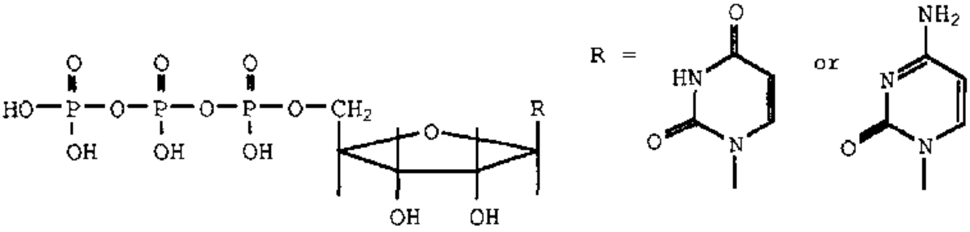
The proton affinity of cobalt(II) oxide has been determined to be 219±5 kcal mol^{-1}; values for the Co^+-OH bond dissociation energy were measured as 71±6 kcal mol^{-1} by a proton transfer method, and 71±3 kcal mol^{-1} from photodissociation studies [266]. The thermal conductivity of the complex [$Co(H_2O)_6$][NO_3]$_2$.nH_2O has been shown to depend linearly upon n, but only for values of $n \geq 5$; a nonlinear relationship is followed for $0 \leq n \leq 5$ [267].

Infra red, ^{31}P n.m.r., and electronic spectroscopy have been used to investigate the association in CCl_4, benzene, or hexane solutions of the complex $[CoL_2]$, in which HL = $H(2\text{-Et-}C_6H_{13})_2PO_4$ [268]. The complex $[Pt(S_2CNR_2)(PhPO)_2H]$, (R = Et; $CHMe_2$), reacts with $[Co(acac)_2]$ to give a product, which, on the basis of spectroscopic evidence, is proposed to have the structure shown in **(58)** [269].

Complexation of the polyphosphate ligand L^{3-}, (H_3L = **(59)**), with cobalt(II) ions has been studied potentiometrically over the temperature range 298-318K; the thermodynamics of complex formation are discussed [270], and should be compared with the results of a related study [271]. Complex formation of Co(II) with adenosine- and histamine-5'-phosphates has also been described [272]. A structural investigation of the coordination of ATP to cobalt(II) ions illustrates that attachment by the α-, β-, and γ-phosphate moieties blocks any potential interaction between the Co^{2+} centre and the adenosine base [273].



(58)



(59)

2.3.2.2 Carboxylate ligands

An investigation, including detailed solubility data, of the formate complex, $[Co(HCO_2)_2].2H_2O$, has lead to the identification of a new species, $K_3[Co_2(HCO_2)_7].2H_2O$ [274, 275].

Low temperature infra red and Raman spectroscopic results for hydrated cobalt(II) acetate has confirmed the presence of one type of carboxylate ligand, and two modes of coordination for the water molecules [276]. The same authors have illustrated the temperature dependence of the infra red and Raman vibrational modes in $[Co(OAc)_2.4X_2O]$, (X = H or D). Two discontinuities, attributed to dynamic processes involving the water molecules, arise at 270±5 and 140±5 K, and a further discontinuity at 213±5 K is explained by considering the dynamics of the methyl group of the carboxylate ligand [277]. Infra red spectroscopic data for $[Co(OAc)_2.2H_2O]$ support the existence of both strong and weak hydrogen bonding [278]. UV-visible absorption spectra for aqueous $[Co(OAc)_2]/[KOAc]$ have been interpreted in terms of the presence of various complexes and cluster structures in solution [279].

The solubility of cobalt(II) acetate in hexane-, benzene-, or cyclohexane-acetic acid mixed solvent systems has been investigated spectrophotometrically; association constants have been determined [280].

The structure of $[Co_2(Cl_2CHCO_2)_4(Me_2NCH_2CH_2NMe_2)(\mu\text{-}H_2O)]$ has been elucidated; each Co(II) ion is in a distorted octahedral site, with two of the four dichloroacetate ligands bridging the metal centres, and one $Cl_2CHCO_2^-$ ligand terminally attached to each metal atom. The bridged Co----Co separation is 3.675(1)Å [281]. A dimeric complex is also proposed as the product of the reaction of 2-ethylhexanoic acid with $[Co(OAc)_2]$ [282].

The thermal decomposition of hydrated cobalt(II) propanoates has been described; details of the decomposition pathway, (the final product of which is the metal oxide), are presented [283]. The reaction of cobalt(II) nitrate with $CH_3CH(Et)(CH_2)_3CO_2Na$ in aqueous solution has been shown to be pH dependent [284].

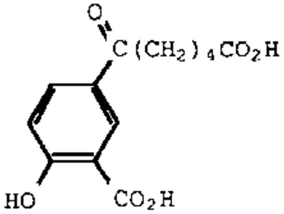
The electronic structure of *trans*-$[Co\{(\pm)HL\}_2(H_2O)_2].2H_2O$, in which $H_2L = HO_2CCH_2CH(OH)CO_2H$, has been discussed in detail, and the results are in agreement with the D_{2h} symmetry observed in the previously reported X-ray structure of the compound [285].

Stability constants for several cobalt(II) citrate complexes have been determined by ^1H n.m.r. techniques [286]. The reaction of $[Co(NH_3)_6]^{2+}$ with tartrate ion to give [Co(tart)] has been followed spectroscopically; coordination of the $tart^{2-}$ ligand is proposed to be *via* the carboxyl-O and the -OH moieties [287]. The preparation and characterisation of the high spin dinuclear complex, $[Co_2L(H_2O)_6)]$, ($H_4L = HO_2CCH_2CH(CO_2H)SCH(CO_2H)CH_2CO_2H$), has been reported; it is suggested that the ligand L^{4-} coordinates *via* the CO_2^- groups, and that water molecules, or bridging hydroxide ions, complete the octahedral coordination sphere about each metal ion [288].

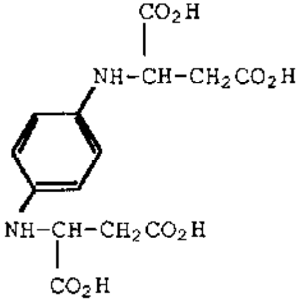
Anhydrous cobalt(II) chloride reacts with R_2NH, (R = Et; ^iPr), and carbon dioxide to give the multicentred complexes $[Co_n(O_2CNR_2)_{2n}]$, the reactivity of which has been discussed. For R = Et, the hexanuclear purple complex has been structurally characterised, and shows an interesting variety of carbamate coordination modes. The complex exhibits three distinct cobalt atom environments, related to the second set of three metal centres by a 2-fold rotation axis; coordination about four of the cobalt ions is essentially trigonal bipyramidal, while two of the ions are octahedrally sited. The average Co----Co distance is 3.178(5)Å [289].

The complex $[Co(salH)_2].4H_2O$ has been prepared in basic solution, and fully characterised [290,291]. Thermal analysis of *trans*-$[Co(salH)_2].4H_2O$ illustrates initial dehydration occurring between 70-140°C, followed by decomposition at 300°C to [Co(sal)], and above 313°C, to Co_3O_4 [291,292]. Stability constants for various $[Co(salH)_2]$ related complexes have been determined, as well as dissociation constants for the protonated ligands [293]. A report of the preparation and characterisation of $[Co(HL)_2]$, (H_2L = (**60**)), proposes that the ligand is bidentate [294].

Complexation studies of H_4L, (**61**), with cobalt(II) ions, have shown that both acidic and neutral complexes may form; stability constants have been determined for these species, and for complexes of other transition metal ions with H_4L [295]. The syntheses and physicochemical characterisation of the dinuclear complexes $[Co(O_2C-C_6H_4-R)_2L]_2$, (R = H, 4-Me, 2-Cl, 4-NO_2; L = quin-*N*-oxide), have been described; unusually low magnetic moments, and anomalies in the electronic spectra suggest the presence of a μ-CO_2 supported Co---Co interaction [296].

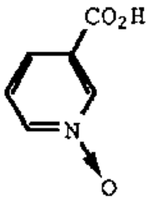


(60)

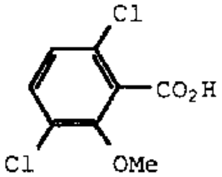


(61)

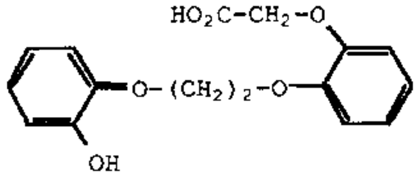
The dicarboxylic acid, 4-HO_2C-C_6H_4-OCH_2CO_2H, (H_2L), has the potential to be either a mono- or bidentate oxygen donor. This flexibility has been the focus of attention in a study of the complexation of H_2L with cobalt(II) and nickel(II) ions; the product of each reaction is *trans*-$[M(HL)_2(H_2O)_4]$, (M = Co or Ni), and the structure of the nickel complex has been confirmed by X-ray analysis [297]. In the same vein, the competition between carboxyl and *N*-oxide functional groups in HL, (**62**), is of interest; the structural elucidation of *trans*-$[CoL_2(H_2O)_4]$ shows the cobalt centre to be in a flattened octahedral site, and attached to the carboxylate portion of the ligand. The *N*-oxide functions are involved in intermolecular hydrogen bonding; inner sphere bond distances are Co-$O_{carboxyl}$ = 2.102(1)Å and Co-O_{water} = 2.072(1) and 2.113(2)Å [298]. The complex *cis*-$[CoL_2(H_2O)_4]$, HL = (**63**), exists as a polymeric material with an overall stoichiometry of $[CoL_2(H_2O)_3]$; the compound is isostructural and isomorphous with $[ZnL_2(H_2O)_3]$, the structure of which has been crystallographically determined [299]. The ligand HL, (**64**), and its salt, $K[HL_2]$, have been prepared, and structurally characterised; $K[HL_2]$ may be converted to $[Co(KL_2)_2]$ by refluxing with cobalt(II) acetate in ethanol. The structures of $[Co(KL_2)_2]$ and the analogous complex, $[Co(RbL_2)_2]$, are discussed [300].



(62)



(63)



(64)

2.3.2.3 Oxalate ligands

The thermal decomposition of cobalt(II) oxalate has been studied by two independent groups. The first work illustrates decomposition of [Co(ox)] to cobalt metal, CoO, and $CoCO_3$; it is noted that reduction of the product system by CO_2 is thermodynamically favourable [301]. The second paper on the subject investigates the catalytic activity of the thermally decomposed [Co(ox)] system, and compares the results with those obtained for the analogous nickel(II) system [302].

The kinetics of the Ce(IV) oxidation of the coordinated oxalate ligand in the complex $[Co(ox)(NH_3)_5]$ have been studied; first order kinetics are obeyed, and a dependence upon $[H^+]$ is observed. The reaction is catalysed by Ag(I) and by Cu(II) ions [303]. In a related piece of work, the same authors report rate and activation parameters for the latter oxidation process [304].

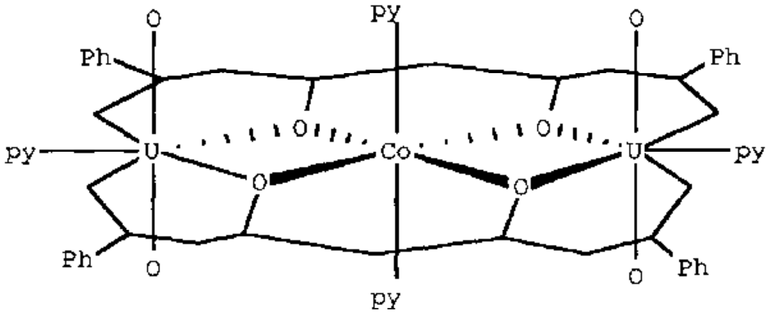
2.3.2.4 β-Diketonate and related ligands

The reaction of $[Co(acac)_2]$ with Ph_2SnCl_2 in pyridine is reported to lead to ligand exchange, and a series of cobalt(II) and tin(IV) mixed ligand complexes; techniques used to monitor the reaction include ^{119}Sn n.m.r. spectroscopy [305]. Related work involving the complexes $[Co(acac)_2(py)_2]$ and $[Co(acac)_2(py)_xCl]$, (x = 1,3), has also been presented [306]. The electrochemical reduction of $[Co(acac)_3]$ to $[Co(acac)_2]$ has been studied in detail, the interest being in the catalytic activity of species present in the system; the growth and decay of transient species is described [307]. The trifluoro- and hexafluoro-acac ligands, H(acac'), react with an equimolar amount of $CoCl_2$ or $Co(NO_3)_2$ and a two molar equivalent of hydrazine to give the complexes $[Co(acac')_2].2N_2H_4$; the products are thermally stable [308]. Solvent extraction studies have been carried out using the ligand L^-, (HL = $C_6H_5C(O)CH_2C(O)CF_3$); the efficiency of extraction of Co(II) and Ni(II) ions in aqueous NaCl with HL in CCl_4 has been measured as a function of the concentration of tetrabutylammonium ion present. In the absence of the organic cation, $[CoL_2]$ is isolated, whereas, with Bu_4N^+ present, the $[CoL_3]$-$[Bu_4N]$ ion pair forms [309].

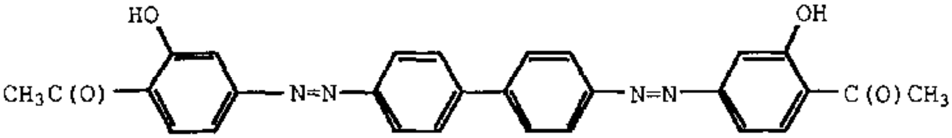
The preparation, X-ray structural characterisation, electrochemical behaviour, and UV-visible spectrum of the complex

$[(UO_2)_2CoL_2(py)_4]$, **(65)**, containing a tetradentate ligand, L^-, have been reported; each U---Co non-bonded contact is 3.5176(31)Å, and within the cobalt's inner coordination sphere, distances are Co-O = 2.040(9), 2.046(8)Å, and Co-N = 2.234(10)Å [310]. Complexation studies of another polychelating ligand, **(66)**, have been described [311].

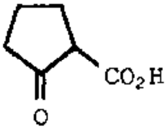
Ligation to cobalt(II) of the cyclopentanone derived ligand, **(67)**, gives the complex $[CoL_2(H_2O)_2]$, the UV-visible spectrum of which has been analysed; the absorption at 500 nm has been assigned to the spin allowed $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition [312]. Thermochemical studies involving the complexes $[Co(H_2L)_2].2ROH$ and $[Co(H_2L)_2].PrOH.H_2O$, (H_3L = **(68)**; R = H, Me, Et, Bu), have been reported; the $Co-O_{alcohol}$ bond dissociation energy is independent of the substituent R, suggesting that there are few steric effects [313].



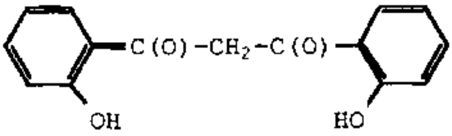
(65)



(66)



(67)

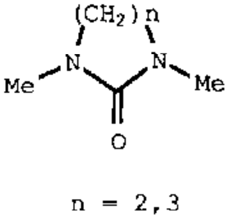


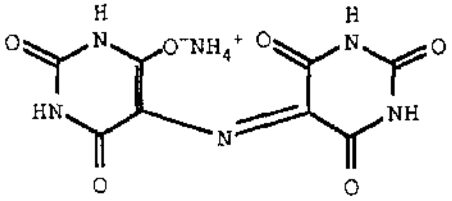
(68)

2.3.2.5 Amide, and amino acid ligands

Complex formation between cobalt(II) ions and

$CH_3C(O)CH_2C(O)NHPh$ has been followed potentiometrically; stepwise chelation occurs, to form initially [CoL], and then $[CoL_2]$ [314]. The structure of the clathrate coordination compound, $[CoBr_2].10(urea)$, has been investigated both by X-ray and neutron diffraction methods; the cobalt ion is octahedrally sited, and is attached to six separate urea molecules *via* Co-O interactions [315]. The preparation and characterisation by spectroscopic and magnetic moment measurements of the tetrahedral, high spin compounds $[CoL_2X_2]$, (X = Cl, Br, I; L = (**69**)), have been reported; each complex is a non-electrolyte in $MeNO_2$, but is partially dissociated in MeCN [316].


(69)


(70)

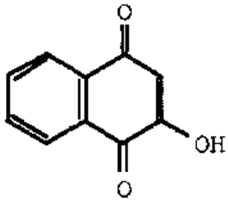
Murexide, H_2L, (**70**), forms two complexes with cobalt(II) ions, pH ≥ 5, *viz.* [CoL] and $[Co(HL)]^+$; equilibria data obtained for the cobalt(II) complexes have been compared with results appertaining to the analogous nickel(II) species [317].

Intramolecular electron transfer from cobalt to ruthenium centres *via* either an amino acid or a dipeptide chain has been studied; the kinetics and temperature dependency of the transfer have been described [318]. The interaction of cobalt(II) ions with glycine and adenosine nucleotides has been studied by using potentiometric titration methods; the formation and decomposition of the complexes have been investigated as a function of pH [319]. Stability constants for Co^{2+}-glyH complexes have been determined, at 35°C and ionic strength 0.1M, by electrophoresis methods [320]. Related work for complexes of $N(CH_2CO_2H)_3$ and serH has also been described [321]. Mono- and bis-cobalt(II) complexes of conalbumin have been prepared in the presence of bicarbonate ion; by using T_1 measurements, proton environments have been assigned in the ^1H n.m.r. spectra of the his and tyr residues [322].

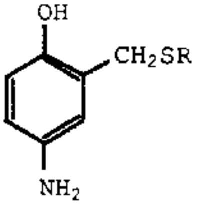
Determinations of thermodynamic parameters for the formation of complexes between $HO_2CCH_2CH_2CH(NH_2)CO_2H$ and cobalt(II) ions in aqueous dioxane over the temperature range 30° to 50°C have been reported [323].

2.3.2.6 *Phenolate ligands*

The stoichiometry of complexes formed between cobalt(II) ions and $3,4\text{-}(HO)_2\text{-}C_6H_4$ has been explored; stability constants have been determined [324]. The complexation of $1,3,5\text{-}(HO)_3\text{-}C_6H_3$ with Co^{2+}(aq) has been followed spectrophotometrically as a function of pH and of metal ion and ligand concentrations [325]. Pyrolysis of

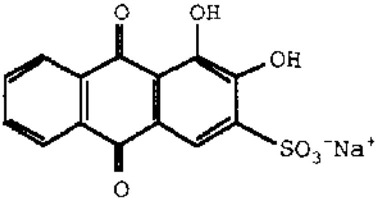


(71)



R = Et,
CH_2Ph,
$p\text{-}C_6H_4$;
X = Me,H,Cl

(72)



(73)

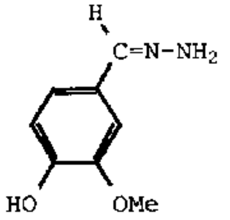
the complex $[CoL_2].nH_2O$, (L = **(71)**), (for which X-ray data is reported), proceeds by loss of water, followed by decomposition; first order kinetics are obeyed for the degradation [326].

Formation of complexes of the type $[CoL_n]$, in which L = 4-nitrocatechol, has been monitored as a function of pH by using potentiometric methods [327]. Structural characterisation of the complex $[Co(\mu_3\text{-}OMe)L(MeOH)]_4$, (HL = 2,4-dinitrophenol), shows the presence of a cubane-like central core, consisting of 4 Co atoms and 4 μ_3-OMe units, ($Co\text{-}O_{OMe}$ = 2.042, 2.094, 2.100Å); each L^- ligand is bidentate, with $Co\text{-}O_L$ = 2.001 and 2.133Å [328]. An associative mechanism has been proposed for the substitution of the ligand **(72)**, with cobalt(II) ions in solution [329]. A series of nineteen non-conducting complexes involving anthraquinone ligands, (e.g. **(73)**), has been prepared and characterised physicochemically [330].

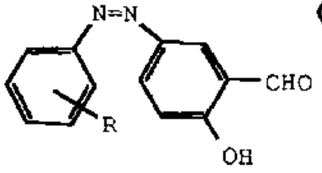
Complexes of the general formula $[CoL_2X_2]$, in which L is a 4-substituted-2,6-dichlorophenolate, have been the subject of a ^{35}Cl n.q.r. spectroscopic study; an inverse correlation between the difference in frequency of the coordinated and non-coordinated o-Cl and the Co-Cl bond length has been illustrated [331].

The reaction of 1-nitroso-2-naphthol, HL, with $[Co(acac)_2]$

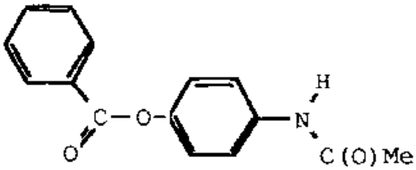
in refluxing aqueous KOH leads to the complex [Co(acac)L].nH_2O, which, on heating to 130-150°C, loses water; treatment of [Co(acac)L].nH_2O with py produces [Co(acac)L(py)$_2$]. Spectroscopic characterisation of the latter complexes suggests octahedral coordination in all cases [332]. The preparation, and characterisation by spectroscopic and magnetic moment measurements of [CoL_2(H_2O)$_2$], (HL = (**74**)), suggests a low-spin, octahedral complex, containing L^- as an O-O donor [333]. Thermodynamic parameters relating to the formation of 1:1 and 1:2 complexes of Co(II) ions with HL, (**75**), have been determined; the results of a solid state infra red study of the complex [CoLCl] imply chelation *via* the phenolic O- and aldehydic O-atoms of the ligand [334]. Finally, potentiometric methods have been used to determine stability constants for the 1:1 and 1:2 complexes of Co(II) ions with HL, (**76**), in 70% (by volume) ethanol over a temperature range of 25-45°C; comparison of these data with thermodynamic parameters measured for related complexes containing other transition metal ions has also been discussed [335].



(**74**)



(**75**) R = H; *o*-, *m*-, *p*-OMe
o-, *m*-, *p*-NO_2



(**76**)

2.3.2.7 *N-oxide ligands*

The preparation and characterisation of the dinuclear complexes [$Co_2(O_2CR)_4L_2$], (R = CH_2Cl, $CHCl_2$, CCl_3; L = quinoline-*N*-oxide) have been reported, along with the magnetic properties of the compounds [336].

2.3.2.8 *Macrocyclic ligands*

Ligand exchange involving [18]-crown-6 ether complexes of cobalt(II) has been reported; the kinetics of the stereochemical rearrangement of the uncoordinated part of the macrocycle in the complex [Co([18]crown-6)(CH_3OH)$_3$]$^{2+}$ are described [337].

2.3.3 *Complexes with oxygen-nitrogen donor ligands*

2.3.3.1 *Ethylenediaminetetraacetic acid and related ligands*

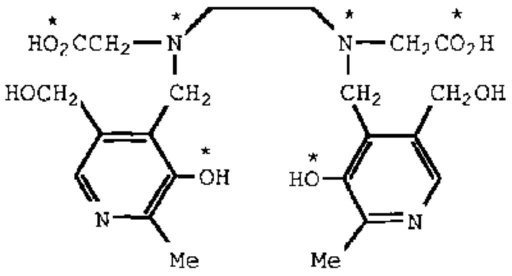
The kinetics of metal exchange reactions between $[Co(edta)]^{2-}$ and Cu(II) ions have been studied; the stability of intermediates has been investigated as a function of the concentration of the $edta^{4-}$ ligand [338]. Related work has been carried out by stopped flow techniques with the dependence of the reaction upon pH being the focus of attention; at a high pH, an associative pathway with a second order rate constant of 37 ± 1 dm^3 mol^{-1} s^{-1} is proposed [339].

A mixed Co(II)-Ni(II) complex of $edtaH_4$ has been found, by use of large angle X-ray scattering, to contain infinite chains of octahedrally coordinated metal ions; the units present are $[Co(H_2O)_6]^{2+}$ and $[Ni(edta)]^{2-}$ [340]. Similarly, characterisation of the dinuclear complex $[Co_2(edta)].6H_2O$ shows the presence of regular chains of $[Co(H_2O)_6]^{2+}$ and $[Co(edta)]^{2-}$ ions [341]. The preference for hydrated versus $edta^{4-}$ coordination spheres of various metal(II) ions including cobalt(II) has also been considered [342].

The kinetics of oxidation of aqueous $[Co(edta)]^{2-}$ by $S_2O_8{}^{2-}$ ions has been studied using spectrophotometric methods, and an overall second order rate equation demonstrated; the dependence of the reaction rate upon pH, ionic strength, and reagent concentration has been investigated [343]. The kinetics of the reversible redox system of $[Ru(NH_3)_5(pz)]^{3+}$ with $[Co(edta)]^{2-}$ has been investigated; mechanistic details reveal that the intermediate complex ion, $[(H_3N)_5Ru(II)\text{-}pz\text{-}Co(III)(edta)]^+$ dissociates *via* electron transfer, with a rate constant of 16.9 s^{-1} at 25°C [344].

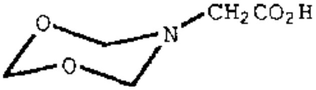
The synthesis of the ligand H_4L, (**77**), and its complexation with cobalt(II) ions have been described; formation constants for the complexes $[Co(H_2L)]$, $[Co(HL)]^-$, and $[CoL]^{2-}$, have been determined to be 8.46, 9.29, and 16.87 respectively, and have been compared with the corresponding equilibrium constants for $edtaH_4$ complexes [345].

Radiolysis, (γ-irradiated), of the complex [CoL], (H_2L = $HO_2CCH_2NHCH_2CO_2H$) has been explored; in addition, reaction of the complex with hydroxide ion shows attack both at the metal and ligand, with the ligand degrading to glyoxylic acid [346].


* = coordination site

(77)

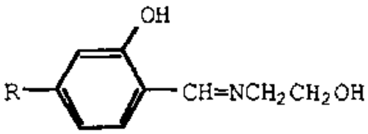
The pink complex $[CoL_2(H_2O)_2]$, (HL = (**78**)), has been prepared and characterised; the analogous Zn(II) complex has been structurally elucidated. $[CoL_2(H_2O)_2]$ reacts with H_2S to liberate glyH [347]. The ligand $\{RC(O)CH_2C(O)CHMeNHCH_2\}_2$, (R = ^tBu, Ph), is capable of presenting either an O_4 or an N_2O_2 donor set to a Co(III) centre depending upon the presence or absence of a secondary ligand, *e.g.* py [347a]



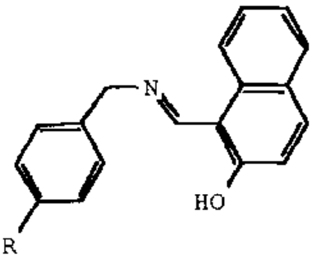
(78)

2.3.3.2 *Imine ligands*

The preparation and spectroscopic characterisation of the complexes $[CoL_2]$, (HL = (**79**)), have been reported [348,349].

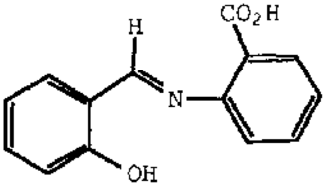


(79) R = H; OH



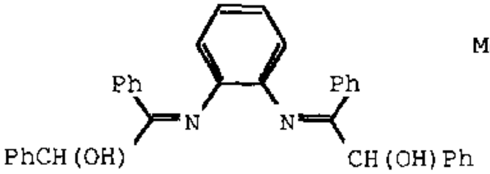
(80) R = H; CO_2Me

Potentiometric studies have been used to monitor the complexation of Co(II) ions with HL or H_2L, ((**80**), R = H or CO_2Me respectively); dissociation constants for ligands, and formation constants for the complexes have been determined [350,351].

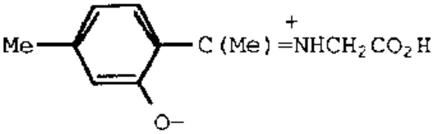


(81)

Complexation of HL, **(81)**, with cobalt(II) ions in coordinating solvents has been investigated by using n.m.r. and e.s.r. spectroscopy; the data has been interpreted to provide an insight into the mechanism for the spin delocalisation onto the ligand [352]. The dinuclear complexes $[Co_2L_2].4H_2O$ in which H_2L = $PhCH(OH)C(Ph)=N-C_6H_4-2-OH)$ or **(82)**, have been synthesised and physicochemically characterised; each metal centre is octahedrally coordinated [353]. Related work has been carried out using the ligand $PhCH(OH)C(Ph)=NCR_2CH(OH)R$, (R = H; Me) [354].



