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STRUCTURAL CHEMISTRY OF TRANSITION METAL COMPLEXES OF OXIMES

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CONTENTS

A. INTRODUCTION

The name oxime is a contraction of oxy-imine, $>$C=NOH. The oxime group is amphiprotic with a slightly basic nitrogen atom and a mildly acidic hydroxyl group. It was Alfred Werner who, in his doctoral work under Hantzsch, clearly recognised[1,2] that the observed isomerism of oximes is due to "the different spatial arrangement" of the groups attached to the C = N moiety. The occurrence of two isomers of benzaldoxime and three isomers of benzildioxime was immediately rationalized.

The most significant early event in the area of transition metal chemistry of oximes took place in 1905 when the Russian chemist, Chugaev* discovered[3] the reaction between nickel(II) salts and dimethylglyoxime, which is the best-known example of a *vicinal* dioxime (henceforth abbreviated as *vic*-dioxime). The list of *vic*-dioximes and transition metals that can participate in complex formation was quickly augmented[4]. Chugaev correctly identified[4] the bidentate nature of *vic*-dioximes although this did not pass without criticism[5]. The chelate ring size, however, remained uncertain and went through the incorrect seven-membered and six-membered formulations to the now well-established five-membered formulation. Detailed accounts of these and other historical developments are well-documented in several places[6-9]. Particular mention should be made of Welcher's treatise[8], which has a large amount of information on the early research on metal complexes not only of *vic*-dioximes but of oximes in general.

The complexes of *vic*-dioximes have yielded through the decades a never-ending series of interesting chemistry[10]. This in turn has stimulated research into the coordination chemistry of ligands having other functions in addition to the oxime function. A vast amount of fascinating chemistry has thus accumulated with fundamental bearings on areas such as structure, stability and reactivity of molecules, analytical chemistry and biochemical models.

In the present article we wish to focus attention on the various structural types among the transition metal complexes of oximes. Structures derived from diffraction work are described in greater detail than those arrived at on the basis of indirect spectroscopic, magnetic and other data. Structural interrelations wherever existent are noted. Discussions of structural types are subdivided according to ligand systems, which are usually identified by functional groups. For example, "carbonyl-oxime" embraces ligands which contain both carbonyl and oxime groups. Where common names exist, these are used as such, e.g. "nitrosophenols". We wish to emphasise that it is *not* the purpose of this article to discuss the complexes of all oximes or of all transition metal ions. In other words it is not an exhaustive report. We have instead concentrated on a few selected systems where considerable structural work has already been done or where such work will be worth doing. Literature coverage is up to late 1972.

The abbreviations used for various ligands are noted in the text in appropriate places. The meanings of some other symbols which appear in the text are collected below:

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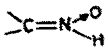
* This, rather than Tschugaeff[3,4], is the correct form of spelling (private communication with Professor J.C. Bailar, Jr.).

oac	acetate
Z	any atom
Y	any organic group
Ar	aryl
Bu	butyl
Et	ethyl
hal^-	halide ion
R	hydrogen, alkyl or aryl
H_nL	ligand with *n* dissociable protons
M	metal
Me	methyl
A and B	monodentate ligands
D	monodentate neutral donor
X^-	mononegative anion
n, m	numbers, usually integers
Ph	phenyl
Pr	propyl
py	pyridine

B. STRUCTURE OF THE OXIME GROUP

The structures of several oximes are accurately known. These are briefly presented in this section with particular reference to the dimensions of the oxime group. Interestingly, the choice between the classical structure I and the nitrone structure II was actively debated[11] as late as 1952. Neutron diffraction work[12] on dimethylglyoxime definitely established the presence of O–H bonds (1.02 ± 0.04 Å) in this compound. It is now generally agreed that the oxime group has the structure I. Oximes are usually associated[12–22] in the solid state *via* O–H···N hydrogen bonds of length ~ 2.8 Å.


I


II

The dimensions of the oxime group in several compounds of known structure are listed in Table 1. The calculated C = N and N–O distances based on covalent radii and electronegativity are 1.27 and 1.44 Å respectively[23]. In most cases the observed C = N distances lie within ± 0.02 Å of the calculated figure. On the other hand observed N–O distances are systematically lower than 1.44 Å and usually lie in the range 1.40 ± 0.02 Å. The anomalous neutron diffraction data[12] of dimethylglyoxime may actually be in error since the work was done in projection. For the sake of comparison the average N–O distances in two *N*-oxides: trimethylamine oxide[24], 1.39 Å and pyridine *N*-oxide[25], 1.35 Å are noted.