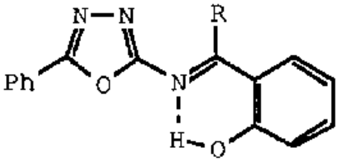
(82)



(83)

By using potentiometric titration methods, the interaction of $Co^{2+}(aq)$ ions with $H_2NC(=NH)N(Me)CH_2CO_2H$ over the temperature range 20° to 40°C has been observed; stability constants for the 1:1 and 1:2 complexes have been determined [355]. The preparation of H_2L, **(83)**, (predominantly existing in its keto-enamine form), and its brown cobalt(II) complex have been reported; the electronic spectrum of the complex, and a magnetic moment of 4.5 BM together imply a high spin tetrahedral metal centre [356]. The complexes $[CoLCl_2(H_2O)_2]$ and $[CoL(OAc)_2]$, in which L is the ligand $PhN=C(SCH_2Ph)N(Ph)C(O)NHPh$, have been synthesised and characterised; interest in these complexes lies in their potential antifungal activity [357].

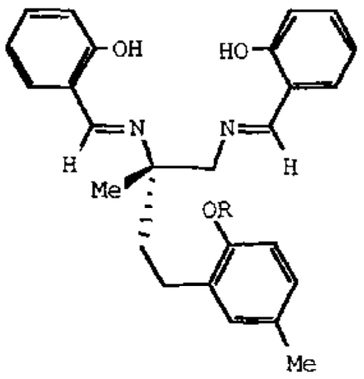
The imine HL, **(84)**, forms the complexes [CoLX], (X = Cl, Br, NO_3) [358], and $[CoL_2(H_2O)_2]$ [359]. For the latter octahedral complex, crystal field parameters have been determined [359].



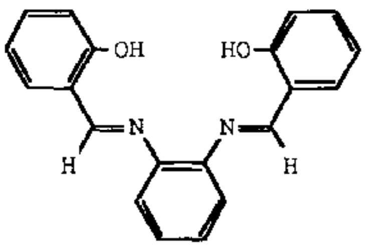
(84) R = H; Me

Complexation with cobalt(II) ions with a variety of Schiff base ligands derived from five substituted salicylaldehydes and $2\text{-}H_2N\text{-}C_6H_4CH_2OH$ has been investigated. Each ligand is proposed to be an O-N-O donor, and the complexes are dimeric non-electrolytes [360].

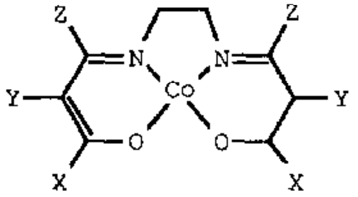
An electrochemical investigation of the complex [Co(salen)] in MeCN and dmf solutions has been presented; the effect of the supporting electrolyte concentration on the electrode kinetics is discussed [361]. The photolysis of [Co(III)(salen)R], (R = Me, Et, Pr, Bu), in 99% glycerin solution, leading to Co-R fission and reduction to [Co(salen)] has been discussed [362]. The one electron oxidation of [Co(salen)] occurs upon treatment of the complex with aryldiazonium salts; other related redox reactions have also been studied [363]. The presence of a phenolic residue on salenH_2 gives the quinquidentate ligands (sal-Hpen)H_2 and (sal-mpen)H_2, **(85)**; preparation of these Schiff bases, and their complexation reactions with transition metal ions, including Co^{2+}, have been described [364]. The dinuclear complex $[Co_2L_2]$, (H_2L = saloph, **(86)**), has been synthesised and characterised; a pseudotetrahedral environment for each metal atom, with no significant Co---Co interaction, is proposed [365]. The magnetic properties of the 5-coordinate complexes [Co(salen)L] and [Co(saloph)L], (in which HL = imidH, bzimidH, or derivatives thereof), have been reported in detail; the magnetic moment of [Co(saloph)(2-Me-imid] is relatively independent of temperature over the range 50-296K, but below 50K, $\mu_{eff.}$ falls significantly. The latter observation is interpreted in terms of zero-field splitting. The X-ray structural elucidation of [Co(saloph)(2-Me-imid] shows that the cobalt atom is 0.452(1)Å out of the plane of the Schiff base ligand; pertinent bond lengths are $Co\text{-}O_{saloph}$ = 1.973(3), 1.977(3)Å, $Co\text{-}N_{saloph}$ = 2.032(4), 2.127(4)Å, Co-N_{imid} = 2.073(4)Å [366]. The degree of interaction of solvent molecules with [Co(saloph)], to give a 5-coordinate species, has been investigated by using ^1H n.m.r. spectroscopy [367].



(85) R = H, Me



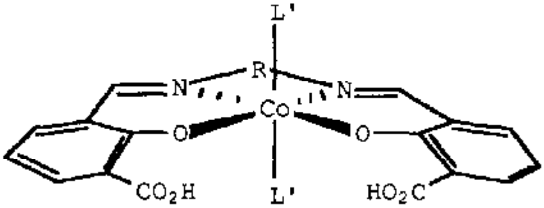
(86)



X	Y	Z
Me	H, Cl, succinimido, PhO	Me
Ph	H, Cl, succinimido	Me
Me	acetyl	H

(87)

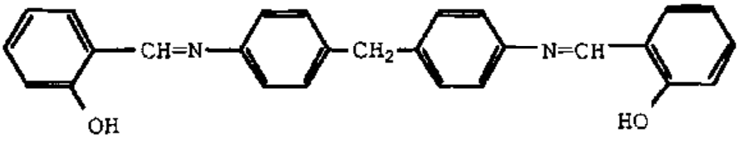
The preparation and characterisation by TGA of the complex [CoL], (H_2L = PhC(O)CH_2C(Me)=N$(CH_2)_2$N=C(Me)CH_2C(O)Ph), have been reported [368]. A series of complexes, **(87)**, has been studied with respect to the ability of each complex to coordinate axial py or molecular oxygen; the determination of redox potentials is reported, and a relationship between these values and the Hammett σ-constants of the substituents X, Y and Z has been developed [369]. High and low spin complexes of type [CoLL'$_n$], **(88)**, containing the Schiff base H_2L, have been studied, with the aim of probing ways of inducing spin crossover; for R = $-CH_2CH_2-$, L' = py, and n = 2, spin crossover is observed [370].



(88) R = $-CH_2CH_2-$, $-CH_2CH_2CH_2-$
L = py, β-picoline, 4-${}^tBu$-py
n = 1,2

The condensation of $HOC(CF_3)_2CH_2COMe$ with the diamines $H_2N\{(CH_2)_2O\}_n(CH_2)_2NH_2$, (n = 1,2), in the presence of Co(II) ions results in the template syntheses of the corresponding cobalt(II) imino complexes. For n = 2, the product has been structurally characterised; the metal ion resides in a distorted octahedral site, with the N-atoms of the N_2O_4 donor set being *trans* to one another. Bond distances within the inner coordination sphere are Co-N = 2.141(4), 2.132(4)Å, and Co-O = 2.317(4), 2.339(4), 1.952(4), 1.933(4)Å, with the ethereal O-atoms participating in the longer Co-O interactions [371].

The deprotonated form of the Schiff base, H_2L, **(89)**, possesses the ability to chelate *via* an O-N donor set to each of two adjacent cobalt atoms; the complex $[Co_2L_2(H_2O)_4]$ has been characterised, and exhibits an abnormally low magnetic moment [372].

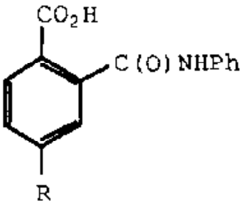


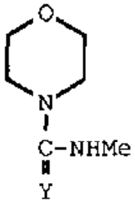
(89)

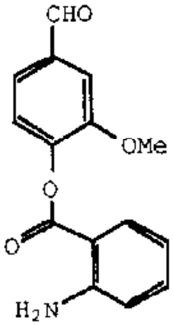
2.3.3.3 *Amido, amino acid, and related ligands*

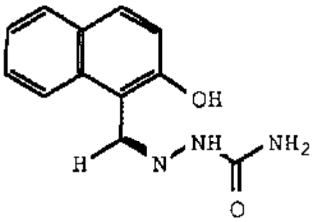
Related to the formation of the dinuclear complex described above is work by the same authors involving the tetradentate ligand $PhNHC(O)CH=C(Me)NH(CH_2)_3NHC(Me)=CHC(O)NHPh$; the complexes $[Co_2L_2X_4]$

in which X = Cl, Br, NO$_3$, or ClO$_4$, have been prepared and spectroscopically characterised [373]. The reaction of cobalt(II) hydroxide with HL, **(90)**, is reported to give the octahedral complex [CoL$_2$(H$_2$O)$_2$] [374]. The compounds [CoLX$_2$] and [CoL$_2$][ClO$_4$]$_2$, (L = **(91)**; X = Cl, Br, NO$_3$, 0.5SO$_4$), have been synthesised and physicochemically characterised; L coordinates *via* the morphilino-N and the (thio)amido-(S)O atoms, and the geometry of the former complex appears to be dependent upon the nature of X$^-$ [375]. Reaction of cobalt(II) ions with L, **(92)**, proceeds endothermically, and the stepwise formation constants of the product complexes at 30°C have been determined [376].


(90) R = H; Me; NO$_2$


(91) Y = O;S


(92)


(93)

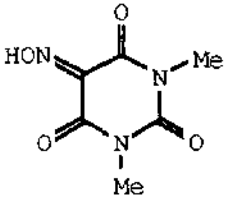
For a series of amido-anthranilic acids, HL, complexes [CoL$_2$(H$_2$O)$_2$] have been prepared and characterised; L$^-$ is consistently bidentate in its mode of chelation, but may either act as an O-N or O-O donor, depending upon the substituents present [377]. The mixed ligand, octahedral complex [CoLL'] in which L = anthranilic acid and L' = 1-nitroso-2-naphthol, has also been reported [378]. Further studies involving anthranilic acid relate to complexes formulated as [CoL$_2$].nH$_2$O and [Co(OH)L].3H$_2$O; spectroscopic and structural investigations have been complimented by thermal analyses [379].

The compound [CoL$_2$], (HL = **(93)**), has been isolated, and it is proposed from physicochemical evidence that the complex is octahedral; ligand field parameters have been reported [380].

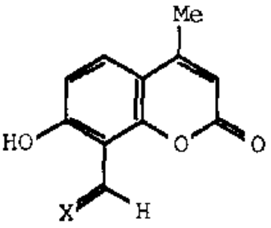
Cobalt(II) carboxypeptidase A has been structurally elucidated using X-ray diffraction methods; Co-N bond lengths are 2.13 and 2.06Å for the his-69 and his-196 residues respectively, and Co-O distances are 2.26 and 2.24Å for the glu-72 residue, and 2.00Å for the Co-OH_2 contact. The Co(II), Ni(II) and Zn(II) carboxypeptidase *A* structures are compared [381]. The mixed ligand complex [CoL(L-lysH.HCl)].nH_2O, (L = L-glutamic acid), has been prepared and characterised by spectroscopic and magnetic moment measurements; results suggest that the complex is octahedral, and that each ligand acts as an O-N donor [382].

2.3.3.4 Oxime ligands

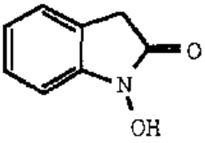
Although the ligands reviewed in this section may be categorised as oximes, their classification as N-O donors arises, on the whole, from the combined presence of the oxime moiety plus another functional group. Thermal decomposition studies, (by infra red spectroscopy and DTGA), of 2-HO-C_6H_4-C(O)NHOH, (HL), and of its complex $[CoL_2].2H_2O$ have shown that both compounds form intermediate *N*-hydroxylactams; kinetic and mechanistic details of the decomposition reactions have been discussed [383]. Conductiometric, potentiometric, and spectrophotometric methods have been applied to an investigation of the reaction of HL, **(94)**, with Co^{2+}(aq) to give the complex $[CoL_3]$ [384].



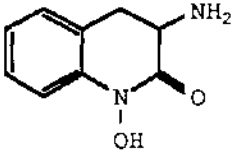
(94)



(95) X = O; N-OH



(96)

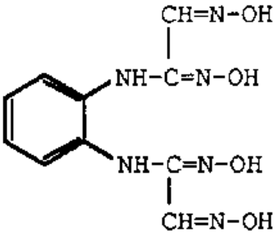


(97)

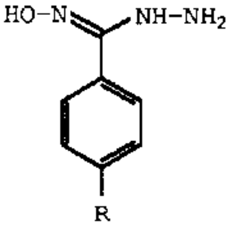
Complex formation between cobalt(II) ions and HL, **(95)**, in 70% (by vol.) aqueous methanol at 35°C has been described; stability constants have been determined, and some differences between the modes of coordination of HL to Co(II), Cu(II), and Ni(II) ions have been established [385].

The high yield syntheses of the pink and yellow complexes, $[Co(HL)_2(H_2O)_2]$, and $[Co(HL)_2]$ respectively, in which the ligands are the cyclic hydroxamic acids HL, **(96)**, and HL', **(97)**, have been reported. Based upon analytical, magnetic susceptibilty, and spectroscopic data, the authors have proposed polymeric structures for the compounds; in the case of HL', one suggestion is that the hydroxamic acid may ligate *via* the amino-N atom to one cobalt(II) centre, and chelate *via* the carbonyl-O and oxime-O atoms to an adjacent metal ion, thus facilitating the construction of chains of $Co(N_2O_6)$-units [386].

Condensation of 1,2-diaminobenzene with *anti*-chloroglyoxime at -5°C is reported to lead to H_4L, (**98**); reaction of the new ligand with Co^{2+} ions produces the binuclear species $[Co_2(H_2L)Cl_2(H_2O)_2]$ which has been spectroscopically characterised [387]. (For related work, the reader is referred to the section of S-O donors [421]). The preparation and infra red spectroscopic characterisation of the complexes $[Co(HL)_2(H_2O)_2]$, (H_2L = (**99**)), have been described; HL^- behaves as a tridentate, weak field ligand for the chloro-derivative, but as a bidentate, strong field ligand for the methyl- and methoxy-derivatives. This difference is attributed to increased electron density localised on the donor atoms when the substituent, R, is Me or OMe as compared to Cl [388]. A report of the preparation, and characterisation by spectroscopic and magnetic susceptibilty measurements of the complexes $[CoL].nH_2O$, (H_2L = 2-X- C_6H_4-C(O)NHN=C(Me)C(Me)=NOH; X = Cl, Me), has appeared; it is suggested that values of $\mu_{eff.}$ = 2.13 and 2.28 BM for X = Cl and Me respectively, are consistent with square planar species [389].



(**98**)

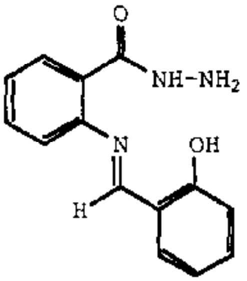


(**99**) R = *p*-Cl; *p*-Me; *p*-OMe

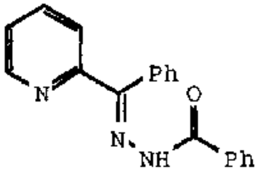
2.3.3.5 Hydrazide, hydrazine, and hydrazone ligands

Cobalt(II) complexes of H_2NNHCO_2H, (HL), and five methyl- and phenyl-derivatives thereof, have been prepared by bubbling carbon dioxide through a solution of $CoCl_2$ and the respective hydrazine; characterisation of $[CoL_2(H_2O)(N_2H_4)]$, $[CoL_2(H_2O)]$, and $[CoL_2]$ indicates octahedral coordination, with $RR'_2NNR''CO_2H$ acting as an N-O donor [390]. Spectroscopic characterisation of the newly synthesised complex $[CoL_3(S_2O_6)].nH_2O$, ($L = NCCH_2C(O)NHNH_2$; n = 1,2), suggests that the metal ion is in an octahedral environment, and that the $S_2O_6^{2-}$ ion is an outer sphere ligand [391]. The same authors have also reported the reactions of CoX_2 with $PhOCH_2C(O)NHNH_2$, (HL), to form the complexes $[Co(HL)_3X_2].nH_2O$, (X = Cl, NO_3, or $0.5SO_4$), and $[Co(HL)_2X_2]$, (X = NCS) [392].

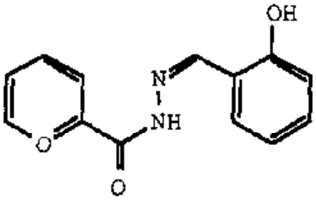
The dinuclear complexes $[M\{Co(HL)_2\}]X_2.nH_2O$, (M = Co, Ni; H_2L = (**100**); X = Cl, Br, I, ClO_4; n = 0,2,4,5), have been described; the central $\{Co(HL)_2\}$ unit coordinates to the second metal atom *via* two *cis*-phenolic-O atoms; infra red spectroscopic results for the isolated $[Co(HL)_2]$ complex, and compared to the dinuclear product, are consistent with the increased coordination number of the phenolic-O atoms [393].



(**100**)



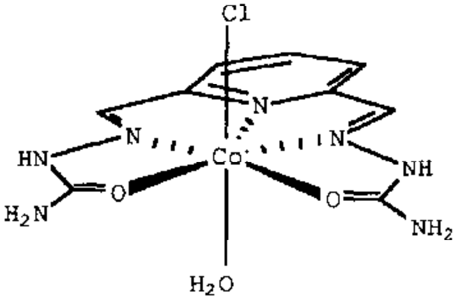
(**101**)



(**102**)

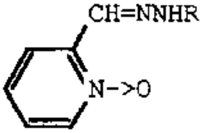
The formation of $[CoL_3]^{2+}$, (L = $2\text{-}H_2NNHC(O)\text{-}py$), from hydrated Co^{2+} ions has been monitored as a function of pH; mechanistic details have been proposed [394]. The preparation and characterisation by spectroscopic, conductance, and magnetic susceptibility data of the complex $[Co(HL)Cl_2]$, (HL = (**101**)), has been described; it is suggested that the ligand acts as a tridentate, N-N-O donor [395]. A similar donor set is offered by $2\text{-}HO\text{-}C_6H_4\text{-}CH{=}NNHC(O)NH_2$, (HL); the high spin, octahedral complex $[CoL_2].nH_2O$ has been synthesised and characterised magnetically and spectroscopically [396]. Complexation of the ligand H_2L, (**102**), with cobalt(II) ions has been investigated; species of type

[Co(HL)Cl].H_2O, [Co(HL)$_2$], and [CoL(H_2O)$_2$] have been formulated on the basis of spectroscopic results [397].



(103)

An interesting 7-coordinate, high spin cobalt(II) complex, **(103)**, has been reported; results of e.p.r. spectroscopy and of low temperature single crystal susceptibilty measurements have been analysed [398]. Steric effects of the heterocyclic part of the ligand L, **(104)**, have been studied; in complexes [CoLX_2], (X = Cl, Br, NO_3, NCS), the metal ion resides either in a five- or six-membered donor set depending upon the nature of the heterocyclic group, R. There is some evidence to support the involvement of the *N*-oxide moiety in Co--Co bridging [399].

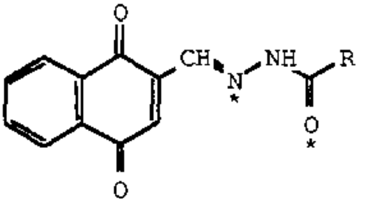


R = 2-py or 2-quin

(104)

The hydrazone MeC(=NNH_2)-C_6H_3-2,4-$(OH)_2$, (HL), has been shown to function as an O-N-N donor to cobalt(II) ions, but this mode of chelation appears to be metal dependent; the complex [$Co_2L_2(H_2O)_2$]Cl_2 has been prepared and physicochemically characterised [400]. A similar mode of chelation has been reported for the ligand EtO_2CCNHN=CH-C_6H_4-2-OH [401]. The complexes [CoL]X_2 and [CoL(ClO_4)][ClO_4]$_2$, (L = RC(O)NHN=CHCH=NNHC(O)R; R = isoquinolyl), have been synthesised and characterised by magnetic moment and spectroscopic measurements; the cobalt atom is proposed to be tetrahedrally coordinated [402].

The dark green complex $[CoLCl_2]$, (L = (**105**)), has been prepared and characterised; values for $\mu_{eff.}$ of 4.52 and 4.31 BM for R = Ph and Me respectively, are consistent with tetrahedral coordination. The octahedral complexes $[CoL_2Cl_2]$ ($\mu_{eff.}$ = 4.95 and 5.12BM for R = Ph and Me respectively) have also been reported [403].



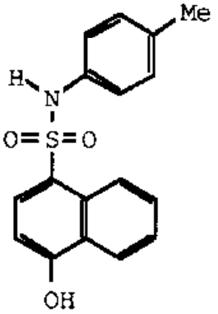
(**105**)

2.3.3.6 *Heterocyclic ligands*

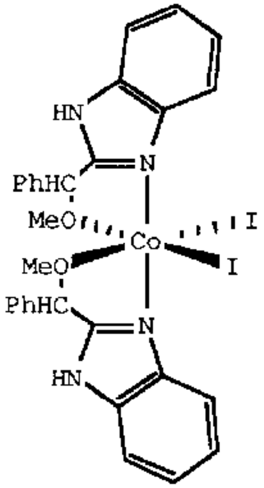
Several heterocyclic ligands containing active, (with respect to coordination), functional groups have been reviewed above, and the interested reader should refer to previous sections.

Complexation of $2\text{-}HOCH_2CH_2\text{-}py$ to give $[CoL_3]X_3$, (X = Cl, Br, I, SCN) has been reported [404]. The kinetics and mechanism of the reaction of HL, ($8\text{-}HO_2CCH_2NH$-quinoline), with Co(II) ions have been studied by using stopped flow techniques; mono- and bis-ligand complexes are formed *via* pathways which involve either HL or L^- [405]. A series of complexes involving 6-substituted derivatives of $2\text{-}MeC(O)CH_2\text{-}py$, (HL), has been prepared; $[CoL_2X_2]$, (X = Cl, Br, NO_3) reacts with NaOH to give the purple complex $[CoL_2]$, with KSCN at 0°C to give the violet complex $[CoL_2(NCS)_2]$, and with KSCN at room temperature to give the yellow-green complex $[CoL_3][Co(NCS)_4]$. Pyrolysis of $[CoL_2X_2]$ at 115°C produces a red-brown complex of formula $[CoL_2]$ [406]. A related investigation utilising the ligand $2\text{-}RC(O)CH_2\text{-}py$, (R = *p*-nitrophenyl; *p*-tolyl), has also been presented [407].

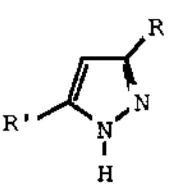
The antibacterial activity of HL, (**106**), has been shown to increase upon complexation of the ligand to cobalt(II) ions; preparations of both HL and $[CoL_2]$ have been reported [408]. Biological significance has also been expressed in connection with the complex $[CoL_2I_2].CH_3C(O)CH_3.2H_2O$, (**107**); characterisation of this complex by X-ray diffraction methods illustrates a distorted octahedral site for the metal ion, with Co-N = 2.097(5), 2.097(5)Å, Co-O = 2.302(4), 2.345(6)Å, and Co-I = 2.775(1), 2.785(1)Å. The observed departure from symmetry is attributed to strain within the chelated rings, and to the bulk of the iodide ligands [409].



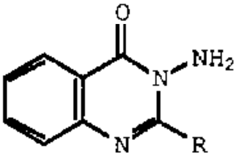
(106)



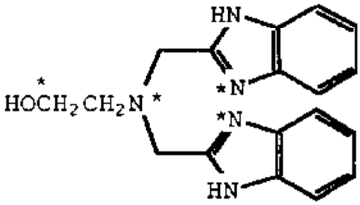
(107)



(108) R ≠ R'; R,R'= Me, C(O)NEt$_2$



(109) R = Me; Ph

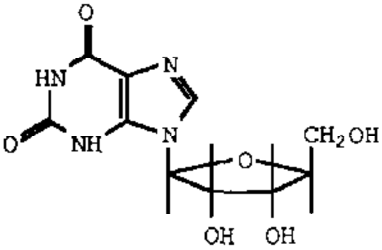


(110)

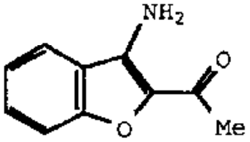
The complexes [CoL$_2$X$_2$].nH$_2$O, (L = **(108)**; X = Cl, Br, I, SCN, 0.5SO$_4$, BF$_4$, NO$_3$, ClO$_4$), have been described; the electronic spectral data suggest the presence of both tetrahedral and octahedral halo-complexes. However, when X$^-$ ≠ halide, only octahedral species are observed [410]. The synthesis and physicochemical characterisation of the complex [CoL(OAc)$_2$], (L = **(109)**), has been described; the ligand appears to be bidentate [411]. The tetradentate ligand, L, **(110)**, forms the complex

$[CoL(NCS)_2]$ which has been structurally elucidated; the thiocyanate ligands are mutually *cis*, and pertinent bond lengths are $Co-O_L$ = 2.262(4)Å, $Co-N_L$ = 2.089(6), 2.089(5), 2.302(6)Å, and $Co-N_{NCS}$ = 2.040(6), 2.086(6)Å [412]. The preparation and spectroscopic characterisation of $[Co(uracil)_2(H_2O)_2]$ have been reported; a shift in the infra red ν_{CO} absorption of uracil has been interpreted in terms of intramolecular hydrogen bonding between the 4-ketonic group and axially coordinated H_2O molecule [413].

Complex formation between cobalt(II) ions, glyH, and xanthosine, H_2L, (**111**), has been monitored by using potentiometric titration; stability constant data for this, and for complexes containing other transition metal ions, have been determined [414]. The preparation of, characterisation by spectroscopic and magnetic susceptibilty measurements of, and determination of ligand field parameters for the octahedral complex $[CoLCl_2]$, (L = (**112**)), have been described [415].



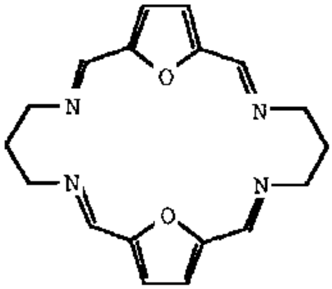
(**111**)



(**112**)

Several complexes containing the ligand 2-amino-py-*N*-oxide have been reported; on standing in air for several days, the blue compound $[Co(HL)Br_2].EtOH$ turns mauve, and the product complex has been spectroscopicaly characterised as $[Co(HL)Br_2].H_2O$. A related complex, $[Co(HL)_4Cl_3].H_2O$, has also been formulated on the basis of spectroscopic data [416].

Since there are few papers reporting purely N-O donating macrocyclic ligands forming Co(II) complexes, a separate section for the complexes $[Co_2L(YR)X_3]$, (L = (**113**); Y = O,S; R = H, alkyl, aryl; X^- = N_3^-, NCS^-), has not been allocated in this review. This new ligand has been prepared *via* a condensation route, and chelation of L to cobalt(II) ions results in the formation of either tetrahedral or trigonal bipyramidal complexes depending upon the nature of the bridging group, YR^-. Structural characterisation of $[Co_2L(OEt)(NCS)_3]$ and $[Co_2L(OMe)(N_3)_3]$ show Co---Co non-bonded separations of 3.119 and 3.195Å respectively [417].



(113)

2.3.4 *Complexes with oxygen-sulphur donor ligands*

The chelating behaviour of the ligands $PhC(O)CH_2C(S)NHPh$ and $PhC(O)CH_2C(S)NR_2$, ($R = {}^iBu$, ${}^nC_6H_{11}$), has been explored; the preparation of 1:3 cobalt(II):L complexes, and stability constants for their formation in dioxane-water solvent systems have been reported [418]. The synthesis, and characterisation by magnetic susceptibity, spectroscopic, and conductance measurements of the compound $[CoL_2(H_2O)_2]$, (L is the S-O chelate PhC(O)NHNHC(S)NHPh), have been described [419]. The related ligands PhC(O)NHC(S)NH(Ar) have also been utilised [420].