TABLE 1

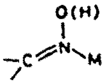
Bond distance (Å) and bond angle (°) data for some oximes

Compound	C = N	N–O	<C–N–O	Ref.
Formaldoxime[a]	1.276	1.408	110	23
Formamidoxime[b]	1.288	1.415	110	13
Acetoxime[b]	1.29	1.36	111	14
Glyoxime[b]	1.284	1.397	111	15
Dimethylglyoxime (i)[c]	1.25	1.32	111	12
(ii)[b]	1.27	1.38	114	16
syn-*p*-Chlorobenzaldoxime[b]	1.260	1.408	111	17, 18
p-Dimethylamino-benzaldoxime[b]	1.264	1.420	121	19
5-Chlorosalicylaldoxime	1.24	1.39	114	20
Pyridoxal phosphate oxime[b]	1.32	1.36	118	21
Cyclohexane-1, 4-dionedioxime	1.276	1.411	112	22

[a] Microwave data.
[b] X-ray diffraction data.
[c] Neutron diffraction data.

C. MODES OF BONDING IN COMPLEXES

As a ligand the oxime group is potentially ambident with possibilities of coordination through nitrogen and/or oxygen atom(s). In the vast majority of complexes coordination actually occurs at nitrogen. Anticipating the results to be described in the later sections, the various proven modes of metal–oxime linking are summarised below in III–VI (electrical charges are not shown).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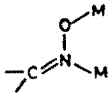
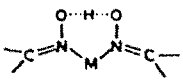
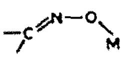

V


IV

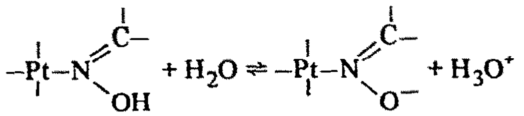

VI

Oximes can react either as such or in the form of the conjugate base. This is what is meant by putting the hydrogen atom in III in parenthesis. This atom may or may not be present. In IV, one oxime group is present as such while the second group is present as the conjugate base; the single hydrogen atom is then shared in the O···H···O bridge. The structural types III and IV are quite common.
Several polynuclear species containing V are also known. In VI the oximate anion is linked to the metal through oxygen. Only a limited number of complexes belonging to this type are known at present.

D. SIMPLE OXIMES

By "simple oximes" are meant ligands which have only one oxime group as the sole coordination site such as acetaldoxime (Hado) and acetoxime (Hato). Hieber and Leutert showed[26,27] many years ago that such oximes react with copper (II), nickel(II) and cobalt(II) salts giving complexes of the type M(oxime)$_n$X$_2$, where n is usually 2 or 4 and X is a halogen. A few cobalt(II) complexes ($n = 4$, X = Cl) were shown to be high-spin[28]. Apart from this there have been very few early physicochemical and structural studies on the complexes of simple oximes. The three-dimensional X-ray structure of Ni(Hado)$_4$Cl$_2$ in the crystalline state was recently reported[29]. The coordination polyhedron is *trans* octahedral NiN$_4$Cl$_2$. The oxime molecules are bound to the metal via nitrogen atoms, the NiN$_4$ fragment being planar (average Ni–N, 2.114; Ni–Cl 2.441; C = N, 1.251; N–O, 1.380 Å and $<$ CNO, 112°). The oxime protons hydrogen-bond with the coordinated chloride ions intramolecularly. The electronic, vibration and PMR spectra of the complex are reported[29] to be in accord with the above structure.

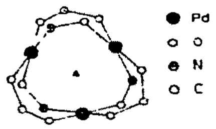
A number of tetracoordinated grossly planar platinum(II) complexes containing Hado and Hato such as *cis*- and *trans*- [Pt(NH$_3$)$_2$(Hato)$_2$] Cl$_2$, *trans*- [Pt(NH$_3$)$_2$(Hado)$_2$] Cl$_2$, [Pt(Hado)$_4$] Cl$_2$, [Pt(Hato)$_4$] Cl$_2$, [Pt(Hato)$_3$Cl] Cl, etc. were described recently[30-33]. The complexes are thermodynamically less stable than the corresponding amine complexes[31], and act as protonic acids due to the dissociation



$$-\overset{|}{\underset{|}{\mathrm{Pt}}}-\mathrm{N}\begin{smallmatrix}\nearrow \overset{|}{\mathrm{C}}- \\ \searrow \mathrm{OH}\end{smallmatrix} + H_2O \rightleftharpoons -\overset{|}{\underset{|}{\mathrm{Pt}}}-\mathrm{N}\begin{smallmatrix}\nearrow \overset{|}{\mathrm{C}}- \\ \searrow \mathrm{O}^-\end{smallmatrix} + H_3O^+ \qquad (1)$$