The condensation of $(CH_2SH)_2$ and *anti*-chloroglyoxime leads to the ligand, H_4L, $CH(=NOH)C(=NOH)SCH_2CH_2SC(=NOH)CH(=NOH)$ which is related structurally to ligand **(98)**; the oligomeric cobalt(II) complex $[Co(H_2L)Cl(H_2O)]_x$ has been prepared, and spectroscopically characterised [421].

2.3.5 *Complexes with oxygen-sulphur-nitrogen donor ligands*

It has been reported that the complex $[CoL(H_2O)]$, (H_2L =

MeC(O)CH_2C(Me)=NNHC(S)OEt), contains L^{2-} functioning as a tridentate ligand *via* the carbonyl-O, the imino-N, and the S-atoms; based on spectroscopic evidence, a tetrahedral geometry is proposed [422]. The preparation, and physicochemical characterisation of the octahedral complex [CoL_2], (HL = 4-R-C_6H_4C(CO_2H)=NNHC(Y)NH2; Y = S, O; R = H, Me), has been described; the ligand appears to be tridentate, with an O-N-Y bonding mode. Ligand field stablisation energies have been calculated [423].

2.3.6 Complexes with sulphur donor ligands

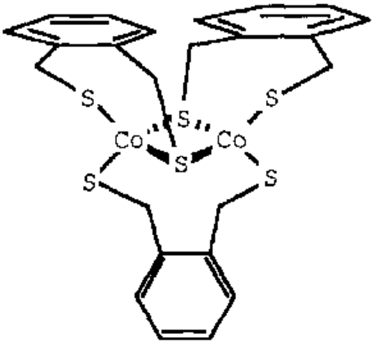
2.3.6.1 Thiolate ligands

The reaction of cobalt(II) chloride with K[$SC_{10}H_{13}$], ($HSC_{10}H_{13}$ = 2,3,5,6-Me_4-C_6H(SH)), in the presence of $^nPr_4$NBr in acetonitrile leads to the formation, (in 70% yield), of the complex [Co($SC_{10}H_{13}$)$_3$(MeCN)][$^nPr_4$N]; structural characterisation of the latter shows a distorted, tetrahedrally sited metal ion, with Co-S = 2.270(1), 2.296(1), 2.267(1)Å, and Co-N = 2.036(4)Å [424].

A proton n.m.r. spectroscopic investigation of cobalt(II)-substituted liver alcohol hydrogenase has been presented [425]. Several complexes of the general type 6-coordinate [CoL_nX_2], (X^- = $(EtS)_2PO_2^-$ or NO_3^-; L = imidH, bipy, py, quin) or 5-coordinate [CoL{$(EtS)_2PO_2$}$_2$] have been prepared; comparisons of the infra red spectra illustrate that both ν_{Co-S} and ν_{Co-N} shift to lower energy on going from the corresponding 5- to 6-coordinate complex, and ν_{Co-S} and ν_{Co-N} shift to higher energy upon an increase in the oxidation state of the cobalt ion in the 6-coordinate complex [426].

The dark green complexes, [Co(H_2L)$_2X_2$], (X = Cl, Br, I, SCN, $MeCO_2$, $EtCO_2$, ClO_4, NO_3, 0.5SO_4) in which H_2L is a dimercaptopiperidine derivative have been prepared and characterised spectroscopically; a bridged structure has been proposed, and conductivity as a function of X has been studied [427]. For the dithiolate ligand, H_2L = 2-$HSCH_2$-$C_6H_4CH_2$SH, complexation with cobalt(II) ions gives the dinuclear dianion [Co_2L_3]$^{2-}$, the structure of which, **(114)**, has been determined; the non-bonded Co--Co distance is 2.786(1)Å, and Co-S distances lie in the range 2.261(2) to 2.310(2)Å [428]. Further dinuclear species are found in the complex ions [$Co_2(SR)_6$]$^{2-}$ in which RSH = EtSH or 2RSH =

$2\text{-}HSCH_2\text{-}C_6H_4CH_2SH$; structural characterisation of the ${}^nBu_4{}^+$ and Et_4N^+ salts for the ethyl thiolate derivative show that the cobalt centres are tetrahedrally disposed, each with two terminal, and two bridging thiolate ligands. Two forms of the complex, *viz anti-* and *syn-*$[Co_2(SEt)_6]^{2-}$, exhibit non-bonded Co----Co separations of 3.045(2) and 3.020(3)Å respectively [429].



(114)

Reaction entropies for redox reactions of the complexes $[Co(R_2dtc)_3]$, (R = alkyl or benzyl), have been determined in acetone, acetonitrile, and dmso, and values compared with those of related systems containing other transition metal ions [430]. The reaction of Et_2NCS_2H, HL, with cobalt(II) bovine carbonic anhydrase has been shown to be pH dependent; at pH 10, no Co(II) extraction is achieved, but at pH values below 7, HL preferentially complexes the metal ion [431]. The complexation of Co(II) ions by $RHNCS_2H$, HL, (R = *o*-, *m*-, or *p*-ClC_6H_4) has been described; spectroscopic and thermal analysis studies are reported [432].

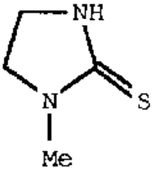
The thiocarboxylate, $PhNHCS_2{}^-$, is reported to behave as a monodentate ligand; complexes with Co(II) ions have been prepared and spectroscopically characterised [433]. Potentiometric and conductiometric titrations have been used to monitor the complex formation between $HS_2CCH_2CS_2H$ and cobalt(II) ions; stability constants for the 1:1 and 1:2 complexes have been measured [434].

2.3.6.2 Thionate ligands

The thermal decomposition, (in several gaseous media), of the complexes $[CoL_2X_2]$, (L = **(115)**; X = Cl, Br, I), has been investigated by using thermogravimetric techniques; values for

ΔH_{fusion} and $\Delta H_{decomp.}$ have been determined, and mechanisms for the decomposition pathways have been proposed [435].

The vacuum sublimation of several cobalt(II) complexes containing thio-β-diketonates has been described [436]



(115)

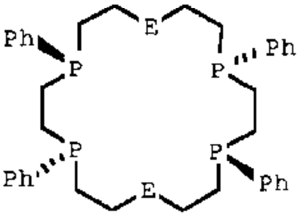
2.3.6.3 *Macrocyclic ligands*

The hexathio-18-crown-6 macrocycle, L, binds to Co(II) to give octahedral $[CoL]^{2+}$ which exhibits *meso*-geometric specificity; magnetic susceptibility and e.s.r. spectroscopic data show there to be a close similarity between $[CoL]^{2+}$ and $[CuL]^{2+}$ [436a].

2.3.7 *Complexes with sulphur-phosphorus donor ligands*

The reaction of $[Co(H_2O)_6][BF_4]_2$ with P_4Se_3 or P_4S_3 in the presence of the tripod-like ligand $(Ph_2CH_2)_3CMe$, (tppme), gives the complex $[Co(tppme)(P_2X)]BF_4.C_6H_6$, (X = S or Se). Structural characterisation of each product shows an octahedrally disposed cobalt ion; the P_2X ring is disordered, and the mean distance between the cobalt atom and an atom in the P_2S ring is 2.270(9)Å. For X = Se, the difference in size between the Se and P atoms introduces asymmetry into the CoP_2Se unit, such that the Co-P/Se distances lie in the range 2.272(6)-2.403(4)Å [437].

The macrocyclic ligand, L, for which one, (δ), of the five diastereomers is (**116**), reacts with Co(II) or Ni(II) ions to give 1:1 complexes; electronic spectral data for the complexes both in solution and in the solid state have been presented. For [CoL], the electronic transitions are independent of state; a 5-coordinate, low-spin cobalt(II) complex is proposed, and this is supported by structural data obtained for the corresponding $[Ni(\delta\text{-}L_{E=S})]$ complex [438].



(116)

2.3.8 *Complexes with nitrogen donor ligands*

2.3.8.1 *Ammine complexes*

The complexes $[Co(NH_3)_6][BF_4]_2$ and $[Co(NH_3)_6][PF_6]_2$ have been structurally characterised; unusually long Co-N average distances of 2.183(2) and 2.187(10)Å are observed for the tetrafluoroborate and hexafluorophosphate salts respectively [439]. An investigation of solid state phase transitions occurring over the temperature range 4.2-80K in crystalline samples of $[Co(NH_{36}]X_2$, (X = Br, I), has been carried out by using e.p.r. spectroscopy [440].

Two accompanying papers have addressed outer sphere association complexes. In the first report, outer sphere complexation of $[Co(bipy)_3]^{2+}$ with NH_3, $MeNH_2$, or $EtNH_2$, has been studied spectrophotometrically, and stability constant data has been recorded; reasons for the observed lower stability of the ammine complex with respect to the amine complexes have been discussed [441]. In the second study, under ambient conditions, outer sphere complexes form when $[Co(NH_3)_3(NO_2)_3]$ is dissolved in 0.1-0.5M solutions of NaF with NaX ,(X = Cl, Br, I), present; stability constants, *K*, have been determined for the complexes, and a linear relationship between *K*, (interestingly, not log*K*), and the radius of X^- has been illustrated [442].

2.3.8.2 *Amino ligands*

Some outer sphere complexes containing $MeNH_2$ and $EtNH_2$ ligands were mentioned in the previous section [441]. The preparation, and characterisation by spectroscopic, magneto-, and X-ray powder diffraction techniques, of $[HCoX_3].3PhNH_2$ and $[HCoXZ_2].3PhNH_2$, (X = Br, I; Z = Cl, Br, I), have been reported; it is proposed that each complex contains a pseudo-tetrahedral $[CoX_3(PhNH_2)]^-$ or $[CoXZ_2(PhNH_2)]^-$ core, with outer sphere $[NH{-}{-}{-}N]^+$ interactions being present [443]. Potentiometric techniques have been used to monitor complexation between cobalt(II) ions and glucosamine; the cobalt(II) compound is found to be less stable than the corresponding Fe(III), Cu(II), and Ni(II)-glucosamine complexes [444].

Compounds of the general formula $[CoL_2(H_2O)_2]X$, (L = en, 1,2-pn, or $HN(CH_2CH_2NH_2)_2$; X = tetrafluoro- or hexafluoro-metal dianions), have been prepared, and characterised *via* spectroscopic methods and magnetic measurements; bonding within the complexes is discussed in terms of crystal field theory, and the orbital overlap within the Co-L bond is compared with, and found to be less than, the metal-ligand overlap in the corresponding manganese(II) complex [445]. The exchange between free and coordinated dmf in the complex cation $[CoL(dmf)]^{2+}$, (L = Me_6-tren), has been shown to proceed *via* an associative pathway, with $k = 51.4 \pm 4.2\ s^{-1}$ at ambient temperature [446]. Reaction of $(o\text{-}H_2NC_6H_4CH{=}NCH_2)_2$, H_2L, with hydrated cobalt(II) salts in thf-EtOH leads to the complexes $[Co_2L(thf)X]X.nH_2O$, (X = Br, I, NO_3; n = 0,1); the results of physicochemical characterisation suggest that the ligand is tetradentate, and adopts a bridging mode, thereby linking the two cobalt(II) centres [447]. In constrast to previous postulates, the complex $[Co_2\{N(SiMe_3)_2\}_4]$ has been shown to be dinuclear in nature; X-ray structural characterisation illustrates an unusual trigonal planar arrangement of N-donor atoms about each cobalt(II) atom. The Co----Co separation in $[Co_2\{N(SiMe_3)_2\}_4]$ is 2.583(1)Å, and Co-N distances are 1.922(5) and 1.910(5)Å for the terminal ligands, and 2.062(4)Å for the bridging amino groups [448].

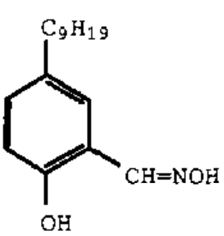
2.3.8.3 Oxime ligands

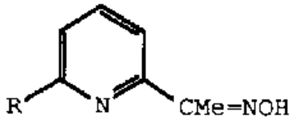
The kinetics and mechanism of the reaction of aqueous cobalt(II) ions with MeC(O)NHOH and its conjugate base have been studied; reactions follow dissociative pathways, with $k_{obs} = (3.59 \pm 0.08) \times 10^4$ and $(4.69 \pm 0.17) \times 10^6\ M^{-1}s^{-1}$ for the neutral and anionic ligand reactions respectively [449].

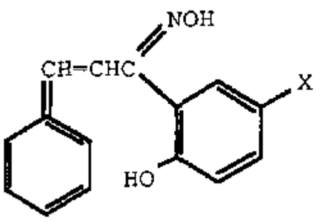
As one would expect, several reported complexes involve the $dmgH_2$ ligand. The reaction of $[Co(dmgH)_2(H_2O)_2]$ with nitrosobenzene is reported to lead to, among other products, cobaloximes; characterisation of the species is not, however, conclusive [450]. The disproportionation of $[Co(dmgH)_2]$ in alkaline solution has been monitored *via* changes in the electronic spectra; competitive covalent hydration is proposed [451]. In pursuit of models for coenzyme-B_{12}, the complex $[CoL(dmgH)_2Et]$, (L = 4-C(=NH)OMe-py), has been prepared and structurally characterised; the two oxime chelates lie in the equatorial plane of an octahedral set of ligands, with Co-N distances ranging from 1.879(4) to 1.887(4)Å [452].

Reaction of diaminoglyoxime, H_2L, with Co(II) ions is reported to lead to the complex $[CoL_{2.5}]Cl_2$; characterisation isby spectroscopic and magnetic susceptibility measurements [453].

Solvent extraction of cobalt(II) ions by the high molecular weight hydroxyoxime, HL, (**117**), in kerosine has been investigated as a function of pH; extraction is irreversible [454]. Partitioning of Co(II) ions between aqueous and chloroform media by 2-propionyl-1-naphthol oxime has been a subject for study; extraction is quantitative and the extraction coefficient maximises at pH 8 [455]. The relative basicities of the ligands (**118**), L_H and L_{Me}, have been measured, and formation constants for the complexes $[Co(L_H)_3]$ and $[Co(L_{Me})_2]$ determined [456]. The synthesis and physicochemical characterisation of complexes of type $[CoL_2Q_2]$, in which L = (**119**), and Q = H_2O or py, have been described; the resulting high-spin, octahedral complexes imply that L is a relatively weak field ligand [457].







(**117**) (**118**) R = H,Me (**119**) X = H,Me,Cl

Preparation and spectroscopic characterisation of the complex $[CoL_2]$, (HL = $1,2-C_6H_4(=NOH)_2$), illustrates the bidentate nature of the ligand [458].

The reaction of $2-H_2NCH_2-C_6H_4-OCH_2CH_2OCH_2CH_2O-C_6H_4-2-CH_2NH_2$ with HON=C(Cl)C(Cl)=NOH produces a new ligand, H_4L; this synthesis, and the complexation of H_4L with cobalt(II) ions to give $[Co(H_3L)_2]$ have been detailed [459].

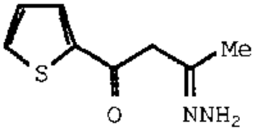
2.3.8.4 Hydrazine, hydrazide, and hydrazone ligands

The preparations of complexes of type $[Co(N_2H_4)_nX_2].mH_2O$, in which X = F, Cl, Br, $0.5SO_4$, n = 2.5, 2, 1.5 and m = 2, 1, 0.5, 0, have been reported; solid state thermal decomposition studies have also been presented for the new compounds [460]. Another hydrazine complex is $[Co(ox)(N_2H_4)].xH_2O$; an infra red and Raman spectroscopic study over the range 400-4000 cm^{-1} has indicated that the hydrazine ligand is bound solely in a bridging mode [461]. The complex $[Co(N_2H_4)_2(NCS)_2]$, containing a bridging hydrazine ligand, has been prepared, and characterised by analytical, spectroscopic, and magnetic measurements; the investigation is complimented by thermal decomposition studies [462]. The relative stabilities of members of a series of cobalt(II) complexes containing N_2H_4 and oxalate ligands have been compared; the stability decreases as the number of hydrazine ligands increases [463].

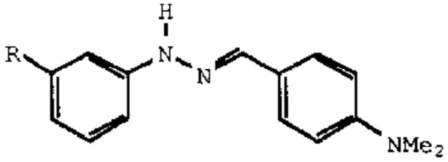
Reaction of $Me(CH_2)_5C(O)NHNH_2$, L, with cobalt(II) ions in the presence of $S_2O_6^{2-}$ ions leads to a 1:3 metal:hydrazide complex, with the $S_2O_6^{2-}$ ion being associated as an outer sphere ligand [464]. For HL = $4-HO-C_6H_4-CH_2CH(NH_2)C(O)NHNH_2$, complexes of formulae $[Co(HL)_2(OH)_2]$, $[Co(HL)_2Cl_2]$ and $[CoL(OH)].nH_2O$ have been prepared and characterised spectroscopically and by measuring magnetic susceptibilities; all compounds are non-electrolytes [465].

The synthesis and characterisation of $[Co(HL)_2Cl_2]$ and $[CoL_2(H_2O)_2]$, (HL = **(120)**), have been reported; ligand field parameters have also been determined [466]. The hydrazone L, **(121)**, behaves as a bidentate ligand in the complexes $[CoL_2Cl_2].2H_2O$ and $[CoL_2(H_2O)Cl]Cl$; the metal ion is in a distorted octahedral environment [467].

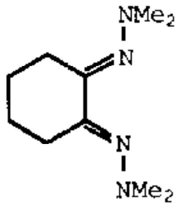
Hydrazone ligand containing complexes include the octahedral $[CoL_2X_2]$, (L = (**122**) or (**123**) for R = Me; X = Cl, NCS), and the tetrahedral $[CoLX_2]$, (L = (**122**), (**123**); X = Cl, NCS); attempts to prepare the corresponding 1:3 complexes have not been successful [468]. Use has been made of the ligand HL, (**124**), as an extracting agent for cobalt(II), nickel(II) and copper(II) ions; the extraction of Co^{2+} is pH dependent, and the efficiency of extraction is less than that of the other metal ions [469].



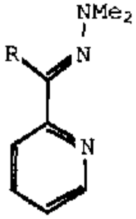
(**120**)



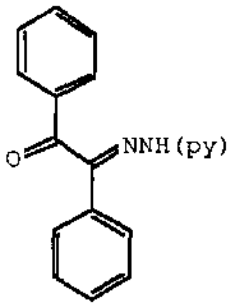
(**121**)



(**122**)

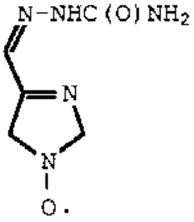


(**123**) R = Me;OH

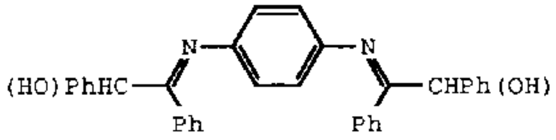


(**124**)

The reaction of cobalt(II) chloride, in aqueous ethanolic media, with HL, (**125**), in alkaline solution, gives a 1:2 complex; octahedral coordination is proposed, with the ligand acting in a tridentate, all N-donor, manner [470].



(125)



(126)

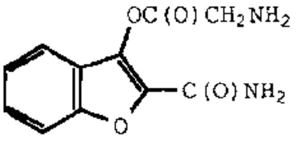
2.3.8.5 *Imine ligands*

Schiff bases, formed from the condensation of *o*-hydroxyacetophenones with en or pn form, 1:1 complexes with cobalt(II) ions; physicochemical characterisation of the products suggests square planar geometries [471]. The preparation and structure of the distorted tetrahedral complex $[CoCl_2L]$, ($L = {}^tBuN{=}CHCH{=}N^tBu$), have been reported; pertinent distances are Co-N = 2.068(5), 2.065(4)Å, and Co-Cl = 2.200(27), 2.228(27)Å. Related complexes, $[CoX_2L]$, (L = RN=CHCH=NR; R = Bz, $c\text{-}C_6H_{11}$, ${}^iPr$; X = Cl, Br) and $[CoX_2L_2]$, (L = PhN=CHCH=NPh; X = Cl, Br) have also been prepared [472].

The new ligand H_2L, **(126)**, has been synthesised, and its complexation with cobalt(II) ions produces a dinuclear species, $[Co_2L_2].4H_2O$, characterised *via* spectroscopic and conductivity data, and magnetic susceptibilty measurements; it is suggested that the Schiff base is tetradentate, with each L^{2-} bridging the two metal cnetres [473]. A series of Schiff bases, H_2L, derived from 3-formylsalicylic acid has been prepared; reaction of H_2L with $[Co(OAc)_2]$ is reported to produce dinuclear complexes, $[Co_2L_2].nH_2O$ with n = 2-4 [474].

2.3.8.6 *Amido, and amino acid ligands*

The preparation and physical characterisation of the complexes $[CoL_2X_2]$, ($L = H_2NC(O)NHC(O)NH_2$; X = Cl, Br, I), have been described [475]. Thermal decomposition of several compounds of general type $[CoL_2X_2]$ in which L is tmu, dmeu (1,3-dimethyl-2-imidazolidone), or dmpu (1,3-dimethyl-hexahydro-2-pyrimidinone) has been shown to be dependent both upon L and X; the relative ease of decomposition decreases as L = tmu > dmeu > dmpu and X = Cl > Br > I, and the observed trends are in line with the relative coordinating abilities of the ligands [476].



(127)

The synthesis of $[CoL_2Cl_2]$, (L = **(127)**), has been reported; spectroscopic characterisation of the complex indicates an octahedral inner coordination sphere, and ligand field parameters have been determined [477].

Characterisation of the complex $[CoCl_2(glyH)_2(H_2O)_2]$ by potentiometric and spectroscopic methods illustrates an N-bonded glyH residue; transitions in the electronic spectrum of the complex have been assigned, and the CFSE calculated [478]. Two accompanying papers are concerned with the thermodynamics of the formation of pheH complexes of cobalt(II) ions. Protonation constants for the ligand, and formation constants for the species $[Co(phe)]^+$ and $[Co(phe)_2]$, have been determined [479], and values of ΔH°, ΔG°, and ΔS° for the same processes have been measured [480].

2.3.8.7 Heterocyclic ligands

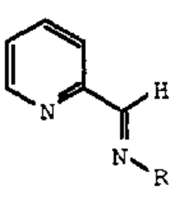
As expected, this section is a large one. The review begins with complexes containing py, bipy, terpy, or phen, progresses through five membered heterocycles, and is completed by a survey of more unusual ligands.

Outer sphere coordination by py has been studied by using ^{1}H n.m.r. spectroscopy in the equilibrium system [481]:

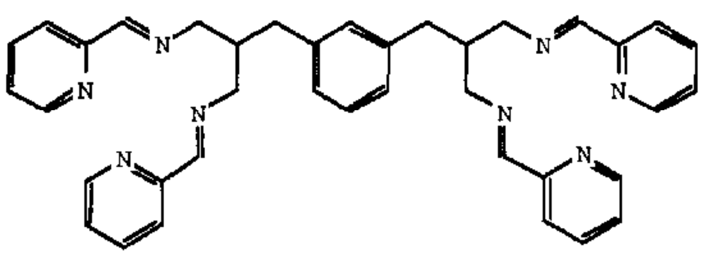
$$[Co(CD_3OD)_6]^{2+} + py \Leftrightarrow [Co(CD_3OD)_6\text{---}py]^{2+}$$

The reaction of cobalt(II) iodide with py is reported to lead to an equilibrium mixture of the tetrahedral complex, $[CoI_2py_2]$, and the octahedral, $[CoI_2py_4]$; increased temperature favours the former, and increased pressure favours the latter complex [481a]. The complexation between cobalt(II) chloride and methyl- or dimethylsubstituted py in acetone solution has been investigated *via* conductivity and spectrophotometric techniques; relative stabilitites of the complexes have been assessed [482]. The compounds $[Co(4\text{-}Me\text{-}py)_3X]X$, (X = Cl, I), have been prepared and characterised spectroscopically and by magnetic susceptibility measurements; in each case, a distorted tetrahedral arrangement of the donor atoms is proposed [483]. The ligand 4-Et-py has been used to extract Co(II) ions in an oxygenated solvent system [484].

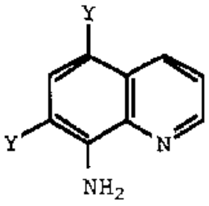
A series of 25 complexes, formed from the reactions of cobalt(II) ions with 2-, 3-, or 4-NC-py, has been characterised, and the thermal decomposition of the compounds described [485]. Characterisation of the newly synthesised complexes, $[CoX_2L]$ in which L = py or RC(O)-derivatives of py, (R = Me, Et), has illustrated a structural dependence upon L and X; the complexes range from being tetrahedral or octahedral through to polymeric in nature, and the variation is attributed to the σ-donating *vs.* π-accepting capabilities of the ligands [486]. The preparation and spectroscopic characteriation of $[Co(OAc)_2L_2]$, (L = 2-, 3-, or 4-R-py with R = OH, NH_2; 3-, or 4-X-py with X = Cl, Br), have been reported; ligand field parameters have been determined for these pseudo-octahedral complexes [487]. Similar complexes with amino-py ligands have also been prepared, and characterised by infrared spectroscopy [488]. The complexes $[Co(HL)_3][ClO_4]_2$ and $[Co(HL)Cl_2]$, (HL = 2-PhHNC(S)NHCH_2-py), have been prepared and spectroscopically characterised as being octahedral and tetrahedral respectively; the ligand, by virtue of an infra red absorption, $\nu_{C=S}$, at 754 cm^{-1}, is shown to persist largely as the thioketo-tautomer [488a]. For several 2-substituted py ligands, complexes of the type $[CoL_2X_2]$, (X = N_3, NCS), have been prepared; the nature of the heterocyclic substititent, (*viz.* CHO, COMe, CO_2Me, CO_2Et) influences the geometrical isomerism exhibited by the thicyanato complex [489].



(128) R = Me; OH

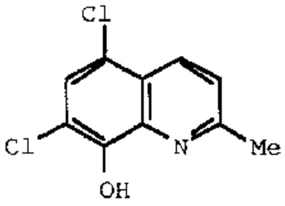


(129)



Y = hal

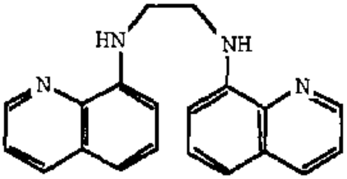
(130)



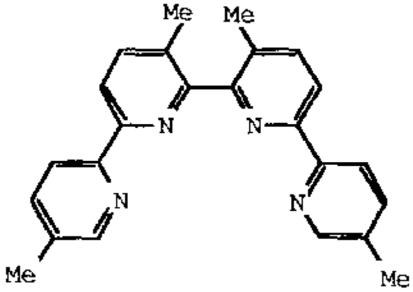
(131)

Several cobalt(II) complexes containing pyridinal imino-ligands have been investigated. Interestingly, the quality of crystals of $[CoL_3][ClO_4]_2$, (L = **(128)** with R = Me), (e.g. result of mechanical grinding), has a significant influence upon their spin-transition properties [490]. Studies aimed at developing paramagnetic shift reagents have utilised cobalt(II) complexes containing ligands derived from **(128)** with R = OH [491]. The octadentate ligand, L, **(129)**, complexes with Co(II) ions to produce a dinuclear species, $[Co_2L]Cl_4$; corresponding nickel(II) and copper(II) complexes have also been prepared and spectroscopically characterised [492].

Reaction of CoX_2(aq), (X = Cl, Br, I, NO_3), with L, **(130)**, is reported to give $[CoX_2L_2]$ or $[CoX_2L]$ depending on X or L [493]. The structure of the red, octahedral complex, $[CoL_2(H_2O)_2]$, in which L is a ligand related to **(130)**, has been determined [493a]. The complexes $[CoL_nX_2]$, (X^- = $(EtS)_2PO_2^-$ or NO_3^-; L = py, bipy, quin, imidH), and $[CoL\{(EtS)_2PO_2\}_2]$ have been synthesised and investigated by infra red spectroscopy [426]. The 2- or 8-Et_2NCH_2-quin ligands, L, form the tetrahedral complex cations $[CoL_2]^{2+}$; structures contrast with those of the corresponding Ni(II) and Cu(II) complexes [494]. The solvent extraction of Co(II) and Ni(II) ions into chloroform by using HL, **(131)**, has been studied as a function of pH; the complex ions $[Co_2L_3(HL)]^+$, $[Co_2L_3(HL)_3]^+$, and the neutral $[Co_2L_4]$ have been identified [495]. Stability constants for cobalt(II)/8-HO-quin complexes , forming in aqueous-dmso solutions, have been determined as a function of dmso concentration [496]. A related study illustrates that $[CoL_2]$, (L = 8-HO-quin), is present in <3% proportions in solutions of [CoL] [497].



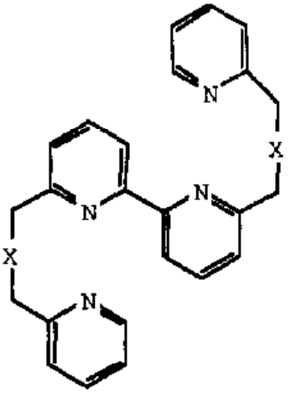
(132)



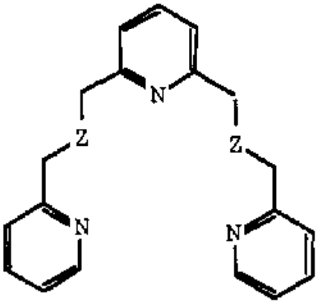
(133)

The quin based ligand, **(132)**, L, reacts with cobalt(II) salts to give [$CoLX_2$], (X = halide, SCN, NO_3); spectroscopic characterisation suggests a distorted octahedral complex with L acting as a tetradentate ligand [498]. The dimethyl-derivative of quaterpyridine, **(133)**, forms 1:1 and 1:2 complexes with Co^{2+} ions; the methyl groups on the backside of the ligand provide an inherent twist at the central C-C bond which renders L a "bis-bipy" donor set, and facilitates the formation of the dinuclear complex [499].

The preparation of the multidentate, open chain ligands, **(134)**, L, and **(135)**, L', and their complexation with cobalt(II) ions has been described; structural characterisation of $[CoL(H_2O)]^{2+}$ and $[CoL'(H_2O)_2]^{2+}$ shows a 7-coordinate, pentagonal bipyramidal geometry in each case [500].



(134) X = O;S;NH;NTs
$C(CO_2Me)_2$;
$CHCO_2Me$



(135) Z = O;S;NH;NTs

Reaction entropies for some complex ion CoL_6^{3+}/CoL_6^{2+} redox couples, (L = NH_3, en, bipy, phen), have been measured; values of

ΔS° for the $Co(bipy)_6{}^{3+}/Co(bipy)_6{}^{2+}$ and $Co(phen)_6{}^{3+}/Co(phen)_6{}^{2+}$ couples are 45 and 37 cal deg^{-1} mol^{-1} respectively [501]. An infrared spectroscopic study of $[Co(bipy)_2][SbCl_6]$ has assigned absorptions to the ν_{Co-N} mode [502]; an accompanying paper describes a similar investigation for the analogous phen complex [503]. The complexes $[CoL_3][H_2PO_4]_2.H_3PO_4$ and $[CoL_2][H_2PO_4]_2$, (L = bipy or phen), have been synthesised and characterised spectroscopically; octahedral and pseudo-tetrahedral species are proposed for the two complex types [504]. The $[Co(bipy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ cations also figure in the complexes $[CoL_3][ML'_2]$, (M = Zn, Cd, Hg; H_2L = HSC(O)CMe=CMeC(O)SH)) [505].

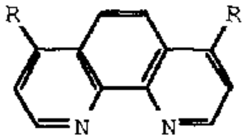
Zeolite Y encapsulated cobalt(II) ions react with bipy or terpy, (L and L' respectively), to give the complexes $[CoL_2]^{2+}$ and $[CoLL']^{2+}$, as well as the oxidised product $[CoLL'(O_2{}^-)]^{2+}$; e.p.r. spectroscopic studies have been reported, and the suitability of the zeolite Y complex containing system as a means of absorbing aerial O_2 has been assessed [506]. The reaction of terpy with $[Co(SeCN)_2]$ in ethanol leads to the formation of the 5-coordinate complex, $[Co(terpy)(SeCN)_2]$, in which the terpy is, as expected, tridentate, and each $SeCN^-$ ion is N-bonded to the metal atom [507]. The kinetics of reduction of ClO_2 by $[Co(terpy)_2]^{2+}$ obey the rate law:

$$\rho = k[Co(terpy)_2{}^{2+}][ClO_2]$$

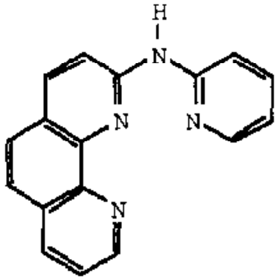
with k = (2.1 ± 0.4) x 10^7 $M^{-1}s^{-1}$ at 25°C [508].

The structure of the complex $[Co(phen)_3][ClO_4]_2.H_2O$ has been determined, and a distorted octahedral array of donor atoms has been confirmed; the average Co-N distance is 2.127(14)Å [509]. Reaction of cobalt(II) ions with phen in the presence of either Eriochrome Azurol S or tetrabromophenolsulphophthalein, L, has led to 1:1:3 and 1:2:1, (Co:L:phen), complexes respectively [510]. Formation constants relating to some protonated cobalt(II) complexes containing the phen ligand have been determined by use of potentiometric titration methods [511]. An investigation of the mechanism by which Co^{2+} ions are transferred from an aqueous phase to a dichloroethane solution of phen has shown that the first step is the diffusion of the ligand into the aqueous layer; the second, and rate determining stage, *viz.* the formation of a 1:1 Co(II):phen complex, is followed by phase transfer of the complex [512].

Reduction potentials, measured with respect to SSCE, for the $[CoL_3]^{2+}/[CoL_3]^{3+}$, (L = (**136**)), redox couples have been determined as 0.404V (R = H), -0.089V (R = Me), and -0.024V (R = $CH(CH_2OH)_2$); detailed discussions of outer sphere electron transfers between Ru(III) or Cu(III) and Co(II) are presented [513]. For a variety of pesticides, L, complexes of the type $[CoL(phen)]^+$ or $[CoL(bipy)]^+$ have been prepared as well as $[CoL_2]$ and $[CoL]^+$; relationships between the complex stability constants and the Hammett σ-values for each pesticide have been exemplified, and the significance of the observed structure/stability/activity correlation has been discussed [514]. By using an SnO_2 glass electrode coated in Δ-$[Ru(phen)_3]^{2+}$-montmorillonite, racemic $[Co(phen)_3]^{2+}$ may be converted to Λ-$[Co(phen)_3]^{2+}$, although specificity is not as high as had been anticipated [514a]. Related work with Δ-$[Ni(phen)_3]^{2+}$-montmorillonite has also been reported [514b].



(**136**) R = H;Me;$CH(CH_2OH)_2$

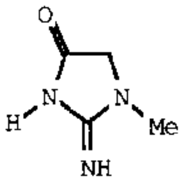


(**137**)

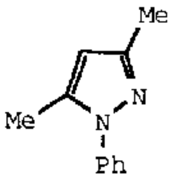
The phen-derived ligand, HL, (**137**), has been prepared. Reaction of HL with Co(II) ions leads to the cationic complex, $[Co(HL)_2]^{2+}$; attempts to prepare the neutral species $[CoL_2]$ are reported to fail on account of accompanying oxidation to Co(III) [515].

The octahedral complex $[CoL_2L'].2H_2O$, (HL = pyrrolidine; L'= en, 1,2-pn), has been synthesised and characterised by physicochemical methods; the complex exhibits antifungal activity [516]. Reaction of each of several cobalt(II) salts with two equivalents of L, (**138**), in aqueous solution, is reported to give $[CoL_2X_2(H_2O)_n]$, (X = Cl, Br, I, NCS; n = 0; or X = HCO_2, $HOCH_2CO_2$, $NCCH_2CO_2$; n = 2); tetrahedral complexes are characteristically blue or green, and octahedral complexes are pink [517].

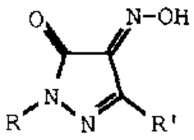
A spectrophotometric study in polar, non-aqueous solvents of the pink, octahedral complex $[Co(3,5\text{-}Me_2\text{-}pzlH)_4(SCN)_2]$ has illustrated a solvent dependent equilibrium between this and the



(138)



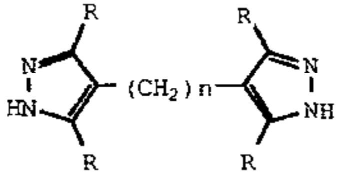
(139)



(140) R = Ph; R' = Me
R = H; R' = Me
R = H; R' = Ph
R = Ph; R' = Ph

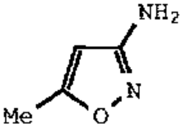
blue, tetrahedral complex, $[Co(3,5\text{-}Me_2\text{-}pzlH)_2(SCN)_2]$ [518]. The preparation and characterisation of $[CoL_2Cl_2]$, (L = 3- or 5-H_2N-pzlH) has been reported; molecular weight determinations suggest that the complex is polymeric [519]. The ligand, L, **(139)**, forms a complex of type $[CoL_2X_2]$, (X = Cl, Br, I, NO_3, NCS), the structure of which, (tetrahedral or octahedral), depends upon the nature of X [520]. The mixed heterocyclic ligand complexes, $[CoL_2(3\text{-}Me\text{-}py)_2]$, in which L is **(140)**, have been prepared, and characterised by spectroscopic and magnetic susceptibility measurements and thermal analyses [521]. Complexes containing coupled pyrazole ligands have been prepared; these compounds are of empirical formula $[CoLX_2].nH_2O$, (L = **(141)**; X = Cl, NO_3; n = 1, 0.5, 0), and structural characterisation for the chloro-complex confirms a dinuclear species supported by bridging heterocyclic ligands [522].

A detailed kinetic study of the reaction between cobalt(II) ions and histamine has been presented; the complex equilibria, established in solution, are found to be pH dependent [523]. Related amino-heterocyclic ligands are L, **(142)**, and L', **(143)**. Results of a variable temperature solution ^1H n.m.r. spectroscopic study of the complex $[CoL_2Br_2]$ have been interpreted in terms of reorientation of the ligand [524]. Reaction of $[Co(NCS)_2].6H_2O$ with L' in EtOH gives *trans*-$[CoL'_4(NCS)_2]$; X-ray structural characterisation of this complex confirms the *trans*-configuration, and average bond lengths are $Co\text{-}N_{L'}$ = 2.182Å, and $Co\text{-}N_{NCS}$ = 2.113Å [525].

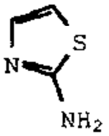


(141) R = Me; n = 0,1

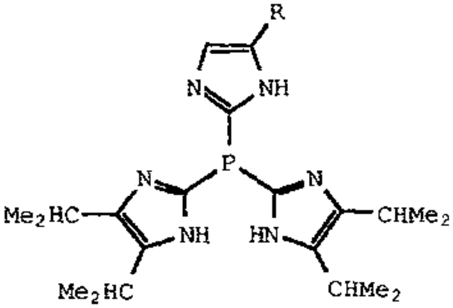
R = H; n = 1



(142)



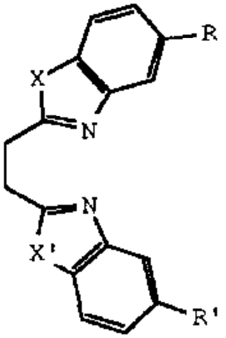
(143)



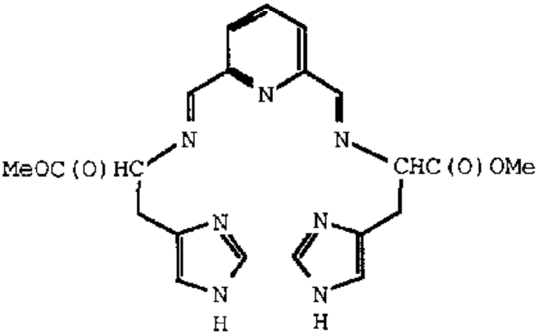
(144)

An interesting phosphine ligand, L, (**144**), has been used in studies aimed at producing biomimetic catalysts for the hydrolysis of *p*-nitrophenyl picolinate; the high solubility of the cobalt(II) complex of L has allowed kinetic studies to be carried out over a large pH range [526]. The coordinating ability of the borohydride anion, $H_2BR_2^-$, (R = imid), has been investigated; the complex $[Co(H_2BR_2)_2]$ has been prepared, and characterised as being octahedral on the basis of spectroscopic data and magnetic moment measurements [527]. Complexation studies of cobalt(II) ions with bzimidH, and some 1-alkyl-derivatives thereof, in dmso, have shown that alkyl substitution has little effect upon the basicity of the complex or upon its stability [528]. Cobalt(II) complexes of other substituted bzimidH ligands have been reported [529,530]. Reactions with a nitrogen-based ligand, L, not unlike (**144**), have been reported; the complex $[CoLCl_2].nH_2O$ has been prepared and spectroscopically characterised, and a trigonal bipyramidal inner coordination sphere has been proposed [531].

The preparation and physicochemical characterisation of $[CoLX_2]$, (L = (**145**); X = Cl, Br, I, NCS), have been described; in each case, the cobalt centre is proposed to be distorted tetrahedral in nature, and coordination appears to be always through the N-donor, rather than the S-donor, sites [532]. The molecular structure of *trans*-[Co(bzt)$_2$(NCS)$_2$(dmf)$_2$], (bzt = benzo-1,3-thiazole), has been determined; the complex is octahedral with pertinent bond lenghts being Co-N$_{bzt}$ = 2.185(2)Å, Co-N$_{NCS}$ = 2.082(2)Å, Co-O$_{dmf}$ = 2.118(2)Å [533].

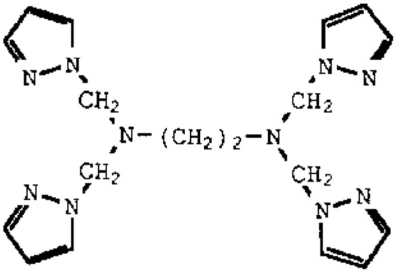


(145)



(146)

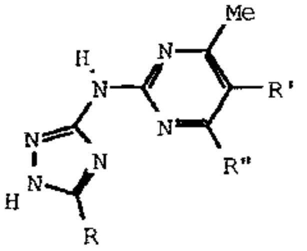
The complex cation, [CoL]$^{2+}$, (L = **(146)**), has been prepared and characterised, and its potential to bind dioxygen is of interest; an X-ray study of the analogous zinc(II) complex shows a severely distorted trigonal bipyramidal geometry with the N$_{axial}$-Co-N$_{axial}$ angle being only 151.1° [534]. Another multidentate



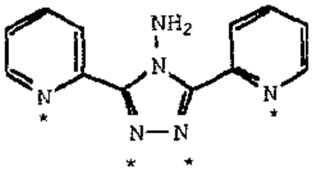
(147)

ligand is shown in **(147)**, L; complexes [CoL]X$_2$, (X = BF$_4$; ClO$_4$), have been synthesised, and their electronic spectra and calculated ligand field parameters are consistent with the presence of an octahedral N$_6$-chromophore [535].

The preparation and spectroscopic characterisation of the complex $[CoLX_2]$, (L = **(148)**; X = Cl, Br), has been described; it is proposed that L coordinates *via* two N-donor atoms, one from each ring [536]. Two cobalt(II) complexes containing the 3-aminotriazole ligand have been reported [537]. The reaction of cobalt(II) bromide or chloride with L, **(149)**, leads to $[Co_2L_2X_2(H_2O)_2]X_2.4H_2O$; the ligand coordinates *via* one triazole nitrogen atom, and a py residue to each metal centre, and, thus, each L bridges the dicobalt unit [538]. The synthesis, and reaction with methanolic $[Co(NCS)_2]$, of LH^+Cl^-, (L = **(150)**), have been reported; the heterocyclic ligand is not incorporated as an inner sphere ligand, and the complexes characterised are formulated either as $[LH][CoCl(NCS)_2(MeOH)]$ or $[LH]_2[CoCl_2(NCS)_2].3MeOH$, depending upon the ligand substituent, R [539].

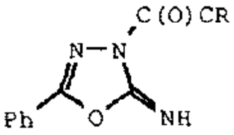


(148) R $=C_6H_{13}$;
R'=H,Et;
R"=OEt,
$NH-C_6H_4$-*p*-Bu



* = coordination site

(149)

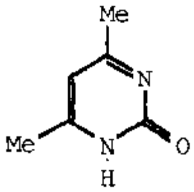


(150) R=Me,Et,Pr

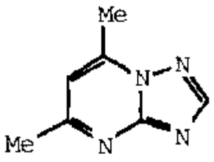
Derivatives of pyrimidine, (pym), have been assessed in terms of their ability to extract cobalt(II) ions from solution [540]. The complex $[Co(pym)_2(NCSe)_2]$ has been prepared and characterised by infra red spectroscopy [541]. Physicochemical characterisation of $[CoL_2Cl_2]$, (L = 2,4-$(H_2NC_3H_6)_2$-6-HO-pym), suggests that L behaves as a monodentate ligand, and that the complex is tetrahedral [542].

Fifteen cobalt(II) complexes of type $[CoXY(HL)_n(H_2O)_m]$, (HL = **(151)**; X and Y = various;), have been prepared and characterised by spectroscopic, conductivity, and magnetic susceptibility data; tetrahedral, square pyramidal, and octahedral structures are proposed [543]. The novel compound $[CoHg(dmtp)_3(SCN)_4(H_2O)]_2$, (dmpt = **(152)**), provides an example of thiocyanate bridged Co and Hg atoms; the heterocyclic ligands are all bound to the cobalt(II) ion [544]. Structural data is available for $[CoL_2(MeOH)_4]$ in which L =

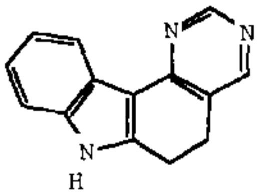
(153); the heterocyclic ligands are *trans* to one another, and pertinent bond lengths are Co-N = 2.158(3)Å, Co-O = 2.077(5), 2.121(3)Å [545].



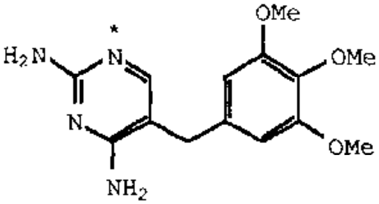
(151)



(152)



(153)



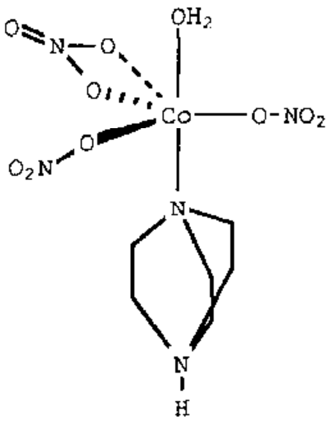
* ligation site

(154)

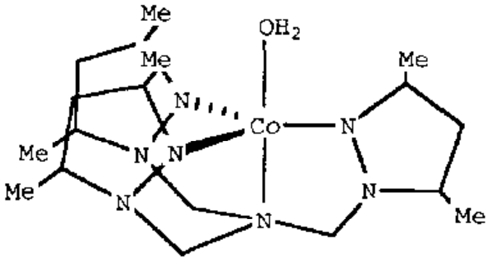
The X-ray structural characterisation of the tetrahedral, ($\mu_{eff.}$ = 4.67 BM), complex $[CoL_2Cl_2]$, (L = **(154)**), has illustated a monodentate bonding mode for the ligand; inner coordination sphere bond distances are Co-N = 2.030(4)Å and Co-Cl = 2.231(2)Å [546].

The coordinating ability of monoquaternised *N*-R-pz^+ ligands has been investigated, and the ligands are shown to be poor σ-donors, but good π-acceptors; the complexes $[CoX_3(N\text{-}R\text{-}pz^+)]$, (X = Cl, Br) have been characterised for R = Me, but $[N\text{-}R\text{-}pz]_2[CoX_4]$ forms when more bulky substituents are present [547].

Two cobalt(II) complexes containing valium-related ligands, L, have been prepared, and spectroscopically characterised; both $[CoL_2(ClO_4)_2].nH_2O$ and $[CoL_2(SO_4)].H_2O$ appear to exhibit acute distortion away from octahedral coordination, towards square planarity [548]. The complex, **(155)**, shows a novel arrangement of ligands, with primary coordination distances being Co-N = 2.207(5)Å, $Co\text{-}O_{nitrate}$ = 2.111(6), 2.060(6), 2.100(6)Å, $Co\text{---}O_{nitrate}$ = 2.44(1)Å, $Co\text{-}O_{water}$ = 2.073(7)Å; individual molecules are linked together *via* O-H---O, N-H---O, and C-H---O interactions [549]. The structural characterisation and an analysis of the spectral properties of the trigonal bipyramidal complex, (**156**), (H atoms omitted for clarity), have been described; the system is a model for cobalt substituted carbonic anhydrase, and it is interesting that the Co-O distance is somewhat short, *viz.* 2.024(7)Å [550]. Two novel trinuclear cobalt(II) complexes containing bridging alkyl-substituted triazole ligands have been prepared; the structure of an analogous Ni(II) complex has been determined [551].



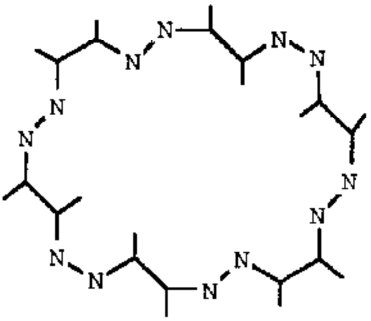
(**155**)



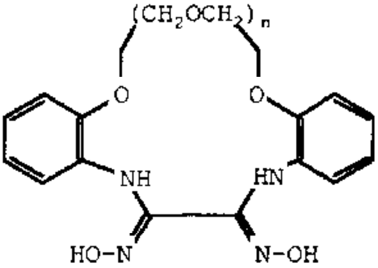
(**156**)

2.3.8.8 *Macrocyclic ligands*

The kinetics of electron transfer during the oxidation of $[Co(sep)]^{2+}$, (sep = (**25**)), by iodine have been investigated; the involvement of I_3^-, which rapidly dissociates to I^- and I_2 within the time scale of the rate determining step, is proposed [552]. Coordination to Co(II) ions of a 24-membered macrocyclic ligand, L, (**157**), (H atoms omitted for clarity), has resulted in the formation of the octahedral complexes $[(Co_2L)X_4].nH_2O$, (X = Br, I, NO_3, SCN); some electrochemistry of the complexes has been described [553]. The presence of a dangling amino-substituent, R, on an otherwise tetradentate macrocycle, (related to (**45**)), increases the coordinating ability of the ligand to pentadentate, but only if the amino-group is not sterically hindered [554]. The potentially macrocyclic ligand, HL, (**158**), apparently prefers to utilise its oxime-N atoms as donor sites in the complex $[Co(HL)_2]$; a square planar geometry is proposed on the basis of infra red and ^1H n.m.r. spectroscopic results [555].



(157)



(158)

Improved syntheses to metal, including cobalt(II), complexes containing quadridentate, macrocyclic ligands have been described; individual ligands are too numerous to list here, but are related to (**42**) or (**129**) [556, 557].

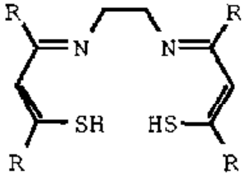
Cobalt(II) complexes invoking porphyrin or phthalocyanine ligands are detailed below. Any non-standard abbreviations used have previously been defined in Section 2.2.7.7. The catalytic properties of [Co(TPP)] and [Co(Pc)], with respect to quadricyclane isomerisation, have been studied [558]. During the course of electrochemical investigations, species of the type $[Co(TPP)(NO)L]^+$ have been observed; formation constants, log *K*, for the complexes are 3.1±0.1, 3.3±0.1, and 5.3±0.2 for L = dmf, dmso, and py respectively [559]. An interesting bridged, heterometallic complex has been characterised and exhibits a nickel(II) Schiff base complex coordinated *via* an imidazole residue to the axial site of [Co(TPP)] [560]. Stopped flow techniques have been used to monitor the complex formation between Co(II) ions and *N*-methylated-$TPPH_2$; the reaction is second order, depending on each reagent, and a value of $\Delta V^{\ddagger} = 8.0 \pm 0.3$ cm^3 mol^{-1} has been determined [561]. In experiments designed to provide models for coenzyme B_{12}, e.p.r. spectra of complexes with spin-labelled py coordinated to [Co(TFPP)], ($TFPPH_2$ = tetra(*p*-trifluoromethyl)porphyrin), have been analysed [562]. Alkoxy-derivatives of $TPPH_2$ have been the subjects for both preparative, [563], and catalytic, [564], investigations. A rather exotic ligand sporting a crown ether-substituted-tri(*p*-chloro)porphyrin has been prepared; reaction with cobalt(II) ions results in the formation of a 1:1 complex [565].

A new, and direct route to peripherally substituted, (R = ^{t}Bu, MeO, NO_2), phthalocyanine complexes of cobalt(II) has been developed; some spectroscopic properties, and the thermal stability of the complexes, have been presented [566]. Polysulphophthalocyanine ligands, H_2Pc' and H_3Pc'', give the complexes [Co(Pc')] and [Co(HPc")], the oligomerisation of which has been described [567]. Gel filtration of some polymeric [CoPc] complexes has allowed separation of two fractions; the first is of low molecular weight and is fluorescent, while the second contains dimeric and polymeric material [568]. The catalytic reduction of CO_2 to CO at a [CoPc]-modified carbon electrode surface has been reported [569]. Mechanistic details for the autooxidation of thiols using polyvinylamine supported [CoPc*], (Pc^*H_2 = tetra(NaO_3S)phthalocyanine), have been discussed [570].

2.3.9 Complexes with nitrogen-sulphur donor ligands

2.3.9.1 Aminothiol and related ligands

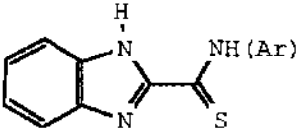
The oxidation of [Co(en)$_2$(2-py-thiol)] by H_2O_2 in acidic solution is reported to give $[Co(en)_2L]^{2+}$, where HL = 2-py-sulphenic acid [571]. Complexation of the ligand, H_2L, **(159)**, has been explored by two independent groups. Firstly, the crystal structure of the complex [CoL], (R = Me), has been determined; the cobalt(II) ion is in a square planar environment, with inner sphere distances of Co-S = 2.155(1), 2.142(2)Å, and Co-N = 1.905(4), 1.910(4)Å [572]. The second paper looks at the electrochemistry of the complex [CoL] in methanol solution, and in the presence of $[Bu_4N][ClO_4]$ [573]. Related chemistry has involved the preparation and characterisation of the covalent complexes, [CoL] and $[Co(H_2L)X_2]$, in which H_2L possesses the same donor set as **(159)**, (X = Cl, Br) [574].



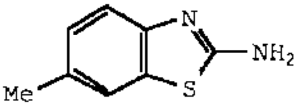
(159) R = Me; CF_3; Ph; *p*-MeO-C_6H_4; *p*-Br-C_6H_4

2.3.9.2 Thioamides and related ligands

The solvent dependence of complex formation between Co(II) ions and $H_2NC(S)NH_2$, (tu), has been studied; aquation of the product $[Co(tu)_4]^{2+}$ ion is accompanied by tetrahedral to octahedral configurational conversion [575]. The preparation and physicochemical characterisation of the complex $[CoL_2(H_2O)_2]$, (HL = PhC(S)NHC(S)NHPh), has been reported, along with an assessment of the fungi-toxicity of HL and of the complex [576]. Related work by the same authors deals with complexation between Co(II) ions and $PhC(SCH_2Ph)=NC(S)NHPh$; again, antifungal activity is a key issue [577].