In some cases the neutralised species, e.g. Pt(Hato)$_2$(ato)$_2$, in which like units are probably disposed in *trans* positions[31] can be readily isolated. The dissociation constants of the complexes catalogued above are known[30,31]. For example, the pK of Hato is ~12 while those of *trans*- [Pt(NH$_3$)$_2$(Hato)$_2$] Cl$_2$ are successively 5.66 and 7.40 at 25°C. The most significant point to note is that the bound oxime is more acidic than the free oxime. This expected phenomenon occurs quite generally in oxime chemistry.

We now refer to a trinuclear palladium(II) complex in which ato acts as a bridging group. Palladium(II) acetate reacts with Hato to produce a red-brown trimeric complex [Pd(oac)(ato)]$_3$. The three palladium(II) atoms constitute[34] an equilateral triangle in which each adjacent pair is held by the oac and ato anions as shown in VII (Me attached to C and =CMe$_2$ attached to N are not shown).



VII

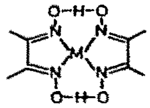
Every palladium(II) atom has a planar O_3N coordination sphere and the molecule has a threefold axis of symmetry. Some average bond distances are : Pd–N, 1.97; Pd–O, 2.00; N–O, 1.37; C=N, 1.31 Å. Acetoximato bridging of the same type as in VII is known[35] to occur in [Z(ato)Me$_2$]$_2$, where Z = B, Al or Ga.

Lastly we make a brief note of some potentially interesting complexes of the trimer of formaldoxime (abbreviated as H_3L). In neutral solutions nickel(II), cobalt(II) and manganese(II) form colourless complexes with this ligand. In strongly alkaline media these are readily oxidised by air to yield[36–38] deeply coloured complexes of composition NiL_2^{2-}, CoL_2^{3-} and MnL_2^{2-}. These can be isolated in the crystalline state as alkali metal salts[37]. These complexes have been examined using spectral, magnetic and polarographic techniques. However, nothing conclusive appears to be known about their structures. In fact, the nature of the ligand H_3L is itself a mystery. One suggestion[39] is that it is $C(CH_2NHOH)_2(=NOH)$. The ions NiL_2^{2-} and CoL_2^{3-} are diamagnetic while MnL_2^{2-} has a magnetic moment of 3.82 B.M. It is speculated[36–38] that the oxidation states of the metal ions in the above complexes are respectively four, three and four. Definitive structural investigations on these systems will be worth undertaking.

E. *vic*-DIOXIMES

(i) General aspects of structure

The detailed structures of a sizeable number of metal *vic*-dioximates are known from X-ray work. In almost all cases the grossly planar moiety VIII is present. Depending on the metal and its oxidation state, VIII may accommodate additional ligands on one or both the axial (i.e. perpendicular to the plane of VIII) positions. Ideally VIII can have the symmetry D_{2h}. In practice the symmetry is often found to be lower due to distortions arising out of peculiarities in bonding or crystal packing. The structures of some molecules[40–56] which contain VIII are summarised in



VIII

TABLE 2
Structure of *vic*-dioxime complexes

Compound	Bond distances in $M(Hvdo)_2$ (Å)				Ref.[a]
	M–N	C = N	N–O	O · · · O	
$Ni(Hg)_2$	1.88	1.29	1.35	2.45	40,41*
	(NiN$_4$ unit is planar but the remainder of the molecule deviates from planarity)				
$Pd(Hg)_2$	1.97	1.30	1.34	2.63	42*
	(Two crystallographically distinct planar molecules occur in the crystal)				
$Pt(Hg)_2$	1.99	1.31	1.35	2.66	43*
	(Planar molecules)				
$Ni(Hdmg)_2$	1.85	1.29	1.36	2.40	44,45
	(Planar molecules stacked one above the other)				
$Pd(Hdmg)_2$	1.96	1.31	1.35	2.59	45
	(Isomorphous with $Ni(Hdmg)_2$)				
$Pt(Hdmg)_2$	1.94	1.32	1.28	3.03	46
	(Isomorphous with $Ni(Hdmg)_2$)				
$Ni(Hmeg)_2$ (α-form)	1.86	1.30	1.35	2.45	47, 48*
	(Planar; β-form is crystallographically quite different)				
$[Cu(Hdmg)_2]_2$	1.95	1.29	1.36	2.66	49, 50*
	(The dimers are centrosymmetric; dimers are formed by interaction of the copper atom of one unit with the oxygen atom of the second unit; copper environment is distorted square pyramidal; a hydrogen atom belonging to a methyl group occupies the sixth position around each copper at 2.93 Å)				

TABLE 2 (continued)

Compound	Bond distances in $M(Hvdo)_2$ (A)				
	M–N	C = N	N–O	O · · · O	Ref.[a]
$[Co(Hdmg)_2(NH_3)_2]NO_3$	1.96	1.22	1.35	2.65	51
	(*Trans* octahedral cation with ammonia in axial positions; $Co(Hdmg)_2$ moiety is nearly planar)				
$Co(Hdmg)_2(py)(C_3H_5O_2)$ ($C_3H_5O_2$ is $-CH_2C(O)OCH_3$)	1.88	1.29	1.37	2.50	52*
	(The methylene carbon of $C_3H_5O_2$ is bonded to cobalt in a position trans to py; $Co(Hdmg)_2$ unit is planar, Co–C and Co–N (axial) are both 2.04 A long)				
$Rh(Hdmg)_2(Cl)(PPh_3)$	1.99	1.30	1.34	2.67	53*
	(Pseudooctahedral with Cl and PPh_3 in trans positions; $Rh(Hdmg)_2$ unit is not strictly planar; Rh–Cl distance is 2.38 A)				
$[Rh(Hdmg)_2(PPh_3)]_2$	1.99	1.30	1.33	2.62	54*
	(Dimerisation occurs via Rh–Rh single bond of length 2.93 A; each rhodium(II) atom is grossly octahedral; the P–Rh–Rh–P chain is practically linear; the grossly planar $Rh(Hdmg)_2$ units are in nearly staggered configuration)				
$Fe(Hniox)_2(Im)_2 . 2H_2O$ (Im is imidazole)	1.94	1.31	1.37	2.67	55
	(Centrosymmetric *trans* octahedral; water molecules are not attached to the metal)				
$Fe(Hdmg)_2(Im)_2 . 2CH_3OH$	1.91	1.32	1.39	2.59	56*
	(Centrosymmetric *trans* octahedral; the chelate rings and imidazole rings are planar. The O···H···O bridge is unsymmetrical, the hydrogen atom being ~ 1 and ~ 1.5 Å away from the two oxygen atoms; the O · · · H · · · O angle is 159°; axial Fe–N is 1.99 A)				

[a] References marked with an asterisk refer to three-dimensional work.
The abbreviations for the ligands are as follows: H_2g, glyoxime; H_2dmg, dimethylglyoxime; H_2meg, methylethylglyoxime; H_2dpg, diphenylglyoxime; H_2niox, cyclohexanedionedioxime; H_2vdo, any *vic*-dioxime.

Table 2. In this Table the bond lengths are *averaged* and then approximated to the second decimal place. While the actual precision of the crystallographic results is higher in several cases, the average values are easy to deal with and will be used as such.

In Table 2, the most accurately known (three-dimensional work) structures are marked by an asterisk. If only these structures are considered, the C = N and N–O distances are found to remain remarkably constant around 1.30 and 1.34 Å respectively. On comparing these distances with those of free oximes (Table 1), two points emerge: (*i*) the N–O distance is considerably shortened on complex formation; (*ii*) the C = N length is not much affected. Another result (not shown in Table 2) is that on complex formation the angle CNO usually opens up by ~ 10° from the free ligand value of ~ 112°. In view of the bond distance data, it may be significant that in going from the alkali metal salts to the transition metal chelates, the N–O stretching frequencies in the infrared are very considerably increased while the effect on the C = N frequency is much less dramatic[57–59].