(160)



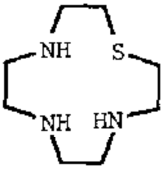
(161)

The reaction of $CoCl_2$ with β-naphthylamine in ethanol with CS_2 present leads to the complex $[CoL_2]$ in which HL is β-naphthylaminedithiocarbamic acid; the complex is reported to be square planar [578]. The preparation and spectral characterisation of $[Co(pytu)_2Cl_2]$, (pytu = pyridyl-2-thiourea) has been described; the ligand coordinates *via* the py-N and thione-S atoms [579]. The reaction of cobalt(II) ions, in methanol solution, with aryl substituted ligands, **(160)**, HL, leads to complexes of type [CoL] [580]. Cobalt(II) complexes involving thiosemicarbazone ligands have also been investigated [581, 582].

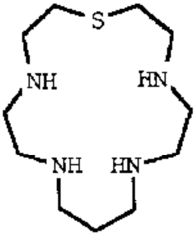
2.3.9.3 Miscellaneous ligands

The heterocyclic ligand, L, **(161)**, forms the complexes $[CoLX_2]$, CoL_2X_2, and $[CoL_4X_2]$, (X = I, NCS, OAc), for which preparative and spectroscopic details have been described [583].

Macrocyclic S-N-donor ligands, **(162)**, L, and **(163)**, L', have been synthesised, and their protonation constants determined. An investigation of the complex formation of these ligands with cobalt(II) ions has been complimented by a study of the kinetics, (using stopped flow techniques), of the uptake of dioxygen by the complex products. The ion $[CoL']^{2+}$ is high spin, and coordinates O_2 rapidly to give a brown, monobridged peroxo-species. On the other hand, a green, μ-peroxo-species formed between dioxygen and $[CoL]^{2+}$ appears to exhibit some μ-superoxo- character [584].



(162)

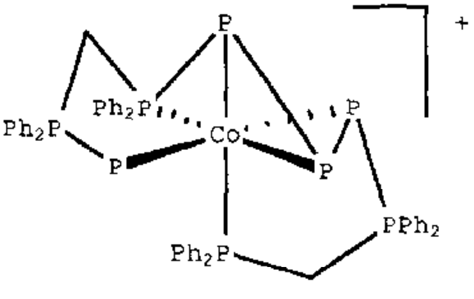


(163)

2.3.10 *Complexes with phosphorus ligands*

Two papers from the same authors have described kinetic results for the reaction of $[CpCoLX]^+$, (X = Cl, Br, I; L = bidentate ligands, e.g. dppe, dppp, dppb, en, bpy), with the phosphites, $P(OMe)_3$ or $P(OEt)_3$; ^1H and ^{31}P n.m.r. spectroscopic data have been used to confirm mechanistic details. It has been concluded that steric control is important in the pre-equilibrium step, and that the rate determining step is electronically controlled [585,586].

An interesting reaction is one between $[Co(BF_4)_2].6H_2O$ and white phosphorus in the presence of dppm; the product has been structurally characterised, **(164)**, and exhibits an open, P_4-chain, with P-P distances of 2.173(3), 2.197(3), and 2.171(3)Å [587].



(164)

2.4 *Cobalt(II)/(III) Complexes with Dioxygen and Related Compounds*

Complexes in this section are organised according to ligands: ammines, amines, macrocyclic N-donors, N-O-donors, Schiff bases, heterocyclic ligands, culminating with $TPPH_2$ and PcH_2.

Structural and spectroscopic studies of the μ-peroxo-complex $[(H_3N)_5Co)_2(O_2)][(NO_3)_2Cl_3].2H_2O$ have confirmed previously presented results, and illustrate that the dioxygen is a good π-acceptor as well as a good π-donor [588]. Aqueous ammoniacal solutions of cobalt(II) ions in the presence of SCN^- ions and dioxygen have been monitored *via* infra red, electronic, and n.m.r. spectroscopic techniques; $[\{Co(NH_3)_4(NCS)\}_2O_2][NCS]_2.4H_2O$ has been identified [589].

The interaction of some cobalt(III) amine, (L = NH_3, ND_3, en, sep, phen, chxn), complexes with the superoxide ion has been observed; the kinetics of the subsequent outer sphere electron transfer reactions obey the rate equation:

$$\rho = k[O_2^-][Co(III)]$$

and the results have been discussed in terms of Marcus theory [590]. The formation of the dioxygen complex ion $[\{(en)LCo\}_2O_2]^{4+}$ requires a conformational change in the ligand L, $(H_2NCH_2)_3CH$; spectral characterisation of this, and related complexes has been reported [591].

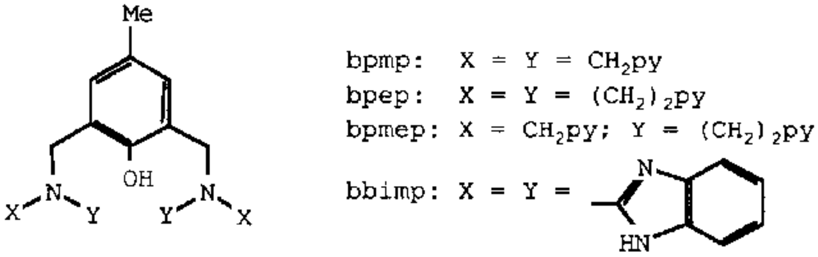
The structure of $[(en)(dien)CoO_2Co(dien)(en)]^{5+}$ has been determined and a planar Co-O-O-Co unit confirmed; Co-N distances range from 1.935(16) to 1.977(18)Å, Co-O = 1.897(12)Å, and O-O = 1.336(17)Å. The authors have correlated structural and electronic properties of some complexes related to the latter ion [592]. A comparison with $[(CN)(tren)CoO_2Co(tren)(CN)]^{2+}$ is instructive; structural parameters include Co-O = 1.898(6)Å and O-O = 1.494(11)Å [593]. Thermochemical studies relating to the uptake of dioxygen by the complex [CoL], (L = tetren), have been reported [594]. The cobalt(II) complexes, $[LCo(O_2)CoL]$ and $[LCo(O_2)(OH)CoL]$, in which L is one of several tri- and pentadentate *N*-benzyltriamine ligands, have been shown to be suitable models for the design of high polymer, oxygen-carrying systems [595]. An investigation of the kinetics of the reversible uptake of O_2 by a histamine containing cobalt(II) complex has given an equilibrium constant of (1.22 ±

0.15) x 10^3 for the process [596]. For the complex, [CoL], (L = $H_2N(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$), the redox rearrangement of the dioxygen adduct has been the subject of study; at 15°C, the rate constant for intramolecular cobalt(II) to cobalt(III) oxidation is $(4.0 \pm 0.2) \times 10^{-4}\ s^{-1}$ [597]. The kinetics and mechanism of autoxidation pathways of Co(II) complexes with pyridyl-containing pentamines have been detailed, and compared and contrasted with other related cobalt dioxygen complexes [597a].

The cobalt(II) cyclam complex, forms the species $[Co_2(cyclam)_2O_2]^{4+}$ and $[Co_2(cyclam)_2O_2(OH)]^{2+}$; heats of reaction relating to the formation of these complex ions have been determined as (-86.1 ± 2.5) and (-132.1 ± 2.2) kJ mol^{-1} respectively [598]. Several discussions covering various aspects of dioxygen uptake by cobalt complexes involving the cyclic ligands **(45)** and **(46)**, or related ligands, have appeared [599-601].

Pulse radiolysis techniques have been applied to the observation of superoxide complexes of $[Co(edta)]^{2-}$ and $[Co(edta)]^-$ [602]. A heterocyclic amine oxide has been gainfully employed as a spin trapping agent for a cobalt(II) dioxygen complex [603].

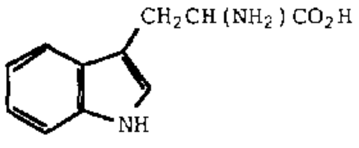
Ligands, HL, defined in **(165)**, form the dinuclear cobalt complexes $[Co_2L(OAc)_2][ClO_4]$, $[Co_2L(OAc)][ClO_4]_2$, $[Co_2L(OH)][ClO_4]_2$ and $[Co_2L(plz)][ClO_4]_2$; for L = bpmp or bpmep, reversible uptake of dioxygen is observed, and equilibrium constants for this process have been determined [604].



(165)

Cobalt(II) complexes of $2\text{-}HO\text{-}C_6H_4\text{-}CH{=}N(CH_2)_nN{=}CH\text{-}C_6H_4\text{-}2\text{-}OH$ and related ligands appear not to bind O_2 [605]. Dioxygen adducts of some [Co(salen)] derivatives have been the subject of resonance Raman spectroscopic investigations; the modes ν_{O-O} and ν_{Co-O} have been assigned at 1146-1143 and 530-515 cm^{-1} respectively [606]. The dimeric nature of the complex $[\{Co(salen)\}_2(O_2^-)]$ in aqueous solution has been established; reaction of this complex with CN^- and NSC^- proceeds *via* initial dissociative exchange of the axially coordinated water molecules, followed by rapid loss of dioxygen [607]. The dioxygen carrying properties of several other cobalt(II) Schiff base complexes have been discussed [608,609].

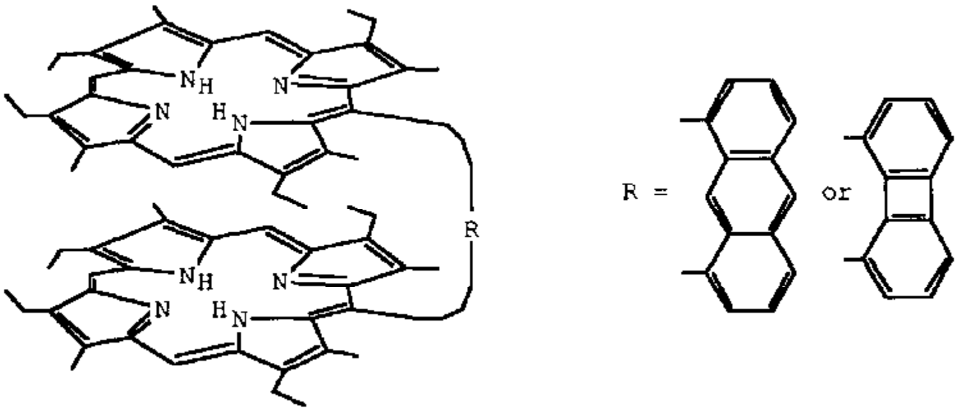
A cobalt-substituted cytochrome *c* peptide, which acts as an artificial dioxygen carrier, has been prepared; e.s.r. spectroscopy has been used to probe the nature of the bound O_2 [609a]. The complex $[Co(phen)L(H_2O)]$, (H_2L = glycyl-DL-ala), binds dioxygen to form a dinuclear species; the coordinated O_2 molecule oxidises the peptide upon thermolysis of the dioxygen containing complex [610]. The same authors have looked at the kinetics of oxygen uptake by $[Co(phen)L(H_2O)]^+$, (L = amino acid) [611], and have measured stability constants for complexes of the type $[L(phen)Co(\mu-O_2)(\mu-OH)Co(phen)L]$ [612]. Some related work reports kinetic and mechanistic details of the decomposition in acidic solution of the complex ion, $[(phen)_2(H_2O)Co(\mu-O_2)Co(H_2O)(phen)_2]^{4+}$ [613]. The reaction of cobalt(II) chloride with HL, (HL = (**166**), in ethanol at pH 6-7, produces $[CoL_2(EtOH)_2]$ which reversibly binds dioxygen at pH 8; the complex $[CoL_2(EtOH)].(O_2).EtOH$ may be isolated over the range pH 9-10 [614].



(**166**)

Two related papers report the formation of silica surface bound cobalt(II) pyridine complexes with either PcH_2 or Schiff base ligands; the dioxygen binding properties of these complexes have been assessed [615,616]. An investigation of the oxidation of carbon monoxide by O_2 over transition metal phthalocyanines shows that the reactivity of [CoPc] is lower than that of [NiPc], but exceeds that of [CuPc] [617]. The pathway of the oxygenation of the ^{t}Bu-derivatised [CoPc] in dmf solution is pH dependent; in neutral solution, a dioxygen adduct is formed reversibly, whereas, in alkaline solution, oxidation of the complex occurs [618].

Porphyrin complexes complete this review of cobalt(II) and cobalt(III) dioxygen species. A resonance Raman spectroscopic study of dioxygen adducts of [Co(TPP)] and derivatives thereof has illustrated the dependence of ν_{O-O} upon the nature of the axial ligands present in the complexes [619]. Reversible binding of dioxygen is reported for the complex [Co(TPP)(PVP)], (PVP = poly-4-vinyl-py), at -78°C; the mechanism of the reaction is discussed [620]. Mechanistic details of the reduction of O_2 by [Co(TPP)] at a graphite electrode surface have been presented [621]. By virtue of its bridgehead unit, the diporphyrin, $TPPH_2$-$TPPH_2$, **(167)**, possesses only limited flexibilty. Thus, the two metal centres of the dinuclear cobalt(II) complex, [Co_2(TPP-TPP)], are beautifully set up to bind dioxygen; the electroreduction of O_2 is catalysed by [Co_2(TPP-TPP)], and the efficiency of the catalyst is effected by the degree of flexibility inherent in the $TPPH_2$-$TPPH_2$ ligand [622].



(167)

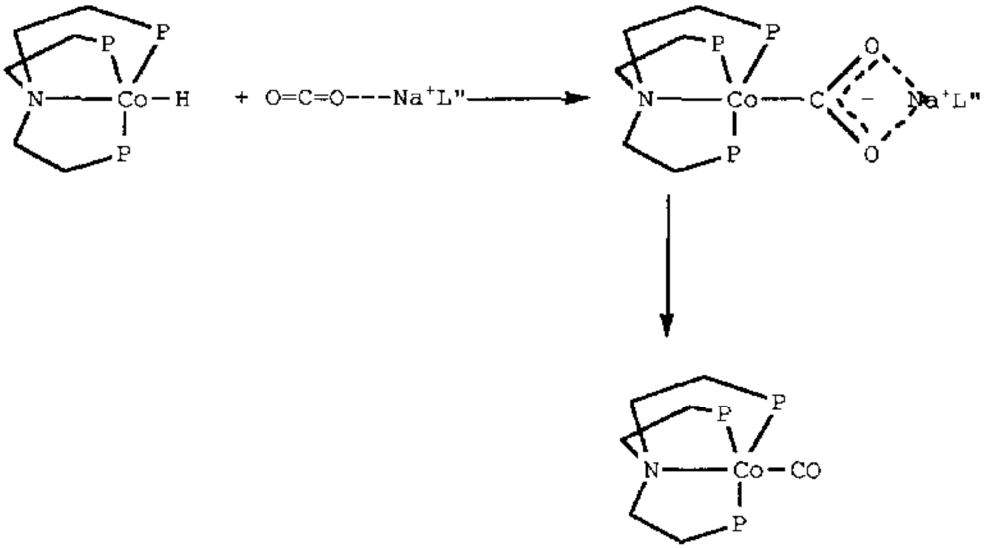
The syntheses of some cyclophane porphyrins, and the spectroscopic characterisation of their Zn(II) complexes have been described; the corresponding cobalt(II) complexes are reported to bind O_2, and the efficiency of this reaction is, significantly, dependent upon the length of the bridging group, $-\{CH_2CH_2C(O)NH-(CH_2)_n-NHC(O)CH_2CH_2\}-$ (n = 6-10, 12, 14) in the porphyrin ligands [623]. Cyclic and differential pulse voltammetry, rotating disc electrode, and spectroelectrochemical techniques have been applied to a study of the complexes [CoL], (H_2L = tetra(4-*N,N',N"*-trimethylanilinium)$TPPH_2$), and their dioxygen carrying properties [624].

2.5 COBALT(I)

Heterocyclic ligands predominate in the reported chemistry of the cobalt(I) ion. In acidic media, the cobalt(I) complex, $[Co(bipy)_3]^+$, is in equilibrium with the cobalt(III) hydride species, $[Co(bipy)_2(H_2O)H]^{2+}$; from kinetic data, a free radical mechanism is implied, and the formation of $[(bipy)H]^\bullet$ in the rate determining step is proposed [625].

Results of a variable temperature, solution ^1H n.m.r. spectroscopic study of the metallaborane $[Co(terpy)(\mu-H)_2BH_2]$ provide an activation energy for terminal/bridge proton exchange of 11.1 ± 0.1 kcal mol^{-1}; for a bidentate BH_4^- ligand, this figure represents the highest barrier so far for such a process [626]. Chemical shift values in the ^{31}P n.m.r. spectra of base-on cobalamins show a far greater variation than do those of the base-off complexes; attempts to rationalise these observations have been presented [627].

In thf solution, [LCoH], (L = $(Ph_2CH_2CH_2)_3N$), does not react with CO_2. However, in the presence of sodium tetraphenylborate, the reaction proceeds to give the complexes $[LCo(CO)][BPh_4]$ and $[L'Co][BPh_4]_2$, where L' is $(Ph_2PCH_2CH_2)_2N(CH_2CH_2P(=O)Ph_2)$. A possible mechanism for the reaction is shown in Scheme 3 [628]. Another cobalt(I) hydride is $[HCoL_4]$ in which L this time is diethylphenylphosphonite; laser flash photolysis of this compound in cyclohexane yields a transient, coordinatively unsaturated species [628a].

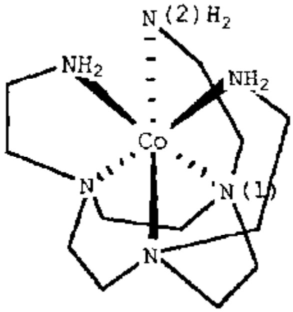


Scheme 3

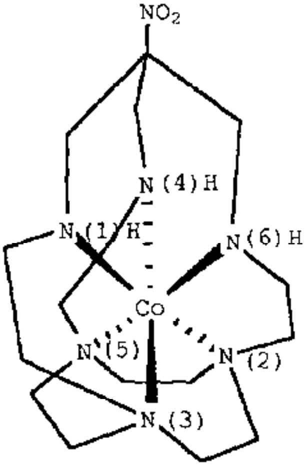
2.6 THEORETICAL INVESTIGATIONS

The degree to which magnetic and spectral properties of a complex are influenced by distorting, (*e.g.* metal ion displacement or angular changes to the ligands), an initially regular ligand array has been investigated [629].

Two references to molecular mechanics calculations have already been made [151,156]. For the complexes **(168)** and **(169)**, structural parameters obtained from molecular mechanical calculations have been compared with those from X-ray analyses; comparitive bond distances are given in Table 6 [630]. Strain energy minimisation calculations have also been applied to some octahedral polyamine complexes such as *mer*-$[CoCl(N\text{-}N)(dien)]^{2+}$, (N-N = en, 1,3-pn, or $(NH_3)_2$) and to the corresponding 5-coordinate residue, *e.g.* *mer*-$[Co(N\text{-}N)(dien)]^{3+}$; the difference in energy between the 5- and 6-coordinate complexes provides useful information applicable to the kinetics of substitution reactions [631]. A simple ligand field model has been used to calculate orbital and state correlation diagrams for 5-coordinate intermediates in the substitution reactions of *cis*- and *trans*-$[Co(en)_2AX]^{n+}$; the leaving group, X, is Cl^-, Br^-, Me_2SO or N_3^-, and the nucleophile, A, is CN^-, NO_2^-, NH_3, Br^-, Cl^-, N_3^-, H_2O, or OH^-. Theoretical results tie in well with those obtained experimentally [632].



(168)



(169)

Table 6. Comparison of calculated and experimental bond lengths in the complexes (**168**) and (**169**) [631].

Complex (**168**)

Bond	Distance from X-ray /Å	Distance from Molecular mechanics /Å
Co-N(1)	1.963(3)	1.974
Co-N(2)	2.009(4)	1.984

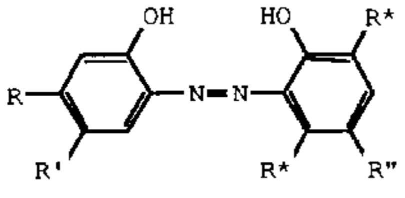
Complex (**169**)

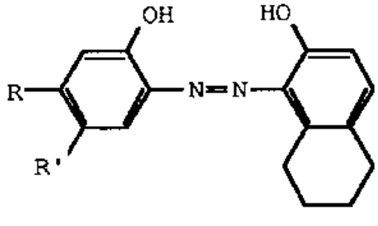
Bond	Distance from X-ray /Å	Distance from Molecular mechanics /Å
Co-N(1)	1.996(6)	1.995
Co-N(4)	1.999(5)	1.995
Co-N(6)	2.001(5)	1.995
Co-N(2)	1.950(6)	1.989
Co-N(3)	1.975(5)	1.989
Co-N(5)	1.961(3)	1.989

By using X-ray diffraction data along with the results of MO calculations, (STO-3G basis set), a correlation between the axial and in-plane bond lengths in sixteen tetragonal, 6-coordinate complexes of type *trans*-$[CoX_2N_4]$ has been developed; the out-of-plane bond distance decreases as the in-plane distance increases [633]. The conformations of some 6-membered cobalt(III) amino acidato chelate rings have been investigated by means of the program *RING;* the output of the program includes torsion angles and puckering parameters [634]. Total energies are also available from the results of extended Hückel calculations. Just such a study has been carried out on the complexes $[(triphos)Co(\eta^2\text{-}CS_2)]$ and $[LCo(\eta^2\text{-}SCNPh)].1.33BuOH$, $(L = (Ph_2PCH_2CH_2)_3N)$; the results are complimented by structural elucidation *via* traditional X-ray diffraction techniques [635]. The electronic structures and total energies of the complexes $[Co(dmgH)_2].nH_2O$, $(n = 0,1)$, have been determined within the constraints of a semi-empirical Mulliken-Wolfsberg-Helmholtz approximation; attempts to rationalise the reactivity patterns of the complexes in terms of the theoretical results are made [636].

A model N_4-ring has been used to represent a porphyrin ligand in a theoretical investigation of some cobalt(III) dioxygen complexes; using an approach which includes configuration interaction, the best description of the dioxygen moiety is found to be that of a superoxide ligand. The O_2^- ion donates electrons into an empty orbital concentrated on the cobalt(III) centre [637].

Calculations using the CNDO/2 approach have included studies of $[Co(phen)L(H_2O)_3]^{2+}$, (L = py, 4-H_2N-py) [638], complexes of type $[CoL_n(H_2O)_{6-n}]^{2+}$, (L = py, 4-H_2N-py) [639], and cobalt complexes with tetraazamacrocyclic ligands [640]. Also within the CNDO/2 method, heats of coordination have been determined for a variety of Co(II), Ni(II), Fe(II), Cu(II) and Zn(II) complexes containing F^-, H_2CO^-, H_2O, NH_3, MeCN, and CO ligands [641].





R = H,Cl,Me,NO_2; R' = H,Cl,Me,OMe,NO_2; R" = Me,OMe; R* = H,Me

(170) **(171)**

Finally, the results of extended Hückel and MNDO/3 calculations relating to cobalt complexes with the azo ligands (**170**) or (**171**) support UV-visible spectroscopic data recorded for the compounds; chelation *via* the azo-N adjoining the least substituted phenyl ring is proposed [642].

2.7 ^{59}Co n.m.r. SPECTROSCOPY

Several papers either focus attention on, or at least make use of, ^{59}Co n.m.r. spectroscopy. The potential of the technique is noted in an investigation of the exchange between solvent and ammine protons, for $[Co(NH_3)_6]^{3+}$ dissolved in dmso in the presence of D_2O and NEt_3 [643]. Related work has looked at nineteen isotopic species lying between the limits of $[Co(NH_3)_6]^{3+}$ and $[Co(ND_3)_6]^{3+}$, as well as thirteen species derived from $[Co(en)_3]^{3+}$; large ^{59}Co n.m.r. spectral chemical shift ranges provide a useful means of analysing the isotopic composition of these complexes [644].

The products of the reactions of $[Co(dien)Cl_3]$ and L, (L = NH_3, en, dien, urea, NCO^-, NCS^-, $S_2O_3{}^{2-}$), have been established by using ^{59}Co n.m.r. spectroscopy, thus illustrating the potential of this experimental technique [645]. The reaction of the complex ion $[\{Co(en)(dien)\}_2O_2]^{4+}$ with iron(II) ions has been monitored by stopped flow methods and by ^{59}Co n.m.r. spectroscopy; the reaction shows two separate initial reduction steps with second order rate constants of 1.07 and 3.04 M^{-1} s^{-1} respectively [646]. A detailed n.m.r. spectroscopic study of the oxygenation of bis(L-histidinato)-cobalt(II) has shown a significant pH dependence of the reaction sequence [647].

Nitrosyl containing complexes have been the focus of attention in one ^{59}Co n.m.r. spectroscopic survey; chemical shifts, which are sensitive to solvent, range from δ 9390 (dmso) for the ^{59}Co nucleus in $[CoL_2(NO)]$, (L = 2-HO-C_6H_4-C(Me)=NOH) to δ 4020 for $[Co(Me)(H_2O)(dmgH)_2]$ [648]. The complexes $[Co(acac)_2(PhacPhSac)]$ and *cis*-C_1-$[Co(acac)(PhacPhSac)_2]$ have been synthesised. Their ^{59}Co n.m.r. spectroscopic signatures illustrate a linear correlation between δ ^{59}Co and the composition of the chromophore, *viz.* CoO_6, CoO_5S, CoO_4S_2, or CoO_3S_3 [649]. ^{59}Co n.m.r. spectroscopy has also gainfully been employed to monitor spin crossover phenomena [650].

REFERENCES

1. R.W. Hay, *Coord. Chem. Rev.*, 71 (1986) 37.
2. C.E. Housecroft, *Coord. Chem. Rev.*, 90 (1988) 111.
3. R.W. Hay, *Mech. Inorg. Organomet. React.*, 2 (1984) 153.
4. Y. Shimura and K. Yamanari, *Kagaku (Kyoto)*, 39 (1984) 68.
5. M.G. Burnett and M.H.M. Abou-El-Wafa, *J. Chem. Soc., Dalton Trans.*, (1984) 2341.
6. P.K. Ghosh, B.S. Brunschwig, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 106 (1984) 4773.
7. F.C. Anson, T.J. Collins, R.J. Coots, S.L. Gipson and T.G. Richmond, *J. Am. Chem. Soc.*, 106 (1984) 5037.
8. M.G. Burnett, *Chem. Soc. Rev.* 12 (1983) 267.
9. H. Inoue and E. Fluck, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.,* 39B (1984) 185.
10. R. Lykvist and R. Larsson, *Z. Phys. Chem. (Leipzig)*, 265 (1984) 633.
11. T.E. Gogoleva, A.A. Marchemko and Yu.A. Sakharovskii, *Kinet. Katal.*, 25 (1984) 234.
12. V.G. Kutsaev, I.A. Potapov, M.B. Rozenkevich, Yu.A. Sakharovskii, G.P. Bulgakova and P.A. Zagorets, *Khim. Vys. Energ.* 18 (1984) 114.
13. R. Palmans, L. Viaene and J. D'Olieslager, *Inorg. Chem.*, 23 (1984) 1792.
14. J. Ribas, M. Serra and A. Escuer, *Inorg. Chem.*, 23 (1984) 2236.
15. G. Schiavon and C. Paradisi, *Inorg. Chim. Acta*, 81 (1983) 219.
16. M.H.M. Abou-El-Wafa and M.G. Burnett, *Polyhedron*, 3 (1984) 895.
17. R. van Eldik, U. Spitzer and H. Kelm, *Inorg. Chim. Acta*, 74 (1983) 149.
18. R. van Eldik and U. Spitzer, *Transition Met.Chem. (Weinheim)*, 8 (1983) 351.
19. V.A. Lunenok-Burmakina, V.B. Emel'yanov, G.G. Lezina, L.I. Grishchenko and S.K. Rubanik, *Ukr. Khim. Zh. (Russ. Ed.)*, 50 (1984) 363.
20. I.D. Isaev, T.V. Stupko, O.Yu. Vybornov and V.E. Mironov, *Koord. Khim.*, 10 (1984) 529.
21. T.P. Dasgupta and G.M. Harris, *Inorg. Chem.* 23 (1984) 4399.
22. N.E. Dixon, W.G. Jackson, G.A. Lawrance and A.M. Sargeson, *Inorg. Synth.* 22 (1984) 103.
23. G. Brewer, S. Drucker, J. Girard, C. Grisham and E. Sinn, *Inorg. Chim. Acta*, 89 (1984) 105.
24. D.R. Jones, L.F. Lindoy and A.M. Sargeson, *J. Am. Chem. Soc.*, 106 (1984) 7807.
25. T.P. Harmony, W.B. Knight, D. Danaway-Mariano and M. Sundaralingham, *Inorg. Chem.*, 23 (1984) 2412.
26. J. Reibenspies and R.D. Cornelius, *Inorg. Chem.*, 23 (1984) 1563.
27. T.P. Harmony, P.F. Gilletti, R.D. Cornelius and M. Sundaralingham, *J. Am. Chem. Soc.*, 106 (1984) 2812.
28. P.R. Norman, P.F. Gilletti, R.D. Cornelius, *Inorg. Chim. Acta*, 82 (1984) L5.
29. A.Okumura, N. Takeuchi, S. Tsuji and N. Okazaki, *Inorg. Chim. Acta*, 74 (1983) 77.