The intramolecular hydrogen bridged O · · · O distances (Table 2) have interesting implications. Hydrogen bonds between oxygen atoms are usually found to occur with O · · · O distances ranging upward from 2.4 Å. An O · · · O distance shorter than 2.4 Å is made improbable by oxygen–oxygen repulsion. The trend of variation of observed O–H distances with O · · · O separations suggests that the hydrogen atom is effectively centred in an essentially symmetric potential in cases where the O · · · O distance is less than 2.5 Å. A case at hand is potassium hydrogen chloromaleate, in which the acidic hydrogen atom was found by neutron diffraction[60] to be symmetrically located in the 2.4 Å long O· · ·O bridge (O· · ·H· · ·O angle, 175°). When the O · · · O separation becomes larger than 2.5 Å, the hydrogen atom is usually situated unsymmetrically in the bridge at about 1 Å from one of the two oxygen atoms. The O · · · O distances of Table 2 suggest that only $Ni(Hg)_2$, $Ni(Hdmg)_2$ and $Ni(Hmeg)_2$ may involve symmetrical hydrogen bridging while the remaining complexes probably have unsymmetrical bridges. Another point of interest is that for a given ligand system the O· · ·O distance increases in the order Ni < Pd < Pt paralleling increase in atomic radii.

The O · · · H · · · O stretching and bending vibrations in VIII are usually observed in the ranges 2200–2400 cm^{-1} and 1600–1800 cm^{-1} respectively[57,58]. Both bands are broad and weak but the bending vibration is more readily observed experimentally. It is significant that crystalline $(Hdmg)_2Cu$ gives rise to[59] two OH frequencies (2650 and 2382 cm^{-1}) corresponding to the two very different (2.526 and 2.694 Å) O· · · O distances of the dimeric complex[50]. On dissolution in chloroform containing *n*-butylamine, only a single O–H frequency is observed[59] at 2375 cm^{-1}. The structure in solution is clearly different from that in the solid state. Most probably a monomeric species (likely to be an *n*-butylamine adduct) having a single O · · · O distance is present in the solution phase.

$Ni(Hdmg)_2$ forms needle-like orthorhombic crystals in which the planar molecules of structure VIII are stacked one above the other such that the nickel atoms form an infinite linear chain along the needle axis. Adjacent molecules in the stack are rotated by 90° and have Ni· · ·Ni separation of 3.245 Å. The chelates

$Pd(Hdmg)_2$, $Pt(Hdmg)_2$ and many other $M(Hvdo)_2$ (M = Ni, Pd) complexes have similar structures. The natures of metal–metal interactions in such chains have been the subject of many investigations. It can be stated that there is little convincing evidence to require the occurrence of appreciable bonding in the ground state along the metal chain. A recent review[61] dealing with this topic is already available.

(ii) Oxidation of $M(Hvdo)_2$ (M = Ni, Pd)

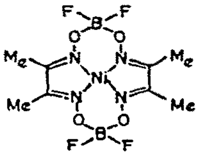
$Ni(Hdmg)_2$ dissolves in strongly alkaline media to give yellow solutions which are believed[62] to contain species such as $Ni(dmg)(OH)^-$ and $Ni(dmg)_2^{2-}$. The latter can be isolated[62] as alkali metal salts, e.g. $Li_2Ni(dmg)_2$. The structure of $Ni(dmg)_2^{2-}$ is probably the same as that of VIII except that the two bridging protons are absent.

Strongly alkaline solutions of $Ni(Hdmg)_2$ (but *not* $Pd(Hdmg)_2$) absorb oxygen with attendant reddening in colour[63,64]. The absorption reaction apparently takes place in two stages[65]. In the first stage a rapid and reversible attachment of oxygen occurs. The bound oxygen can be removed[64,65] by heating, or by bubbling an inert gas through the solution. The second stage is slower and involves[65] an irreversible oxidation leading to the "decomposition" of the complex. The nature of the oxidation product(s) is not known; nickel(IV) species have been postulated[66]. More definite is the nature of the red substance obtained by oxidising a mixture of nickel(II) and H_2vdo with, for example, iodine in strongly alkaline media. This reaction has been studied using ion migration[67], ion exchange[67,68], electrochemical [66,69] and photometric[70] techniques. The general conclusion is that nickel(IV) species are formed. Diamagnetic crystals of composition[71] $K_2Ni(dmg)_3 \cdot 6H_2O$ can be isolated from complexation and oxidation reactions among nickel(II) salts, H_2dmg, KOH and I_2. The anion $Ni(dmg)_3^{2-}$ is probably of the tris(bidentate) pseudooctahedral type. Other examples of the stabilisation of higher (i.e. > 2) valence states of nickel by oxime ligands can be found in Sections D, I and M.