29a. I.I. Creaser, G.P. Haight, R. Peachey, W.T. Robinson and A.M. Sargeson, *J. Chem. Soc., Chem. Commun.*, (1984) 1568.

30. N. Sahu, P.C. Rath and N.K. Mohanty, *Indian Chem. Soc.*, 60 (1983) 1027.

31. E. Kremer, G. Cha, M. Morkevicius, M. Seaman and A. Haim, *Inorg. Chem.*, 23 (1984) 3028.
32. M.S. Ram, J.R. Barber and E.S. Gould, *Inorg. Chem.*, 23 (1984) 1989.
33. P. Kalidoss and V.S. Srinivasan, *J. Chem. Soc., Dalton Trans.*, (1984) 2631.
34. R. Marcec, M. Orhanovic, J.A. Wray and R.D. Cannon, *J. Chem. Soc., Dalton Trans.*, (1984) 663.
35. A. Hammershøi, A.M. Sargeson and W.L. Steffen, *J. Am. Chem. Soc.*, 106 (1984) 2819.
36. N.H. Williams and J.K. Yandell, *Aust. J. Chem.*, 36 (1983) 2377.
37. T.T.-T. Li and M.J. Weaver, *J. Am. Chem. Soc.*, 106 (1984) 6107.
38. T.T.-T. Li, H.Y. Liu and M.J. Weaver, *J. Am. Chem. Soc.*, 106 (1984) 1233.
39. H. Ito, *Tokushima Diagaku Kyoyobu Kiyo, Shizen Kagaku*, 16 (1983) 1.
40. H.F. Lee, H.C. Lee, C.S. Tam, K.K. Cheung and W.C. Fu, *Hsiang-Kang Ch'iu Hui Hsueh Yuan Hsueh Pao*, 9 (1982) 111.
41. I.G. Murgulescu amd G. Mincu, *Rev. Roum. Chim.*, 28 (1983) 779.
42. S.K. Sarkar, P.K. Tarafdar, A. Roy and S. Aditya, *J. Indian Chem. Soc.*, 60 (1983) 1142.
43. M.J. Blandamer, J. Burgess and E.-E.A. Abu-Gharib, *Transition Met. Chem. (Weinheim)*, 9 (1983) 193.
44. J. Burgess and E.-E.A. Abu-Gharib, *Transition Met. Chem. (Weinheim)*, 9 (1983) 234.
45. M.B. Davies, *Inorg. Chim. Acta*, 92 (1984) 141.
46. T. Tominaga, K. Tanabe and J. Takanaka, *J. Solution Chem.*, 13 (1984) 563.
47. V.E. Mironov, I.D. Isaev, V.M. Leont'ev, V.A. Fedorov and N.P. Samsonova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 26 (1983) 1185.
48. K. Ohkubo, K. Yamashita and S. Sakaki, *J. Mol. Catal.*, 22 (1983) 165.
49. K. Ito, H. Isono, E. Iwamoto and Y. Yamamoto, *Inorg. Chem.*, 23 (1984) 850.
50. N.A. Lewis and A.M. Ray, *Inorg. Chem.*, 23 (1984) 3649.
51. N.A. Lewis and A.M. Ray, *Inorg. Chem.*, 23 (1984) 3699.
52. Y. Kitamura and R. van Eldik, *Transition Met. Chem. (Weinheim)*, 9 (1983) 257.
53. B. Hajek, D. Sykorova and J. Chyba, *Collect. Czech. Chem. Commun.*, 49 (1984) 680.
54. S.S. Isied and A. Vassilian, *J. Am. Chem. Soc.*, 106 (1984) 1732.
55. R.B. Patel and J.K. Verma, *J. Indian Chem. Soc.*, 60 (1983) 1094.
56. A.T. Pilipenko and N.A. D'yachenko, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 27 (1984) 533.
57. D.J. Radanovic, *Coord. Chem. Rev.*, 54 (1984) 159.
58. E. Brücher, Cs.E. Kukri and R. Király, *Inorg. Chim. Acta*, 95 (1984) 135.
59. A.M. Lannon, A.G. Lappin and M.G. Segal, *Inorg. Chem.*, 23 (1984) 4167.
60. H. Okazaki, K. Tomioka and H. Yoneda, *Inorg. Chim. Acta*, 74 (1983) 169.
61. M. Haner, A.F. Eidson, D.W. Darnall and E.R. Birnbaum, *Arch. Biochem. Biophys.* 231 (1984) 477.
62. H. Ogini and H. Isago, *Chem. Lett.* (1984) 561.
63. L.H. O'Connor and K.H. Pearson, *Synth. React. Inorg.*

Met.-Org. Chem. 14 (1984) 217.
64. E.B. Chuklanova, T.N. Polynova, A.V. Sobolev and M.A. Porai-Koshits, *Koord. Khim.* 10 (1984) 255.
65. G.A. Sigel and J.A. Weyh, *Inorg. Chem.*, 23 (1984) 3246.
66. S. Yano, T. Murata, M. Asami, M. Inoue, M. Yashiro, M. Kosaka and S. Yoshikawa, *Inorg. Chem.* 23 (1984) 4127.
67. V.E. Stel'mashok and A.L. Poznyak, *Zh. Neorg. Khim.* 29 (1984) 1046.
68. C.A. Chang, E.N. Duesler and R.E. Tapscott *Inorg. Chim. Acta* 85 (1984) 73.
69. K. Bernauer and P.Pousaz, *Helv. Chim. Acta* 67 (1984) 796.
70. M.F. Summers, L.G. Marzilli, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc.*, 106 (1984) 4478.
71. Y. Fujii, T. Kobayashi, M. Matsufuru and S. Takahashi, *Bull. Chem. Soc. Jpn.*, 56 (1983) 3608.
72. L.D.Dave and A.E. Komala, *J. Indian Chem. Soc.*, 61 (1984) 164.
73. Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, 57 (1984) 2650.
74. Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, 57 (1984) 47.
75. A. Neves, W. Herrmann and K. Weighardt, *Inorg. Chem.*, 23 (1984) 3435.
76. N.R. Brodsky, N.M. Nguyen, N.S. Rowan, C.B. Storm, R.J. Butcher and E. Sinn, *Inorg. Chem.*, 23 (1984) 891.
77. F. Jursik, J. Franc, J. Arnoldova and B. Hajek, *Collect. Czech. Chem. Commun.*, 49 (1984) 1665.
78. M. Yamaguchi, M. Saburi and S. Yoshikawa, *J. Am. Chem. Soc.*, 106 (1984) 8295.
79. V.P. Tarasov, T.Sh. Kapanadze, G.V. Tsintsadze, I.B. Baranovskii, S.A. Petrushin and Yu.A. Buslaev, *Dokl. Akad. Nauk. SSSR*, 276 (1984) 382.
80. K. Yamanari and Y. Shimura, *Chem. Lett.*, (1984) 761.
81. K. Okamoto, T. Konno, M. Nomoto, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1494.
82. B. Singh, B.P. Yadava and R.C. Aggarwal, *Indian J. Chem., Sect. A*, 23A (1984) 441.
83. R. Mukherjee and A. Chakravorty, *Inorg. Chem.*, 23 (1984) 4755.
84. Y. Akihiko, *J. Phys. Chem.* 88 (1984) 305.
85. I. Lin, A. Hsueh and D. Dunaway-Mariano, *Inorg. Chem.*, 23 (1984) 1692.
86. S. Ohba and Y. Saito, *Acta Crystallogr., Sect. C*, 40C (1984) 398.
87. M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, 56 (1983) 2958.
88. K. Okamoto, M. Suzuki, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 56 (1983) 3513.
89. K. Okamoto, M. Kanesaka, M. Nomoto and J. Hidaka, *Chem. Lett.* 12 (1983) 1861.
90. T. Konno, K. Okamoto and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 56 (1983) 2631.
91. M.A. Ali and R.N. Bose, *Polyhedron*, 3 (1984) 517.
92. S.K. Mondal, P. Paul, R. Roy and K. Nag, *Transition Met. Chem.(Weinheim)*, 9 (1984) 247.
93. N.K. Kaushik, G.R. Chhatwal and A.K. Sharma, *J. Therm. Anal.* 26 (1983) 309.
94. S. Muthuswamy and D. Venkappayya, *J. Inst. Chem. (India)* 56 (1984) 129.
95. C.A. Tsipis, M.P. Sigalas and C.C. Hadjikostas, *Z. Anorg. Allg. Chem.*, 505 (1983) 53.

96. G. Kartha and K.V. Krishnamurthy, *Proc.-Indian Acad. Sci., Chem. Sci.,* 92 (1983) 437.
97. B.M. Ondo, J.P. Barbier and R.P. Hugel, *Inorg. Chim. Acta,* 77 (1983) L211.
98. J. Doherty, J. Fortune, A.R. Manning and F.S. Stephens, *J. Chem. Soc., Dalton Trans.,* (1984) 1111.
99. W.P. Schaefer, *Acta Crystallogr., Sect. C,* 39C (1983) 1610.
100. M. Sundaralingam and T.P. Harmony, *J. Biomol. Struct. Dyn.,* 2 (1984) 55.
101. S. Balt, C.R.P. MacColl,. *Anorg. Allg. Chem.,* 513 (1984) 208.
102. L. Dubicki and B. Williamson, *Inorg. Chem.,* 23 (1984) 3779.
103. A.V. Mahajani and N. Arora, *J Indian Chem. Soc.,* 60 (1983) 1099.
104. J.G. Russell and R.G. Bryant, *J. Phys. Chem.,* 88 (1984) 4298.
105. D. Rehorek and E.G. Janzen, *Z. Chem.,* 24 (1984) 228.
106. E.V. Boldyreva, M.I. Tatarintseva and N.Z. Lyakhov, *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.,* (1984) 24.
107. E.V. Boldyreva and N.Z. Lyakhov, *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.,* (1984) 21.
108. E.V. Boldyreva and N.Z. Lyakhov, *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.,* (1984) 18.
109. R. Tsuchiya, A. Uehara and T. Nakayama, *Bull. Chem. Soc. Jpn.* 56 (1983) 3284.
110. G.J. Ferraudi and J.F. Endicott, *J. Phys. Chem.,* 88 (1984) 4444.
111. S. Balt and H.J. Gamelkoorn, *Inorg. Chim. Acta,* 86 (1984) L61.
112. S. Balt, W.E. Renkema and H. Ronde, *Inorg. Chim. Acta,* 86 (1984) 87.
113. W.G. Jackson, C.N. Hookey, M.L. Randall, P. Comba and A.M. Sargeson, *Inorg. Chem.,* 23 (1984) 2473.
114. M.C. Ghosh, P. Bhattacharya and P. Banerjee, *Transition Met. Chem. (Weinheim),* 9 (1984) 68.
115. M.F. Amira, F.M. Abdel-Halim, N.H. Ismail and M.M. Elsemongy, *Curr. Sci.,* 52 (1983) 1190.
116. Y. Kitamura, R. van Eldik and H. Kelm, *Inorg. Chem.,* 23 (1984) 2038.
117. M.C. Ghosh and P. Banerjee, *J. Coord. Chem.,* 13 (1984) 237.
118. G. Yeshoda, S. Alwar, S. Bangaru and V. Thiagarajan, *Indian J. Chem., Sect. A,* 23A (1984) 564.
119. A.C. Dash, S. Khatoon and R.K. Nanda, *Indian J. Chem., Sect. A,* 22 (1983) 940.
120. J. M. Harrowfield, L. Spiccia and D.W. Watts, *Aust. J. Chem.,* 36 (1983) 1923.
121. A. Hammershøi, D. Geselowitz and H. Taube, *Inorg. Chem.,* 23 (1984) 979.
122. S.W. Barr and M.J. Weaver, *Inorg. Chem.,* 23 (1984) 1657.
123. W.C. Kupferschmidt and R.B. Jordan, *J. Am. Chem. Soc.,* 106 (1984) 991.
124. M.N. Bishnu, R.N. Banerjee and D. Banerjea, *Indian J. Chem., Sect. A,* 22 (1983) 948.
124a. N.J. Curtis, K.S. Hagen and A.M. Sargeson, *J. Chem. Soc., Chem. Commun.,* (1984) 1571.
125. S. Balt, H.J. Gamelkoorn, C.R.P. Mac-Coll and W.E. Rankema, *Transition Met. Chem.(Weinheim),* 9 (1984) 224.
126. G.A. Lawreance, K. Schneider and R. van Eldik, *Inorg. Chem.,* 23 (1984) 3922.
127. U.B. Goli and E.S. Gould, *Inorg. Chem.,* 23 (1984) 221.
128. Y. Yoshikawa and K. Yamasaki, *J. Indian Chem. Soc.,* 59 (1982) 1250.
129. N.K. Blagovestov, A.K. Pyartman, Yu.B. Solov'ev and V.E.

Mironov, *Koord. Khim.*, 10 (1984) 355.

130. A.K. Pyartman, S.D. Manolov and M.V. Sofin, *Koord. Khim.*, 10 (1984) 837.
131. A.K. Pyartman, S.D. Manolov and M. Genchev, *Koord. Khim.*, 10 (1984) 974.
132. N.K. Blagovestov, A.K. Pyartman, S.A. Miroshnichenko and Yu.B. Solov'ev, *Koord. Khim.*, 10 (1984) 1079.
133. P. Yang, J. Lin, J. Li and D. Liu, *Shanxi Daxue Xuebao, Ziran Kexueban*, 21 (1983) 45.
134. A. Beltran-Porter and E. Martinez-Tamayo, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 703.
135. K. Miyoshi, K. Watanabe, Y. Toda and H. Yoneda, *Bull. Chem. Soc. Jpn.*, 56 (1983) 3845.
136. Y. Yoshikawa, Y. Masuda, H. Yamatera and S. Utsuno, *J. Mag. Res.*, 58 1984) 473.
137. O. Grancicoá and V. Holba, *Transition Met. Chem. (Weinheim)*., 9 (1984) 322.
138. Y. Kitamura, S. Nariyuka and T. Kondo, *Bull. Chem. Soc. Jpn.*, 57 (1984) 285.
139. K. Koshy and T.P. Dasgupta, *J. Chem. Soc., Dalton Trans.*, (1984) 2781.
140. C.H. Langford, A.Y.S. Malkhasian and D.K. Sharma, *J. Am. Chem. Soc.*, 106 (1984) 2727.
141. S.K. Bose, S. Chatterjee and A. Roy, *J. Indian Chem. Soc.*, 61 (1984) 29.
142. M.H.M. Abou-El-Wafa and M.G. Burnett, *Inorg. Chim. Acta*, 86 (1984) L7.
143. V. Holba, V. Harcarova and M. Tarnovska, *Chem. Zvesti* 37 (1983) 721.
144. A.C. Dash, *Indian J. Chem., Sect.A*, 23A (1984) 421.
145. K.P. Dubey and M.L. Bhat, *Bull. Soc. Chim. Fr.*, (1983) 170.
146. K.P. Dubey and M.L. Bhat, *J. Indian Chem. Soc.*, 61 (1984) 119.
147. T. Ramasami and J.F. Endicott, *Inorg. Chem.*, 23 (1984) 2917.
148. P. Jones, R.S. Vagg and P.A. Williams, *Inorg. Chem.*, 23 (1984) 4110.
149. A. Watson, A.R. Gainsford and D.A. House, *Inorg. Chim. Acta*, 86 (1984) L11.
150. H. Ogino and K. Ohata, *Inorg. Chem.*, 23 (1984) 3312.
151. T.W. Hambley and G.H. Searle, *Acta Crystallogr., Sect. C*, 40C (1984) 383.
152. S. Yamada, M. Umehara, M. Ishii and M. Nakahara, *Nippon Kagaku Kaishi*, (1983) 1733.
153. A.C. Dash, *Indian J. Chem., Sect.A*, 23A (1984) 94.
154. R.A. Kenley, R.H. Fleming, R.M. Laine, D.S. Tse and J.S. Winterle, *Inorg. Chem.*, 23 (1984) 1870.
155. K. Tomioka, U. Sakaguchi and H. Yoneda, *Inorg. Chem.*, 23 (1984) 2863.
156. G.R. Brubaker and D.W. Johnson, *Inorg. Chim. Acta*, 83 (1984) 155.
157. Y. Yamamoto and H. Kudo, *Bull. Chem. Soc. Jpn.*, 57 (1984) 287.
158. Y. Yamamoto, S. Shimokawa and E. Yamada, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1153.
159. R.J. Geue, T.W. Hambley, J.M. Harrowfield, A.M. Sargeson and M.R. Snow, *J. Am. Chem. Soc.*, 106 (1984) 5478.
160. R. van Eldik, A.C. Dash and G.M. Harris, *Inorg. Chim. Acta*, 77 (1983) L143.
161. A.T.H. Lenstra, J.F.J. Van Loock and S.K. Tyrlik, *Bull. Pol. Acad. Sci., Chem.*, 31 (1983) 23.
162. A.T.H. Lenstra, H.J. Geise and S.K. Tyrlik, *Acta*

Crystallogr., Sect. C, 40C (1984) 749.

163. M. Pizzey, L. Mihichuk, R.J. Barton and B.E. Robertson, *Can. J.Chem.,* 62 (1984) 285.
164. Yu.Ya. Kharitonov, V.N. Shafranski, I.V. Dranka and A.A. Stratulat, *Koord. Khim.* 10 (1984) 359.
165. I.V. Dranka, Yu.Ya. Kharitonov, V.N. Shafranski and A.A. Stratulat, *Zh. Neorg. Khim.* 29 (1984) 138.
166. T. Okamoto, S. Yamamoto, A. Ohno and S. Oka, *Bull. Inst. Chem. Res., Kyoto Univ.,* 61 (1983) 64.
166a. N. Bresciani-Pahor, L.G. Marzilli, L. Randaccio, P.J. Toscano and E. Zangrando, *J. Chem. Soc., Chem. Commun.,* (1984) 1508.
167. S. Kinsoshita, H. Wakita and I. Masuda, *Bull. Chem. Soc. Jpn.,* 57 (1984) 1818.
168. G. Marcu, C. Varhelyi, M. Somay and E. Kiss, *Stud. Univ. Babes-Bolyai, [Ser.] Chem.,* 28 (1983) 29.
169. D. Borchardt and S. Wherland, *Inorg. Chem.,* 23 (1984) 2537.
170. Z.N. Egorova, N.N. Proskina, N.E. Bulusheva, A.V. Senakhov, T.N. Fioletova, O.A. Bologa, M.I. Stolbyrya, Zh.Yu. Vaisbein, Ya.A.Grukov and G.I. Makarova, *Izv. Akad. Nauk. Mold. SSR., Ser. Biol. Khim. Nauk.,* (1984) 59.
171. C. Natarajan and A.N. Hussain, *Transition Met. Chem. (Weinheim),* 9 (1984) 18.
172. K.L. Brown, E.P. Kirren and L.-Y. Lu, *Inorg. Chim. Acta,* 84 (1984) 199.
173. A. Wasey, R.K. Bansal, B.K. Puri, F. Kamil and S. Chandra, *Transition Met. Chem. (Weinheim),* 8 (1983) 341.
174. Yu. Simonov, V.E. Zavodnik, L.P. Sharova, A.A. Dvorkin, S.A. Dijachenko and A.I. Statsenko, *Zh. Strukt. Khim.,* 25 (1984) 102.
175. V.N. Parmon and L.B. Volodarskii, *Zh. Strukt. Khim.,* 24 (1983) 60.
176. S. Siripaisarnparnpipat and E.O. Schlemper, *J. Coord. Chem.,* 13 (1984) 281.
177. T. Kurihara, A. Uchida, Y. Ohashi, Y. Sasada and Y. Ohgo, *J. Am. Chem. Soc.,* 106 (1984) 5718.
178. K. Tomioka, T. Kashihara, U. Sakaguchi and H. Yonedi, *CHem. Lett.,* (1984) 1047.
179. H.C. Mishra, G. Mishra and L.N. Choubey, *J. Indian Chem. Soc.,* 60 (1983) 521.
180. A.E. Shvelashvili, E.N. Zedelashvili and L.Sh. Charelishvili, *Zh. Neorg. Khim.,* 29 (1984) 1030.
181. M.P. Teotia, I. Singh, P. Singh and V.B. Rana, *Synth. React. Inorg. Met.-Org. Chem.,* 14 (1984) 603.
182. K. Okamoto, H. Maki and J. Hidaka, *Bull. Chem. Soc. Jpn.,* 57 (1984) 595.
183. A. Pasini, *Gazz. Chim. Ital.,* 113 (1983) 793.
184. F. Pavelcik, *J. Coord. Chem.,* 13 (1984) 299.
185. C.N. Elgy and C.F. Wells, *J. Chem. Soc., Faraday Trans. I,* 79 (1983) 2367.
186. I.M. Sidahmed and C.F. Wells, *J. Chem. Soc., Dalton Trans.,* (1984) 1969.
187. J.A. Chambers, T.J. Goodwin, M.W. Mulqi, P.A. Williams and R.S. Vagg, *Inorg. Chim. Acta,* 88 (1984) 193.
188. J.A. Chambers, T.J. Goodwin, M.W. Mulqi, P.A. Williams and R.S. Vagg, *Inorg. Chim. Acta,* 81 (1984) 55.
189. J.A. Chambers, T.J. Goodwin, M.W. Mulqi, P.A. Williams and R.S. Vagg, *Inorg. Chim. Acta,* 75 (1983) 241.
190. T.J. Goodwin, P.A. Williams and R.S. Vagg, *J. Proc. R. Soc., N.S.W.,* 117 (1984) 1.
191. Y. Masuda and H. Yamatera, *J. Phys. Chem.* 88 (1984) 3425.
192. A.K. Pyartman and S.D. Manolov, *Koord. Khim.,* 10 (1984) 526.

193. M.B. Munroe, D.R. Boone and R.N. Kust, *Polyhedron.*, 3 (1984) 49.

194. T. Ohno and S. Kato, *J. Phys. Chem.*, 88 (1984) 1670.

195. R.R. Ruminski and J.D. Peterson, *Inorg. Chim. Acta*, 88 (1984) 63.

196. S.K. Chapman, C.V. Knox, P. Kathirgamanathan and A.G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1984) 2769.

197. A. Tatehata and S. Natsume, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1419.

198. J.K. Barton and A.L. Raphael, *J. Am. Chem. Soc.*, 106 (1984) 2467.

199. A.C. Dash, B. Mohanty and S.K. Mohapatra, *Indian J. Chem., Sect. A*, 23A (1984) 312.

200. S.K. Mohapatra, K.S. Prakash and U.L. Prasana, *J. Inorg. Biochem.*, 21 (1984) 287.

201. M.F. Hoq and R.E. Shepherd, *Inorg. Chem.*, 23 (1984) 1851.

202. M. Saburi, Y. Yokowo and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1235.

203. J.M. Pickard, *J. Hazard. Mater.*, 9 (1984) 121.

204. U. Sakaguchi, K. Tomioka and H. Yoneda, *Chem. Lett.*, (1984) 349.

205. M.E. Gross, C.E. Johnson, M.J. Maroney and W.C. Trogler, *Inorg. Chem.*, 23 (1984) 2968.

206. J. Lichtig, M.E. Sosa and M.L. Tobe, *J. Chem. Soc., Dalton Trans.*, (1984) 581.

207. T. Ramasami and J.F. Endicott, *Inorg. Chem.*, 23 (1984) 3324.

208. M. Nonoyama and K. Sakai, *Inorg. Chim. Acta*, 72 (1983) 57.

209. R. Bembi, V.K. Bhardwarj, R. Singh, R. Singh, K. Taneja and S. Aftab, *Inorg. Chem.*, 23 (1984) 4153.

210. J. Giusti, S. Chimichi, M. Ciampolini, M. Sabat and D. Masi, *Inorg. Chim. Acta*, 88 (1984) 51.

211. R.W. Hay, R. Bembi and D.A. House, *J. Chem. Soc., Dalton Trans.*, (1984) 1921.

212. R.W. Hay, R. Bembi and D.A. House, *J. Chem. Soc., Dalton Trans.*, (1984) 1927.

212a. D.A. House, M. Harnett, W.T. Robinson and M.C. Couldwell, *J. Chem. Soc., Chem. Commun.*, (1984) 979.

213. R.W. Hay, R. Bembi, F. McLaren and W.T. Moodie, *Inorg. Chim. Acta*, 85 (1984) 23.

213a. M.F. Manfrin, N. Sabbatini, L. Moggi, V. Balzani, M.W. Hoseini and J.M. Lehn, *J. Chem. Soc., Chem. Commun.*, (1984) 555.