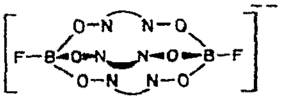
Lastly we record the species obtained by reacting $M(Hvdo)_2$ (M = Ni, Pd, Pt) with bromine and iodine in nonaqueous solvents. Compounds such as $Ni(Hdpg)_2X$ (X = Br, I)[72,73] and $Ni(Hdmg)_2Br_2$ (ref. 73) were originally believed to contain nickel atoms of valency higher than two. More recently crystals of $M(Hdpg)_2X$ were examined using partial X-ray data[74]. The crystal structure is basically the same[74] as that of $M(Hdpg)_2$. In the structure of $M(Hdpg)_2$ there are channels surrounded by phenyl groups. One suggestion[74] is that in $M(Hdpg)_2X$, halogen *molecules* are included in these channels and are held by charge-transfer interactions. Other workers have likened the complexes to the starch–iodine complex, thereby implying that I_3^- is present[75]. Whatever are the details of the structure, it is clear that $M(Hdpg)_2X$ is not a molecular species and contains mainly metal(II). The $M(Hdpg)_2I$ complexes, $Ni(Hdpg)_2I$ in particular, are slightly paramagnetic[74,75]. This is attributed[75] to lattice defects associated with the presence of some metal (III).

(iii) Encapsulation, clathro chelates and trigonal prismatic geometry

Ni(Hdmg)$_2$ readily reacts[76] with boron trifluoride etherate to yield Ni(BF$_2$dmg)$_2$ of structure IX, in which the ligand is macrocyclic. A similar reaction between Co(Hdmg)$_3$ and boron trifluoride etherate yields[77] [Co{(BF)$_2$(dmg)$_3$}] BF$_4$, in which the bicyclic macrocycle shown schematically in X completely encapsulates the cobalt(III) atom. This complex is an example of a clathro chelate[78] since the metal atom is surrounded by the ligand cage. The corresponding cobalt(II) clathro chelate Co{(BF)$_2$(dmg)$_3$} is readily obtained[79] by reducing the cobalt(III) analogue with sodium iodide. It is low-spin.



IX

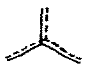


X

The three-dimensional X-ray structures of both the complexes are known[80]. In the cobalt(II) complex the CoN$_6$ coordination polyhedron is found to have the uncommon trigonal prismatic geometry. Octahedral and trigonal prismatic geometries can be distinguished by defining the twist angle ϕ as shown in XI and XII, in which the two geometries are projected along three-fold axes. In the cobalt(II) complex under discussion, $\phi = 8.6°$, so that it can be considered to be a slightly distorted XII. On the other hand, in the cobalt(III) complex, $\phi = 45°$. This defines the complex as a distorted XI. The average Co–N, O–N and C = N distances are[80], respectively, cobalt(III): 1.89, 1.36, 1.29; cobalt(II): 1.94, 1.37, 1.30 Å.

O_h, $\phi = 60$

XI



D_{3h}, $\phi = 0$

XII

There have been many studies in recent years on the factors which determine the relative stabilities of octahedral and trigonal prismatic geometries[81–84]. In absence of compulsions from steric and/or crystal packing forces the octahedral geometry is practically universally favoured. Unusual in this regard are some metal tris(dithiolene) complexes and their selenium analogues, which are grossly trigonal prismatic in geometry[81]. Apart from these, trigonal prismatic geometry, where it exists[81,83], is forced by the requirements of the ligand cage as in the case of X. Even then, low-spin d^6 ions resist trigonal prismatic geometry, at least in part for crystal field stabilisation reasons[82,84]. This is apparent in the structure of the cobalt(III) complex of X. In addition the size of the metal ion affects the structure. For a given ligand, decrease in the ionic size of the metal ion may increase the twist angle as the metal ion seeks to optimise metal–ligand distances. Often it is difficult to separate the crystal field and ionic size effects since they act in the same direction[82]. Other examples of trigonal prismatic complexes are cited in Section I.