214. P. Doppelt, J. Fischer and R. Weiss, *Inorg. Chem.*, 23 (1984) 2958.

215. M. Hoshino, S. Konishi and M. Imamura, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1713.

216. M. Kohno, H. Ohya-Nishiguchi, K. Yamamoto and T. Sakurai, *Bull. Chem. Soc. Jpn.*, 57 (1984) 932.

217. Z. Gasyna, W.R. Browett and M.J. Stillman, *Inorg. Chem.*, 23 (1984) 382.

218. P. Doppelt, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, 106 (1984) 5188.

219. J. Setsune and D. Dolphin, *Organometallics*, 3 (1984) 440.

220. C. Tait, D. Holten and M. Gouterman, *J. Am. Chem. Soc.*, 106 (1984) 6653.

221. T. Mlodnicka, J. Haber, I. Apostol and J. Poltowicz, *Oxid. Commun.* 5 (1983) 189.

222. T. Mlodnicka, J. Haber, I. Apostol and J. Poltowicz, *J. Mol. Catal.*, 26 (1984) 239.

223. V.E. Maizlish, A.B. Korzhenevskii and V.N. Klyuev, *Khim. Geterotsikl. Soedin*, (1984) 1257.

224. J. Abwao-Konya, A Cappelli. L. Jacobs, M. Krishnamurthy and M. Smith, *Transition Met. Chem. (Weinheim)*, 9 (1984) 270.
225. T.S. Kurtikyan, M.B. Ordyan and N.S. Enikolopyan, *Khim. Geterotsikl. Soedin*, (1984) 82.
226. B.D. Berezin, S.V. Kharitonov, R.A. Petrova, T.I. Potopova and S.A. Lapshina, *Koord. Khim.*, 10 (1984) 931.
226a. Z. Dokuzovic, D. Pavlovic, S. Aserger and I. Murati, *J. Chem. Soc., Chem. Commun.*, (1984) 1060.
227. Y. Kushi and H. Yoneda, *Kagaku (Kyoto)*, 39 (1984) 492.
228. I.I. Creaser, J.D. Lydon, A.M. Sargeson, E. Horn and M.R. Snow, *J. Am. Chem. Soc.*, 106 (1984) 5729.
229. R.J. Geue, M.G. McCarthy and A.M. Sargeson, *J. Am. Chem. Soc.*, 106 (1984) 8283.
230. C.-Y. Mok, A.W. Zanella, C. Creutz and N. Sutin, *Inorg. Chem.*, 23 (1984) 2891.
231. H. Barrera and J. Suades, *Transition Met. Chem. (Weinheim)*, 9 (1984) 342.
232. K. Nakabayashi, K. Doi, M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, 57 (1984) 989.
233. I. Murase, S. Ueno and S. Kida, *Bull. Chem. Soc. Jpn.*, 56 (1983) 2748.
234. K. Yamanari, N. Takeshita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1227.
235. K. Yamanari and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 56 (1983) 2283.
236. L.R. Gahan, G.A. Lawrance and A.M. Sargeson, *Inorg. Chem.*, 23 (1984) 4369.
237. N.K. Singh, S.C. Srivastva and R.C. Aggarwal, *Indian J. Chem., Sect. A*, 22A (1983) 704.
238. M. Mohan and M. Kumar, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 615.
239. S. Ghosh, P.K. Ray, S.R. Saha and A.P. Koley, *Indian J. Chem., Sect. A*, 23A (1984) 745.
240. T. Ohishi, S. Ohba, K. Kashiwabara, Y. Saito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 57 (1984) 877.
241. V.H. Houlding and V.M. Miskowski, *Inorg. Chem.*, 23 (1984) 4671.
242. U. Geiser, R.D. Willett and R.M. Gaura, *Acta Crystallogr., Sect. C*, 40C (1984) 1346.
243. D.X. West, T.J. Parsons and R.K. Bunting, *Inorg. Chim. Acta*, 84 (1984) 7.
244. A. Musinu, G.,Paschina, G. Piccaluga and M. Magini, *J. Chem. Phys.*, 80 (1984) 2772.
245. V.A. Prokuev and E.A. Belousov, *Zh. Neorg. Khim.*, 29 (1984) 1771.
246. I.S. El-Yamani and El-S.I. Shabana, *Transition Met. Chem. (Weinheim).*, 9 (1984) 199.
247. M.A. Bañares, A. Angoso and E. Rodriguez, *Polyhedron*, 3 (1984) 363.
248. C. Fischer, H. Wagner and V.V. Bagreev, *Polyhedron*, 2 (1983) 1141.
249. S. Zhao and H. Wang, *Fezi Kexue Yu Huaxue Yanjiu*, 4 (1984) 415.
250. M. Ichihashi, H. Wakita and I. Masuda, *J. Solution Chem.*, 13 (1984) 505.
251. S.J. Carter, B.M. Foxman and L.S. Stuhl, *J. Am. Chem. Soc.*, 106 (1984) 4265.
252. O.I. Kuntyi, L.N. Kryvlyuk and A.I. Zhirov, *Koord. Khim.*, 9 (1983) 1680.
253. M.B. Mooiman and J.M. Pratt, *J. Mol. Catal.*, 27 (1984) 367.
254. S.P. Perlepes, T.F. Zafiropoulos, D. Raptis and A.G. Galinos,

Monatsh. Chem., 114 (1983) 1355.

255. S.T. Malinovskii, Yu.A. Sinonov, T.I. Malinovskii, V.E. Zubareva, D.G. Batyr and I.M. Reibel, *Kristallografiya*, 29 (1984) 466.
256. B. Das and P.C. Roy, *J. Inst. Chem. (India)*, 56 (1984) 121.
257. L. Chen, H. Zhao and Z. He, *Huaxue Xuebao*, 42 (1984) 925.
258. W.G. Jackson and C.N. Hookey, *Inorg. Chem.*, 23 (1984) 668.
259. W. Grzybkowski and M. Pilarczyk, *J. Chem. Soc., Faraday Trans. 1*, 79 (1983) 2319.
260. J. Rimbault, J.C. Pierrard and R.P. Huget, *Nouv. J. Chim.*, 7 (1983) 653.
261. W.G. Jackson and C.M. Begbie, *Inorg. Chem.*, 23 (1984) 659.
262. R.J. Barton, D.G. Holah, H. Shengzhi, A.N. Hughes, S.I. Khan and B.E. Robertson, *Inorg. Chem.*, 23 (1984) 2391.
263. C. Benelli, D. Galteschi and C. Zanchini, *Inorg. Chem.*, 23 (1984) 798.
264. K.A.R. Salib and R.A. Bucher, *Transition Met. Chem. (Weinheim)*, 8 (1983) 360.
265. J.E. House,Jr. and G.L. Jeyaraji, *J. Therm. Anal.*, 29 (1984) 41.
266. C.J. Cassady and B.S. Freiser, *J. Am. Chem. Soc.*, 106 (1984), 6177.
267. A. Mascas and S. Sternberg, *Rev. Roum. Chim.*, 29 (1984) 165.
268. E.S. Stoyanov and V.A. Mikhailov, *Koord. Khim.*, 10 (1984) 518.
269. J.R. Allen, G.H.W. Milburn, T.A. Stephenson and P.M. Veitch, *J. Chem. Res., Synop.*, (1983) 215.
270. P.R. Reddy, K.V. Reddy and M.M.T. Khan, *Indian J. Chem., Sect. A*, 22A (1983) 959.
271. P.R. Reddy, K.V. Reddy and M.M.T. Khan, *Indian J. Chem., Sect. A*, 22A (1983) 999.
272. N.K. Davidenko, P.A. Manorik and E.I. Lopatina, *Koord. Khim.*, 10 (1984) 187.
273. R. Chini, M. Sabat, M. Sundaralingam, M.C. Burla, A. Nunzi, G. Polidori and P.F. Zanazzi, *J. Biomol. Struct. Dyn.*, 1 (1983) 633.
274. S.M. Portnova, E.V. Petrova, A.K. Lyashchenko and I.N. Lepeshkov, *Zh. Neorg. Khim.*, 28 (1983) 2952.
275. E.V. Petrova, A.K. Lyashchenko, A.F. Borina and S.M. Portnova, *Zh. Neorg. Khim.*, 28 (1983) 3158.
276. G.S. Raghuvanshi and D.P. Khandelwal, *Appl. Spectrosc.*, 38 (1984) 710.
277. G.S. Raghuvanshi and H.D. Bist, *Chem. Phys. Lett.*, 103 (1984) 507.
278. M. Ristova and B. Soptrajanov, *J. Mol. Struct.*, 115 (1984) 355.
279. A.F. Borina, A.K. Lyashchenko and V.R. Timofeeva, *Koord. Khim.*, 10 (1984) 204.
280. O.A. Golubchikov, I.M. Kazakova and B.D. Berezin, *Zh. Fiz. Khim.*, 57 (1983) 2740.
281. M. Ahlgren, R. Hamalainen and U. Turpeinen, *Finn. Chem. Lett.*, (1983) 125.
282. V.H.K. Chu, *J. Chin. Chem. Soc. (Taipei)*, 31 (1984) 23.
283. P.S. Bassi, H.S. Jamwal and B.S. Randhawa, *Thermochim. Acta*, 71 (1983) 15.
284. I. Dreveni, O. Berkesi and J.A. Andor, *Acta Phys. Chem.*, 29 (1983) 211.
285. Z. Yongfeng, L. Jianmin, C. Feng and G. Jiugao, *Inorg. Chim. Acta*, 87 (1984) L25.
286. Yu.I. Sal'nikov, F.V. Devyatov, N.E. Zhuravleva and D.V. Golodnitskaya, *Zh. Neorg. Khim.*, 29 (1984) 2273.

287. Yu.B. Yakovlev, E. Jumbuu and R.A. Ninburg, *Zh. Neorg. Khim.*, 29 (1984) 809.

288. S.K. Tiwari, D.P.S. Rathmore and R. Prakash, *J. Indian Chem. Soc.*, 61 (1984) 108.

289. D.B. Dell'Amico, F. Calderazzo, F. Giovannitti and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, (1984) 647.

290. Yu.Ya. Kharitonov and Z.K. Tuiebakkhova, *Koord. Khim.*, 9 (1983) 1512.

291. Yu.Ya. Kharitonov and Z.K. Tuiebakkhova, *Koord. Khim.*, 10 (1984) 376.

292. Yu.Ya. Kharitonov and Z.K. Tuiebakkhova, *Zh. Neorg. Khim.*, 29 (1984) 1217.

293. J.K. Sthapak, V.P. Gupta and D.D. Sharma, *J. Indian Chem. Soc.*, 60 1983) 705.

294. M.N. Patel and M.R. Chaudhari, *Proc.-Indian Acad. Sci., Chem. Sci.*, 93 (1984) 65.

295. B.R. Rios, J.F. Diaz and R.R. Barroso, *An. Quim., Ser.B*, 80 (1984) 37.

296. N. Kumar, P.L. Kacharo, A.K. Gandotra and R. Kant, *Indian J. Chem., Sect. A*, 23A (1984) 608.

297. C.H.L. Kennard, G. Smith, E.J. O'Reilly and P.T. Manoharan, *Inorg. Chim. Acta*, 82 (1984) 35.

298. H. Knuuttila, *Acta Chem. Scand. A*, 37A (1983) 697.

299. G. Smith, E.J. O'Reilly and C.H.L. Kennard, *Aust. J. Chem.*, 36 (1983) 2175.

300. D.L. Hughes and J.N. Wingfield, *J. Chem. Soc., Dalton Trans.*, (1984) 1187.

301. V.V. Trubinskii and V.A. Sharov, *Zh. Fiz. Khim.*, 58 (1984) 1610.

302. X. Wang, X. Xin and A. Dai, *Gaodeng Xuexiao Huaxue Xuebao*, 5 (1984) 141.

303. A.C. Dash, R.K. Nanda and P. Mohanty, *Indian J. Chem., Sect.A*, 23A (1984) 11.

304. A.C. Dash, R.K. Nanda and P. Mohanty, *Indian J. Chem., Sect.A*, 23A (1984) 162.

305. A.G. Stepanov and V.M. Nekipelov, *React. Kinet. Catal. Lett.*, 24 (1984) 351.

306. A.G. Stepanov and V.M. Nekipelov, *React. Kinet. Catal. Lett.*, 24 (1984) 357.

307. C.W. Anderson and K.R. Lung, *Inorg. Chim. Acta*, 85 (1984) 33.

308. Zh.N. Bublik, S.V. Volkov and E.A. Mazurenko, *Zh. Neorg. Khim.*, 29 (1984) 132.

309. T. Sekine. R. Murai and H. Konno, *Solvent Extr. Ion Exch.*, 2 (1984) 213.

310. R.L. Lintvedt, B.A. Schoenfelner, C. Ceccarelli and M.D. Glick, *Inorg. Chem.*, 23 (1984) 2867.

311. H.B. Suthar and J.R. Shah, *J. Macromol. Sci., Chem. Ser.A*, A21, (1984) 29.

312. M.A. Banares, A. Angoso, J.L. Manzano, B. Macias and V. Rives, *Spectrosc. Lett.*, 17 (1984) 197.

313. F. Teixidor, A. Llodet and J. Casabo, *Thermochim. Acta*, 79 (1984) 315.

314. M.M. Shoukry, *Rev. Roum. Chim.*, 29 (1984) 283.

315. Kh. Suleimanov, A.S. Antsyshkina, V.Ya. Dudarev, L.V. Fykin and M.A. Porai-Koshits, *Koord. Khim.*, 10 (1984) 1272.

316. M.K. Kuya, A.D. Pereira, E. Giesbrecht and K. Sono, *An. Acad. Bras. Cienc.*, 56 (1984) 147.

317. C.O.'Mara, J. Walsh and M.J. Hynes, *Inorg. Chim. Acta*, 92 (1984) L1.

318. S.S. Isied and A. Vassilian, *J. Am. Chem. Soc.*, 106 (1984) 1726.

319. P.A. Manorik and N.K. Davidenko, *Zh. Neorg. Khim.*, 28 (1983) 2551.

320. P. Prasad, H.L. Yadav, S. Singh, P.C. Yadav and K.L. Yadava, *J. Electrochem. Soc. India* 32 (1983) 377.

321. S. Singh, P.C. Yadav, H.L. Yadava, R.K. Singh, M. Gupta and K.L. Yadava, *Natl. Acad. Sci. Lett. (India)*, 6 (1983) 229.

322. I. Bertini, C. Luchinat, L. Messori and A. Scozzafava, *Eur. J. Biochem.*, 141 (19840 375.

323. P.S. Relan and K.K. Girdhar, *Haryana Agric. Univ. J. Res.*, 14 (1984) 14.

324. T. Kiss and A. Gergely, *Acta Chim. Hung.*, 114 (1983) 249.

325. G.A. El-Inany, F.M. Ebeid and S.M. Abu-El-Wafa, *Egypt. J. Chem.*, 26 (1983) 145.

326. S.S. Sawhney and R.M. Sati, *Thermochim. Acta* 70 (1983) 373.

327. P. Hakkinen, *Finn. Chem. Lett.*, (1984) 59.

328. Yu.A. Simonov, V.K. Bel'skii, G.S. Matuzenko and N.V. Gerbeleu, *Kristallografiya*, 29 (1984) 82.

329. B.G. Rarog, V.A. Ivanov, V.M. Potekin, M.V. Nesterov and E.G. Savel'eva, *Zh. Obshch. Khim.*, 54 (1984) 161.

330. M.S. Masoud, M.S. Tawik and S.E. Zayan, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 1.

331. R. Meyer, J. Gagliardi and G. Wulfsberg, *J. Mol. Struct.*, 111 (1983) 311.

332. R.C. Aggarwal, R. Bala and R.L. Prasad, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 171.

333. P.B. Chakrawarti and P. Khanna, *J. Indian Chem. Soc.*, 61 (1984) 112.

334. H.A. Dessouki, R.M. Issa, A.K. Ghoniem and M.M. Moustafa, *J. Indian Chem. Soc.*, 61 (1984) 286.

335. V.K. Jaitly and B.S. Pannu, *J. Indian Chem. Soc.*, 60 (1983) 791.

336. N. Kumar, P.L. Kachroo, R. Sachar and R. Kant, *Proc. Indian Natl. Sci. Acad., Part A*, 49 (1983) 557.

337. F.L. Dickert and W. Gumbrecht, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 39B (1984) 69.

338. E. Mentasti, *J. Chem. Soc., Dalton Trans.*, (1984) 903.

339. D.J. Boban and I.J. Gal, *Glas. Hem. Drus. Beograd.*, 48 (1983) 239.

340. A. Mosset, J. Galy, E. Coronado, M. Drillon and D. Beltran, *J. Am. Chem. Soc.*, 106 (1984) 2865.

341. E. Coronado, M. Drillon, D. Beltran and J.C. Bernier, *Inorg. Chem.*, 23 (1984) 4000.

342. E. Escrivá, A. Fuertes and D. Beltran, *Transition Met. Chem. (Weinheim)*, 9 (1984) 184.

343. T.R. Amb, R.K. Nandwana and S.K. Solanki, *Cienc. Cult. (Sao Paulo)*, 35 (1983) 1942.

344. G.C. Seaman and A. Haim, *J. Am. Chem. Soc.*, 106 (1984) 1319.

345. C.H. Taliaferno, R.J. Motekaitis and A.E. Martell, *Inorg. Chem.*, 23 (1984) 1188.

346. E.V. Srisankar, N.C. Saha, P.C. Mandal and S.N. Bhattacharyya, *J. Chem. Soc., Dalton Trans.*, (1984) 1629.

347. S.-B. Teo and S.-G. Teh, *Inorg. Chim. Acta*, 91 (1984) L17.

347a. R.P. Kreh, A.E. Rodriguez and S.P. Fox, *J. Chem. Soc., Chem. Commun.*, (1984) 130.

348. Z. Wu, Z. Yen, J. Liu and Y. Chan, *Huazhang Shiyuan Xuebao, Ziran Kexueban*, (1983) 55.

349. H. Wang, Z. Luo, Z. Wu, Z. Yen and W. Guo, *Huazhang Shiyuan Xuebao, Ziran Kexueban*, (1983) 88.

350. M.S. Mayadeo, A.G. Vaidya and N.G. Ghatpande, *J. Indian Chem. Soc.*, 61 (1984) 450.

351. M.S. Mayadeo and A.G. Vaidya, *J. Indian Chem. Soc.*, 60 (1983)

708.

352. G.E. Jackson and L.G. Scott, *S. Afr. J. Chem.*, 36 (1983) 120.

353. B.B. Mahapatra and S.K. Pujari, *J. Chem. Technol. Biotechnol., Chem. Technol., Ser. A* , 33A (1983) 187.

354. B.B. Mahapatra, B. Patel, D. Satyanarayana and S.K. Pujari, *Acta Chim. Hung.*, 114 (1983) 217.

355. R.S. Saxena and M.K. Sharma, *J. Indian Chem. Soc.*, 60 (1983) 543.

356. N.S. Biradar, V.L. Roddabasanagoudar and T.M. Aminabhavi, *Polyhedron*, 3 (1984) 575.

357. B. Singh, B.P. Yadava and R.C. Aggarwal, *Indian J. Chem., Sect.A*, 23A (1984) 575.

358. B.B. Mahapatra and D. Panda, *Indian J. Chem., Sect.A*, 23A (1984) 256.

359. K.C. Satpathy, B.B. Jal and R. Mishra, *Transition Met. Chem. (Weinheim)*, 9 (1984) 8.

360. A. Syamal and B.K. Gupta, *Rev. Roum. Chim.*, 28 (1983) 805.

361. A. Kapturkiewicz and B.Behr, *J. Electroanal. Chem. Interfacial Electrochem.*, 163 (1984) 189.

362. G.A. Shagisultanova and A.V. Maslov, *Zh. Neorg. Khim.*, 29 (1984) 1197.

363. N. Farrell, M.N.de O. Bastos and A.A. Neves, *Polyhedron*, 2 (1983) 1243.

364. W. Kanda, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 56 (1983) 3268.

365. P.S. Zacharias, J.M. Elizabathe and A. Ramachandraiah, *Indian J. Chem., Sect.A*, 23A (1984) 26.

366. B.J. Kennedy, G.D. Fallon, B.M.K.C. Gatehouse and K.S. Murray, *Inorg. Chem.*, 23 (1984) 580.

367. K. Mitiga, C.T. Mitiga and M. Iwaizumi, *J. Chem. Soc., Dalton Trans.*, (1984) 1195.

368. S.Z. Haider, K.M.A. Malik, A. Hashem, M.S. Khan and M.A. Islam, *J. Bangladesh. Acad. Sci.*, 8 (1984) 37.

369. K. Kasuga, Y. Iida, Y. Yamamoto, M. Aihara and M. Kudo, *Inorg. Chim. Acta*, 84 (1984) 113.

370. J. Zarembowitch and O. Kahn, *Inorg. Chem.*, 23 (1984) 589.

371. E. Konefal, S.J. Loeb, D.W. Stephan and C.J. Willis, *Inorg. Chem.*, 23 (1984) 538.

372. B.B. Mahapatra and D. Panda, *Transition Met. Chem. (Weinheim)* 9 (1984) 280.

373. B.B. Mahapatra and D. Panda, *Transition Met. Chem. (Weinheim)* 9 (1984) 117.

374. C.L. Sharma, S.S. Narvi and R.S. Arya, *Acta Chim. Hung.*, 114 (1983) 349.

375. M. Ramalingam and D. Venkappayya, *J. Inst. Chem. (India)*, 56 (1984) 2.

376. P.B. Chakrawarti and P. Khanna, *J. Indian Chem. Soc.*, 61 (1984) 416.

377. V. Ravinder, S.J. Swamy, S. Srihari and P. Lingaiah, *Indian J. Chem., Sect.A*, 23A (1984) 219.

378. R.C. Aggarwal, R. Bala and R.L. Prasad, *Indian J. Chem., Sect.A*, 22A (1983) 955.

379. R.K. Gridasova and L.I. Shevernovskaya, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 26 (1983) 1423.

380. M.S. Patil, H.O. Deore, M.M. Kulkarni and J.R. Shah, *J. Indian Chem. Soc.*, 60 (1983) 817.

381. K.D. Hardman and W.N. Lipscomb, *J. Am. Chem. Soc.*, 106 (1984) 463.

382. A.K. Jain, K.D. Jain and A.K. Ojha, *Indian J. Phys. Nat. Sci.*, 4 (1984) 25.

383. F. Capitan, D. Gazquez, A.F. Cueto and L.F. Capitan-Vallvey,

Thermochim. Acta, 75 (1984) 313.

384. M.A.R. Moilna, J.M.S. Peregrin, J.D.L. Gonzalez and C.V. Calahorro, *An. Quim., Ser.B*, 79 (1983) 383.
385. K.J. Charyulu, P. Ettaiah, K.L. Omprakash, A.V.C. Pal and M.L.N. Reddy, *Indian J. Chem., Sect.A*, 23A (1984) 668.
386. B. Hutchinson, S. Sample, L. Thompson, S. Olbricht, J. Crowder, D. Hurley, D. Eversdyk, D. Jett and J. Bostick, *Inorg. Chim. Acta*, 74 (1983) 29.
387. A. Kocak and O. Bekaroglu, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 753.
388. M.M. Mostafa, K.M. Ibrahim and M.N.H. Moussa, *Transition Met. Chem. (Weinheim)*, 9 (1984) 243.
389. M.M. Mostafa, M.A. Khattab and K.M. Ibrahim , *Transition Met. Chem. (Weinheim)*, 9 (1984) 282.
390. A.K. Srivastava, A.L. Varshney and D.R. Singh, *Acta Cienc. Indica, [Ser.] Phys.*, 9 (1983) 62.
391. R.I. Machkhoshvili, G.Sh. Mitaishvili and N.I. Pirtskhalava, *Zh. Neorg. Khim.*, 29 (1984) 970.
392. R.I. Machkhoshvili, D.P. Metreveli, G.Sh. Mitaishvili and R.N. Shchelokov, *Zh. Neorg. Khim.*, 29 (1984) 1020.
393. S.N. Poddar and B.C. Kundu, *Indian J. Chem., Sect. A*, 23A (1984) 488.
394. J.M. Hernando and T. Prieto, *An. Quim., Ser.A*, 79 (1983) 525.
395. R.L. Dutta and M.M. Hossain, *Indian J. Chem., Sect. A*, 23A (1984) 30.
396. Y. Kumar, S. Chandra, R.P. Singh and A.K. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 185.
397. B. Singh, R.N. Singh and R.C. Aggarwal, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 815.
398. I. Morgenstern-Badarau, *Inorg. Chem.*, 23 (1984) 2725.
399. A.E. Landers and D.J. Phillips, *Inorg. Chim. Acta*, 86 (1984) 77.
400. V. Jayatyaga, V. Ranabaore, B.B. Kumar and M.C. Ganorkar, *J. Indian Chem. Soc.*, 60 (1983) 724.
401. R.C. Aggarwal, N.K. Singh and R.P. Singh, *J. Indian Chem. Soc.*, 60 (1983) 789.
402. R.C. Khulbe, Y.K. Bhoon and R.P. Singh, *J.Indian Chem.Soc.*, 61 (1984) 194.
403. M.A. Khattab and M.S. Solinian, *Transition Met. Chem. (Weinheim).*, 8 (1983) 285.
404. P.K. Sharma and P. Acharya, *Acta Cienc. Indica, [Ser.] Chem.*, 9 (1983) 61.
405. Y. Hara, K. Okamoto, J. Hidaka and H. Einaga, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1211.
406. A. El-Dissouky, G.S. Mohamed and L.S. Refaat, *Transition Met. Chem. (Weinheim).*, 9 (1984) 23.
407. A. El-Dissouky and L.S. Refaat, *Inorg. Chim. Acta*, 87 (1984) 213.
408. G.D. Tiwari and M.N. Mishra, *J. Indian Chem. Soc.*, 60 (1983) 698.
409. M.V. Capparelli, M. Goodgame, A.C. Skapski and B. Piggott, *Inorg. Chim. Acta*, 92 (1984) 15.
410. N. Saha, A.K. Adak and K.M. Datta, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 731.
411. K.L. Reddy, S. Srihari and P. Lingaiah, *J. Indian Chem. Soc.*, 60 (1983) 1020.
412. K. Takahashi, Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn*, 57 (1984) 2628.
413. P. Ghosh, T.K. Mukhopadhyay and A.R. Sarkar, *Transition Met. Chem. (Weinheim).*, 9 (1984) 46.
414. P.R. Reddy and M.H. Reddy, *Polyhedron* 2 (1983) 1171.

415. A.C. Hiremath, M.B. Halli and N.V. Huggi, *Indian J. Chem., Sect. A.* 23A (1984) 72.

416. A.E. Landers and D.J. Phillips, *Inorg. Chim. Acta*, 74 (1983) 43.

417. M.G.B. Drew, F.S. Esho, A. Lavery and S.M. Nelson, *J. Chem. Soc., Dalton Trans.*, (1984) 545.

418. E. Ludwig, E. Uhlemann and F. Dietze, *Z. Anorg. Allg. Chem.*, 512 (1984) 181.

419. A.M. Shallaby, M.M. Mostafa and A.A. El-Asmy, *Acta Chim. Hung.*, 114 (1983) 9.

420. C.L. Sharma and V.P. Mishra, *Acta Chim. Hung.*, 114 (1983) 3.

421. M. Kocak and O. Bekaroglu, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 689.

422. N.K. Singh, S.C. Srivastava and R.C. Aggarwal, *J. Indian Chem. Soc.*, 60 (1983) 622.

423. S. Chandra and K.K. Sharma, *Transition Met. Chem. (Weinheim)*, 9 (1984) 1.

424. S.A. Koch, R. Fikar, M. Millar and T. O'Sullivan, *Inorg. Chem.*, 23 (1984) 121.

425. I. Bertini, M. Gerber, G. Lanini, C. Luchinat, W. Maret, S. Rawer and M. Zeppezauer, *J. Am. Chem. Soc.*, 106 (1984) 1826.

426. I.M. Oglezneva and V. Kirichenko, *Zh. Strukt. Khim.*, 25 (1984) 164.

427. H. Barrera and F. Teixidor, *Polyhedron*, 2 (1983) 1165.

428. W. Tremel, B. Trebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 634.

429. K.S. Hagen and R.H. Holm, *Inorg. Chem.*, 23 (1984) 418.

430. J.E.J. Schmitz and J.G.M. van der Linden, *Inorg. Chem.*, 23 (1984) 3298.

431. L. Morpurgo, A. Desideri, A. Rigo, P. Viglino and G. Rotiolo, *Biochem. Biophys. Acta*, 746 (1983) 168.

432. N.K. Kaushik, B. Bhushan and A.K. Sharma, *Transition Met. Chem. (Weinheim)*, 9 (1984) 250.

433. K.S. Arulsamy, R.F.N. Ashok and U.C. Agarwala, *Indian J. Chem., Sect. A*, 23A (1984) 127.

434. R.S. Saxena and A. Gupta, *J. Indian Chem. Soc.*, 61 (1984) 210.

435. E.S. Raper, *J. Therm. Anal.*, 25 (1982) 463.

436. T. Honjo and S. Shima, *Bull. Chem. Soc. Jpn.*, 57 (1984) 293.

436a. J.R. Hartman, E.J. Hintsa and S.R. Cooper, *J. Chem. Soc., Chem. Commun.*, (1984) 386.

437. M. Di Vaira, M. Peruzzini and P. Stoppioni, *J. Chem. Soc., Dalton Trans.*, (1984) 359.

438. M. Ciampolini, N. Nardi, P. Dapporto and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, (1984) 995.

439. S. Kummer and D. Babel, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 39B (1984) 1118.

440. J. Pichet and J. Stanowski, *Acta Phys. Pol., Ser. A*, 65 (1984) 173.

441. I.D. Isaev, T.V. Stupko, O.Yu. Vybornov and V.E. Mironev, *Zh. Neorg. Khim.*, 29 (1984) 1207.

442. I.D. Isaev, T.V. Stupko and V.E. Mironev, *Zh. Neorg. Khim.*, 29 (1984) 1211.

443. T.F. Zafiropoulis, A.G. Galinos and S.P. Perlepes, *J. Coord. Chem.*, 13 (1984) 197.

444. M. Genchev, S. Manolov and S. Zhekov, *Koord. Khim.*, 10 (1984) 168.

445. R.K. Jain, S.N. Misra, N. Sudhindra and G.K. Joshi, *Indian J. Pure Appl. Phys.* 21 (1983) 736.

446. S.F. Lincoln, A.M. Hounslow, D.L. Pisaniello. B.G. Doddridge, J.H. Coates, A.E. Merbach and D. Zbinden, *Inorg. Chem.*, 23

(1984) 1090.

447. R. Pastorek, F. Brezina and H. Hennebergova, *Acta Univ. Palacki. Olomuc., Fac. Rerum. Nat.*, 76 (1983) 27.

448. B.D. Murray and P.P Power, *Inorg. Chem.*, 23 (1984) 4584.

449. L.A. Dominey and K. Kustin, *Inorg. Chem.*, 23 (1984) 103.

450. H. Stepowska, A. Korda, S.K. Tyrlik, N. Gyor and A. Rockenbauer, *Arab Gulf J. Sci. Res.*, 2 (1984) 55.

451. L.I. Simándi, É. Budó-Záhonyi and S. Németh, *Inorg. Chim. Acta*, 77 (1983) L203.

452. L.G. Marzilli, M.F. Summers, J.H. Ramsden, N. Bresciani-Pahor and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, (1984) 511.

453. L.I. Vasil'eva, V.L. Varand, L.A. Sheludyakova and S.V. Larionov, *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.*, (1984) 41.

454. L. Calligaro, A. Mantovani, U. Belluco and M. Acampora, *Polyhedron*, 2 (1983) 1189.

455. A.P. Argekar and Z.R. Turel, *J. Radioanal. Nucl. Chem.*, 86 (1984) 45.

456. P.W. Beaupre and W.J. Holland, *Mikrochim. Acta*, 2 (1984) 1.

457. C. Natarajan and M. Palaniandavar, *Proc.-Indian Acad. Sci., [Ser.]: Chem. Sci.*, 92 (1983) 265.

458. I.I. Kalinichenko, N.M. Titov and M.G. Ivanov, *Zh. Neorg. Khim.*, 29 (1984) 2010.

459. A.E. Zongur and O. Bekaroglu, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 881.

460. B. Banerjee, P.K. Biswas and N.R. Chaudhuri, *Thermochim. Acta*, 76 (1984) 47.

461. E.A. Nikonenko, I.N. Marenkova, I.I. Olikov and L.N. Margolin, *Zh. Neorg. Khim.*, 29 (1984) 1027.

462. K.C. Patil, J.P. Vittal and C.C. Patel, *Proc.-Indian Acad. Sci., Chem. Sci.*, 92 (1983) 83.

463. V.A. Sharov and V.A. Larikov, *Zh. Neorg. Khim.*, 29 (1984) 248.

464. G.Sh. Mitaishvili, R.I. Machkhoshvili and N.I. Pirtskhalava, *Soobshch. Akad. Nauk. Gruz. SSR*, 113 (1984) 529.

465. T.R. Rao, M. Sahay and R.C. Aggarwal, *Indian J. Chem., Sect. A*, 23A (1984) 214.

466. B. Singh, R.N. Singh and R.C. Aggarwal, *Indian J. Chem., Sect. A*, 23A (1984) 480.

467. Y.M. Temerk, S.A. Ibrahim and M.M. Kamal, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 39B (1984) 812.

468. D. Demertzi, D. Nicholls and K. Tracey, *Inorg. Chim. Acta*, 85 (1984) 143.

469. S.A. Berger, *Mikrochim. Acta*, 3 (1983) 333.

470. L.A. Patrina, V.I. Ovcharenko and S.V. Larionov, *Zh. Neorg. Khim.*, 29 (1984) 1605.

471. B.A. Kushekar and D.D. Khanolkar, *Indian J. Chem., Sect.A*, 22 (1983) 881.

472. M.C. Barral, E. Delgado, E. Gutiérrez-Puebla, R. Jimenez-Aparcio, A. Monge, C. Del Pino and A. Santos, *Inorg. Chim. Acta*, 74 (1983) 101.

473. B.B. Mahapatra, D. Panda and B.K. Patel, *Acta Chim. Hung.*, 115 (1984) 131.

474. R. Pastorek, F. Brezina and L. Dvorakova, *Z. Chem.*, 24 (1984) 102.

475. N. Mabiala, J.P. Narbier and R.P. Hugel, *Polyhedron*, 3 (1984) 99.

476. K. Sone, M. Kikuchi, K. Ogasawara, M.K. Kuya and A.D. Pereira, *Bull. Chem. Soc. Jpn.*, 57 (1984) 3005.

477. A.C. Hiremath, M.B. Halli and N.V. Huggi, *J. Indian Chem. Soc.*, 61 (1984) 191.

478. M. Castillo E. Ramirez, *Transition Met. Chem. (Weinheim)*, 9 (1984) 268.

479. M. Ganteaume and M. Decressac, *Themochim. Acta*, 80 (1984) 35.

480. M. Ganteaume and M. Decressac, *Themochim. Acta*, 80 (1984) 51.

481. J.R. Vriesenga and G.H. Fairchild, *Inorg. Chim. Acta*, 82 (1984) L21.

481a. K. Kojima, T. Miyashita and J. Matsuda, *Bull. Chem. Soc. Jpn.*, 57 (1984) 879.

482. M. De Moraes, M. Molina, C. Melios and J.O. Tognolli, *An. Acad. Bras. Cienc.*, 55 (1983) 257.

483. G. Narain, P.R. Shukla and S.T. Spees, *J. Indian Chem. Soc.*, 60 (1983) 1088.

484. E. Bezak and B. Lenarcik, *Pol. J. Chem.*, 57 (1983) 383.

485. J.R. Allan and P.M. Veitch, *J. Therm. Anal.*, 27 (1983) 3.

486. C.-C. Su and S.-M. Huang, *Transition Met. Chem. (Weinheim)*, 9 (1984) 220.

487. M.T.P. Leite, *Rev. Port. Quim.*, 25 (1983) 197.

488. G.V. Tsintsadze, T.K. Dzhashiashvili, Ts.P. Mgaloblishvili, M.M. Abashidze and M.I. Lochoshvili, *Soobshch. Akad. Nauk. Gruz. SSR*, 112 (1983) 77.

488a. M.M. Mostafa and D.X. West, *Transition Met. Chem. (Weinheim)*, 8 (1983) 304.

489. M.A.S. Goher, A.A. Hasanein and S.M. Soliman, *Bull. Soc. Chim. Fr.*, (1984) 169.

490. E.W. Müller, H. Spiering and P. Gütlich, *Inorg. Chem.*, 23 (1984) 119.

491. J.W. Faller, C. Blankenship and S. Sena, *J. Am. Chem. Soc.*, 106 (1984) 793.

492. B.C. Whitmore and R. Eisenberg, *Inorg. Chem.*, 23 (1984) 1624.

493. M. Izquierdo, J. Casabó, C. Diaz and J. Ribas, *Synth. React. Inorg. Met.-Org. Chem.*, 13 (1983) 843.

493a. J.M. Castresana, M.P. Elizalde, J.M. Arrieta, G. Germain and J.-P.Declercq, *Acta Crystallogr., Sect. C*, 40C (1984) 763.

494. V.V. Skopenko, V.N. Zaitsev and A.K. Trofimchuk, *Ukr. Khim. Zh. (Russ. Ed.)*, 50 (1984) 451.

495. A. Izquierdo, R. Compano and E. Bars, *Mikrochim. Acta*, 2 (1984) 343.

496. V.P. Vasil'ev, G.A. Zaitseva and N.V. Provova, *Zh. Obshch. Khim.*, 54 (1984) 1079.

497. V.P. Vasil'ev, G.A. Zaitseva, N.V. Provova and E.B. Vorob'eva, *Zh. Obshch. Khim.*, 54 (1984) 2085.

498. J. Ribas, C. Diaz and J. Casabó, *Polyhedron*, 3 (1984) 357.

499. J.-M. Lehn, J.-P. Sauvage, J. Simon, R. Ziessel, C. Piccinni-Leopardi, G. Germain, J.-P. Declercq and M. van Meerssche, *Nouv. J. Chem.*, 7 (1983) 413.

500. G.R. Newkome, V.K. Gupta, F.R. Fronczek and S. Pappalardo, *Inorg. Chem.*, 23 (1984) 2400.

501. J.T. Hupp and M.J. Weaver, *Inorg. Chem.*, 23 (1984) 256.

502. I. Lupu, *Bul. Univ. Brasov., Ser. C*, 23 (1981) 215.

503. I. Lupu, *Bul. Univ. Brasov., Ser. C*, 23 (1981) 209.

504. M.S. Sastry, T. Kesavadas and G.S. Rao, *Indian J. Chem., Sect. A*, 22A (1983) 993.

505. R.C. Aggarwal, M.K. Singh and B. Singh, *Indian J. Chem., Sect. A*, 22A (1983) 778.

506. K. Mizuno, S. Imamura and J.H. Lunsford, *Inorg. Chem.*, 23 (1984) 3510.

507. B. Das and P.C. Roy, *J. Inst. Chem. (India)*, 56 (1984) 145.

508. D.M. Stanbury and L.A. Lednicky, *J. Am. Chem. Soc.*, 106 (1984) 2847.

509. D. Boys, C. Escobar and O. Wittke, *Acta Crystallogr., Sect. C*, 40C (1984) 1359.

510. N.L. Shestidesyatnaya and L.V. Gaevskaya, *Ukr. Khim. Zh. (Russ. Ed.)*, 50 (1984) 275.
511. R. Ghose, *Indian J. Chem. Soc., Sect. A*, 23A (1984) 493.
512. Z. Yoshida and H. Freiser, *Inorg. Chem.*, 23 (1984) 3931.
513. C.A. Koval, R.L.A. Pravata and C.M. Reidsema, *Inorg. Chem.*, 23 (1984) 545.
514. R. Sahai and S.S.S. Kushwaha, *J. Indian Chem. Soc.*, 61 (1984) 205.
514a. A. Yamagishi and A. Aramata, *J. Chem. Soc., Chem. Commun.*, (1984) 452.
514b. A. Yamagishi, *J. Chem. Soc., Chem. Commun.*, (1984) 119.
515. A.S. Abushamleh, H.A. Goodwin, C.G. Benson and G.J. Long, *Aust. J. Chem.*, 37 1984) 281.
516. R. Baniwar, O.P. Shrivastava and N.K. Soni, *J. Indian Chem. Soc.*, 60 (1983) 825.
517. S. Muralidharan, K.S. Nagaraja and M.R. Udupa, *Transition Met. Chem. (Weinheim)*, 9 (1984) 218.
518. A. Anagnostopoulous and S. Hadjispyrou, *Polyhedron*, 3 (1983) 251.
519. B. Banerjee, S.K. Nandi, S.R. Chaudhuri and B. Sur, *Indian J. Chem., Sect. A*, 22A (1983) 875.
520. M.P.D. Mallioli, C.B. Melios, A.C. Massabni and M. Molina, *Rev. Chim. Miner.*, 21 (1984) 45.
521. N.R. Shah and J.R. Shah, *J. Indian Chem.Soc.*, 60 (1983) 1092.
522. A. Cuadro, J. Elguero, P. Navarro, E. Royer and A. Santos, *Inorg. Chim. Acta*, 81 (1984) 99.
523. M.R. Feliz and A.L. Capparelli, *J. Phys. Chem.*, 88 1984) 300.
524. K.V.G. Reddy, K.V.R. Chary, B.A. Sastry, G. Ponticelli and R. Pinna, *Indian J. Phys., A*, 58 (1984) 50.
525. E.S. Raper, J.R. Creighton, R.E. Oughtred and I.W. Nowell, *Inorg. Chim. Acta*, 87 (1984) 19.
526. R.S. Brown, M. Zamkanei and J.L. Cocho, *J. Am. Chem. Soc.*, 106 (1984) 5222.
527. S.A.A. Zaidi, T.A. Khan and Z.A. Siddiqi, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 717.
528. V.I. Dulova and L.F. Petrash, *Koord. Khim.*, 10 (1984) 89.
529. C.P. Prabhakaran and R. Krishnan, *Indian J. Chem., Sect.A*, 23A (1984) 605.
530. G.N. Mukherjee, *Indian J. Chem., Sect.A*, 23A (1984) 496.
531. T. Sakurai, H. Oi and A. Nakahara, *Inorg. Chim. Acta* 92 (1984) 131.
532. G.C. Wellan, D.V. Bautista, L.K. Thompson and F.W. Hartstock, *Inorg. Chim. Acta*, 75 (1983) 271.
533. E.S. Raper, R.E. Oughtred, J.R. Creighton and I.W. Nowell, *Inorg. Chim. Acta*, 87 (1984) 201.
534. L. Castella, M.E. Silver and J.A. Ibers, *Inorg. Chem.*, 23 (1984) 1409.
535. F.B. Hulsbergen, W.L. Driessen, J. Reedjik and G.C. Verschoor, *Inorg. Chem.*, 23 (1984) 3589.
536. A.V. Ivashchenko, O.N. Garicheva and T.N. Ivanova, *Koord. Khim.*, 9 (1983) 1508.
537. T.G. Leonova, L.G. Lavrenova, S.V. Larionov, V.N. Ikorskii and Z.A. Grankina, *Izv. Sib. Otd. Akad. Nauk. SSSR., Ser. Khim. Nauk.*, (1984) 82.
538. F.S. Keij, R.A.G. de Graaf, J.G. Haasnoot and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, (1984) 2093.
539. R. Mueller and R. Ackermann, *Z. Chem.*, 24 (1984) 295.
540. A.V. Ivashchenko and V.N. Avilina, *Koord. Khim.*, 9 (1983) 1627.
541. H. Nham and L. Thuan, *Tap. Chi. Hoa Hoc*, 22 (1984) 18.
542. A. Kircheiss and H. Weber, *Z. Chem.*, 23 (1983) 446.

543. R. Baltistuzzi and G. Peyronel, *Z. Anorg. Allg. Chem.*, 509 (1984) 192.

544. M.B. Cingi, A.M.M. Lanfredi, A. Tiripicchio, J.G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta*, 86 (1984) 137.

545. P.B. Viossat, N.-H. Dung, J.-C. Lancelot and M. Robba, *Acta Crystallogr., Sect. C*, 40C (1984) 935.

546. F. Demartin, M. Manassero, L. Naldini and M.A. Zoroddu, *Inorg. Chim. Acta*, 77 (1983) L213.

547. W.L. Darby and L.M. Vallarino, *Inorg. Chim. Acta*, 75 (1983) 65.

548. J.A. Real and J. Borras, *Synth. React. Inorg. Met.-Org. Chem.*, 14 (1984) 857.

549. P.B. Viossat, S. Bénazeth, P. Khodadad and N. Rodier, *Acta Crystallogr., Sect. C*, 40C (1984) 1340.

550. C. Benelli, I. Bertini, M. DiVaira and F. Mani, *Inorg. Chem.*, 23 (1984) 1422.

551. G.A. van Albada, R.A.G. de Graaff, J.G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 23 (1984) 1404.

552. N. Rudgewick-Brown and R.D. Cannon, *J. Chem. Soc., Dalton Trans.*, (1984) 479.

553. B.K. Mohapatra and B. Sahoo, *Indian J. Chem., Sect.A*, 23A (1984) 844.

554. A.K. Basak and T.A. Kadem, *Helv. Chim. Acta*, 66 (1983) 2086.

555. K. Karadeniz and O. Bekaroglu, *Synth. React. Inorg. Met.-Org. Chem.*, 13 (1983) 1029.

556. D.St.C. Black and N.E. Rothnie, *Aust. J. Chem.*, 36 (1983) 2387.

557. D.St.C. Black and N.E. Rothnie, *Aust. J. Chem.*, 36 (1983) 2395.

558. K. Maruyama, H. Tamiaka and S. Kawabata, *Chem. Lett.*, (1984) 743.

559. S. Kelly, D. Lançon and K.M. Kadish, *Inorg. Chem.*, 23 (1984) 1451.

560. G. Brewer and E. Sinn, *Inorg. Chim. Acta*, 87 (1984) L41.

561. S. Funahashi, Y. Yamaguchi and M. Tanaka, *Inorg. Chem.*, 23 (1984) 2249.

562. S.S. Eaton, P.M. Boymel, B.M. Sawant, J.K. More and G.R. Eaton, *J. Magn. Reson.*, 56 (1984) 183.

563. F. Gao, Y. He, X. Wang, D. Yao, H. Xu and M. Wang, *Huaxue Xuebao*, 41 (1983) 966.

564. D.A. Scherson, S.L. Gupta, C. Fierro, E.B. Yeager, M.E. Kordesch, J. Eldridge, R.W. Hoffman and J. Blue, *Electrochim. Acta*, 28 (1983) 1205.

565. Q. Zheng, X. Wu and C. Niu, *Wuhan Daxue Xuebao, Ziran Kexueban*, (1984) 119.

566. J. Metz, O. Schneider and M. Hanack, *Inorg. Chem.*, 23 (1984) 1065.

567. V.N. Parmon, G.L. Elizarova, L.G. Matvienko, N.V. Lozhkina and V.E. Maizlish, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1984) 1735.

568. L.Y. Johansson and R. Larsson, *Chem. Scr.*, 23 (1984) 48.

569. C.M. Lieber and N.S. Lewis, *J. Am. Chem. Soc.*, 106 (1984) 5033.

570. W.M. Brouwer and A.L. German, *J. Mol. Catal.*, 22 (1984) 297.

571. M. Kita, K. Yamanari and Y. Shimura, *Chem. Lett.*, (1984) 297.

572. R. Cini, A. Cinquantini, P.L. Orioli, C. Mealli and M. Sabat, *Can. J. Chem.*, 62 (1984) 2908.

573. A. Kotocova, D. Valigura and P. Fodran, *Proc. Conf. Coord. Chem.*, 9 (1983) 189.

574. R. Roy, P. Paul and K. Nag, *Transition Met. Chem. (Weinheim)*,

9 (1984) 152.
575. U.B. Ceipidor, V. Carunchio, A.M. Girelli and A. Messina, *Inorg. Chim. Acta*, 75 (1983) 237.
576. B. Singh, B.P. Yadava and R.C. Aggarwal, *Indian J. Chem., Sect. A*, 23A (1984) 332.
577. B. Singh, B.P. Yadava and R.C. Aggarwal, *J. Chem. Eng. Data*, 29 (1984) 343.
578. K.S. Siddiqi, M.A.A. Shah, S.A.A. Zaidi, *Indian J. Chem., Sect. A*, 22A (1983) 812.
579. S.K. Nandi, B. Banerjee, S. Roychowdhury and B. Sur, *Indian J. Chem., Sect. A*, 23A (1984) 1073.
580. B.A. Bovykin, L.G. Romanovskaya, A.P. Ranskii, I.A. Zanina and E.P. Artynkhova, *Vopr. Khim. Khim. Tekhnol.*, 73 (1983) 22.
581. C.L. Jain, P.N. Mundley and R. Benjamin, *J. Indian Chem. Soc.*, 61 (1984) 84.
582. R.C. Mishra, B.K. Mohapatra and D. Panda, *J. Indian Chem. Soc.*, 60 (1983) 782.
583. M.R. Chaurasia and P. Shukla, *J. Indian Chem. Soc.*, 60 (1983) 1011.
584. M. Kodama, T. Koike, N. Hoshiga, R. Machida and E. Kimura, *J. Chem. Soc., Dalton Trans.*, (1984) 673.
585. S.J. Landon and T.B. Brill, *Inorg. Chem.*, 23 (1984) 4177.
586. S.J. Landon and T.B. Brill, *Inorg. Chem.*, 23 (1984) 1266.
587. F. Cecconi, C.A. Ghilardi, S. Midollini and A. Orlandini, *J. Am. Chem. Soc.*, 106 (1984) 3667.
588. V.M. Miskowski, B.D. Santarsiero, W.P. Schaefer, G.E. Ansok and H.B. Gray, *Inorg. Chem.*, 23 (1984) 172.
589. B.V. Fal'kovskii, E.V. Makhonina, M.B. Rozenkevich and Yu.A. Sakkarovskii, *Koord. Khim.*, 9 (1983) 1528.
590. M.S. McDowell, J.H. Espenson and A. Bakac, *Inorg. Chem.*, 23 (1984) 2232.
591. C. Romig, C.L. Brooks, J.J. Deyoung and R.C. Beaumont, *Inorg. Chim. Acta*, 86 (1984) 13.
592. D.D. Dexter, C.N. Sutherby, M.W. Grieb and R.C. Beaumont, *Inorg. Chim. Acta*, 86 (1984) 19.
593. S. Fallab and M. Zehnder, *Helv. Chim. Acta*, 67 (1984), 392.
594. S. Cabanti, N. Ceccanti and P. Gianni, *J. Chem. Soc., Dalton Trans.*, (1984) 307.
595. R.J. Motekaitis, A.E. Martell and D.A. Nelson, *Inorg. Chem.*, 23 (1984) 275.
596. V.P. Vasil'ev and I.P. Gus'kov, *Zh. Neorg. Khim.*, 29 (1984) 2014.
597. A. Kufelnicki and S. Petri, *Pol. J. Chem.*, 56 (1982) 31.
597a. C. Raleigh and A. Martell, *J. Chem. Soc., Chem. Commun.*, (1984) 335.
598. S. Cabanti, N. Ceccanti and G. Conti, *Inorg. Chim. Acta* 89 (1984) L21.
599. K. Kumar and J.F. Endicott, *Inorg. Chem.*, 23 (1984) 2447.
600. M. Munakata and J.F. Endicott, *Inorg. Chem.*, 23 (1984) 3693.
601. R.W. Hay and R. Bembi, *Inorg. Chim. Acta*, 86 (1984) 65.
602. A. Lecheheb, M. Takakubo, J. Faure and J. Belloni, *Electr. Fr., Bull. Dir. Etud. et Rech., Ser. A., Nucl., Hydraul., Therm.*, (1983) 103.
603. D.E. Hamiliton, R.S. Drago and J. Telser, *J. Am. Chem. Soc.*, 106 (1984) 5353.
604. M. Suzuki, H. Kanatomi and I. Murase, *Bull. Chem. Soc. Jpn.*, 57 (1984) 36.
605. Y. Ozkalay, Y. Sarikahaya and F. Sarikahaya, *Chim. Acta Turc.*, 11 (1983) 291.
606. K. Bajdor, K. Nakamoto, H. Kanatomi and I. Murase, *Inorg.*

Chim. Acta, 82 (1984) 207.

607. S.C.F. Au-Yeung and D.R. Eaton, *Inorg. Chem.*, 23 (1984) 1517.
608. B. Jezowska-Trzebiatowska, P. Chimielewski and A. Vogt, *Inorg. Chim. Acta*, 83 (1984) 129.
609. A. Nishinaga, H. Tomita and H. Ohara, *Chem. Lett.*, (1983) 1751.
609a. S. Kawanishi and S. Sano, *J. Chem. Soc., Chem. Commun.*, (1984) 1628.
610. D.M. Palade, V.V. Shapovalov, I.D. Ozherel'ev and I.V. Lanina, *Zh. Neorg. Khim.*, 28 (1983) 3067.
611. D.M. Palade, V.V. Shapovalov and V.S. Semykin, *Zh. Neorg. Khim.*, 28 (1983) 2284.
612. D.M. Palade, V.V. Shapovalov and V.S. Semykin, *Zh. Neorg. Khim.*, 28 (1983) 987.
613. D.M. Palade and V.V. Shapovalov, *Zh. Neorg. Khim.*, 28 (1983) 2562.
614. P. Spacu, L. Patron and A. Contescu, *Rev. Roum. Chim.*, 29 (1984) 99.
615. K. Tashkova and A. Andreev, *Inorg. Chim. Acta*, 84 (1984) 31.
616. K. Tashkova and A. Andreev, *J. Mol. Struct.*, 115 (1984) 55.
617. B.V. Roumanovbskii and T.G. Borisova, *Oxid. Commun.*, 6 (1984) 157.
618. A.S. Dubrovina, A.I. Malkova and V.I. Tupikov, *Koord. Khim.*, 10 (1984) 1207.
619. K. Bajdor, J.R. Kincaid and K. Nakamoto, *J. Am. Chem. Soc.*, 106 (1984) 7741.
620. H.K. Chae, C.S. Han and H. Chon, *Taehan Hwahakhoe Chi*, 28 (1984) 114.
621. D.A. Buttry and F.C. Anson, *J. Am. Chem. Soc.*, 106 (1984) 59.
622. C.K. Chang, H.Y. Liu and I. Abdalmuhdi, *J. Am. Chem. Soc.*, 106 (1984) 2725.
623. H. Ogoshi, H. Sugimoto, M. Miyake and Z. Yoshida, *Tetrahedron*, 40 (1984) 579.
624. D. Ozer, R. Parash, F. Broitman, U. Mor and A. Bettelheim, *J. Chem. Soc., Faraday Trans. I*, 80 (1984) 1139.
625. C. Creutz, H.A. Schwarz and N. Sutin, *J. Am. Chem. Soc.*, 106 (1984) 3037.
626. D.J. Wink and N.J. Cooper, *J. Chem. Soc., Dalton Trans.*, (1984) 1257.
627. K.L. Brown, J.M. Hakimi and D.W. Jacobsen, *J. Am. Chem. Soc.*, 106 (1984) 7894.
628. C. Bianchini and A. Meli, *J. Am. Chem. Soc.*, 106 (1984) 2698.
628a. S. Oishi, K. Tajime, A. Hosaka and I. Shiojima, *J. Chem. Soc., Chem. Commun.*, (1984) 607.
629. A.P. Bogdanov, V.V. Zelentsov, A.A. Shul'ga, A.P. Malyshkin and V.V. Volkov, *Dokl. Akad. Nauk. SSSR*, 275 (1984) 899.
630. S.G. Taylor, M.R. Snow and T.W. Hambley, *Aust. J. Chem.*, 36 (1983) 2359.
631. D.A. House and R.G.A.R. Maclagan, *Aust. J. Chem.*, 37 (1984) 239.
632. L.G. Vanquickenborne and K. Pierloot, *Inorg. Chem.*, 23 (1984) 1471.
633. T. Ito, M. Kato and H. Ito, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1556.
634. R. Herak and S. Kalman, *Glas. Hem. Drus. Beograd.*, 48 (1983) 343.
635. C. Bianchini, D. Masi, C. Mealli and A. Meli, *Inorg. Chem.*, 23 (1984) 2838.
636. D.G. Batyr, F.A. Spatar, S.S. Budnikov and I.B. Bersuler, *Koord. Khim.*, 9 (1983) 1452.
637. J.E. Newton and M.B. Hall, *Inorg. Chem.*, 23 (1984) 4627.

638. L.I. Savranskii, O.N. Miroshnikov, A.T. Pilipenko and V.L. Sheptun, *Koord. Khim.*, 10 (1984) 350.

639. A.T. Pilipenko, L.I. Savranskii and O.N. Miroshnikov, *Dokl. Akad. Nauk. SSSR*, 275 (1984) 1126.

640. I.P. Beletskii and K.B. Yatsimirskii, *Teor. Eksp. Khim.*, 19 (1983) 643.

641. V.M. Pinchuk, V.A. Korobskii and L.B. Shevardina, *Zh. Neorg. Khim.*, 29 (1984) 1111.

642. F. Feichtmayr and H. Pfitzner, *Liebigs Ann. Chem.*, (1980) 2055.

643. J.G. Russell, R.G. Bryant and M.M. Kreevoy, *Inorg. Chem.*, 23 (1984) 4565.

644. S.H. Peterson, R.G. Bryant and J.G. Russell, *Anal. Chim. Acta*, 154 (1983) 211.

645. V.P. Tarasov, T.Sh. Kapanadze, I.B. Baranovskii, G.V. Tsintsadze, S.G. Drobyshev and Yu.A. Buslaev, *Koord. Khim.*, 10 (1984) 368.

646. S.C.F. Au-Yeung and D.R. Eaton, *Can. J. Chem.*, 62 (1984) 2127.

647. D.R. Eaton and J.D. Weegar, *Inorg. Chim. Acta*, 93 (1984) 73.

648. J. Bultitude, L.F. Larkworthy, J. Mason, D.C. Povey and B. Sandell, *Inorg. Chem.*, 23 (1984) 3629.

649. N. Juranic, *Inorg. Chim. Acta*, 93 (1984) L37.

650. G. Navon and W. Kläui, *Inorg. Chem.*, 23 (1984) 2722.