(iv) Cobalt complexes containing $Co(Hvdo)_2^{n\pm}$ *(n = 0, 1)*

In recent years the structure and reactivity of this class of complexes have received a great deal of attention. This is mainly because of the recognition[85,86] that many chemical reactions of vitamin B_{12} can be simulated by such complexes, often surprisingly closely. The majority of studies are limited to the $Co(Hdmg)^{n\pm}$ species. The $Co(Hdmg)_2^{n\pm}$ moiety has been named "cobaloxime" by analogy with "cobalamin", which is another name of vitamin B_{12}. Since the cobaloximes, together with their rhodium and iridium analogues, will be the subject matter of a separate review article*, we shall summarise only briefly the salient features of the structural chemistry of $Co(Hvdo)_2^{n\pm}$ complexes. No mention of rhodium complexes will be made beyond what is in Table 2.

The cobalt(II) complexes[87–89] belong mainly to two types. The simpler type is $Co(Hdmg)_2(D)_2$ (D = H_2O, py, PPh_3, $AsPh_3$ (etc.)). These low spin ($S = \frac{1}{2}$) complexes are most likely to have a *trans* octahedral structure in which the $Co(Hdmg)_2$ fragment of structure VIII defines the basal plane. The other type has the stoichiometry $Co(Hdmg)_2(D)$. In the solid state this type is diamagnetic and is presumably dimeric with a Co–Co bond. The structure of an analogous rhodium (II) complex is known (Table 2). The cobalt(II) dimers dissociate in solution yielding paramagnetic ($S = \frac{1}{2}$), presumably pentacoordinated, monomers[89,90]. The unpaired electron in both types of paramagnetic complexes is believed[90,91] to lie in the d_{z^2} orbital.

In strongly alkaline media, the cobalt(II) species undergo disproportionation[89] to diamagnetic cobalt(I) and cobalt(III) species, e.g.

$$Co(Hdmg)_2(PPh_3)_2 + OH^- \rightarrow Co(Hdmg)_2(PPh_3)^- + Co(Hdmg)_2(PPh_3)(OH) \qquad (2)$$

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* *Coord. Chem Rev.*, to be published.

If reducing agents (e.g. $NaBH_4$) are present, the reduction cobalt(III) → cobalt(I) occurs and the deep blue cobalt(I) complex alone is obtained. In general, the cobalt(I) complexes are formulated[92] as $Co(Hvdo)_2(D)^-$ with a pentacoordinated metal atom. They form[93] labile π-complexes of the type $Co(Hvdo)_2(D)(olefin)^-$ in which the olefin is believed to lie *trans* to D. The $Co(Hvdo)_2(D)^-$ species are extremely strongly nucleophilic and reactions[92] such as (S_N2 mechanism)

$$Co(Hvdo)_2(D)^- + RX \rightarrow Co(Hvdo)_2(D)(R) + X^- \qquad (3)$$

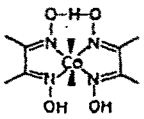
provide an effective route for the synthesis of organocobalt species, $Co(Hvdo)_2(D)(R)$, which contain trivalent cobalt. The cobalt–carbon bond in these complexes is quite stable although photochemical[94] and chemical[95] cleavage can sometimes occur.

The $Co(Hvdo)_2(D)(R)$ complexes belong to the large class of cobalt(III) chelates of general formula $Co(Hvdo)_2(A)(B)^{m\pm}$. The ligands A and B can be either neutral or anionic. When A and/or B are ambident in nature, attachment to cobalt usually occurs via the more polarisable atom[96–99].

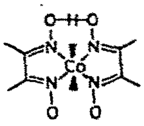
The $Co(Hvdo)_2(A)(B)^{m\pm}$ complexes almost universally have *trans* octahedral geometry. Two accurately known structures are listed in Table 2. Further, X-ray data for $Co(Hdmg)_2(NH_3)(Cl)$ (ref. 100) and $NH_4[Co(Hdmg)_2(SeCN)_2].3H_2O$ (ref. 97) are said to be in accord with *trans* geometry. The occurrence of the grossly planar hydrogen bonded $Co(Hvdo)_2^+$ moiety and hence of the *trans* octahedral geometry of $Co(Hvdo)_2(A)(B)^{m\pm}$ can be very conveniently demonstrated from infrared data[101–103], the characteristic O ··· H ··· O bending being observed in the region 1700–1800 cm^{-1}. The stretching vibration can also be detected with some difficulty[99,104] around 2300 cm^{-1}.

In some cases isomerism of $Co(Hvdo)_2(A)(B)^{m\pm}$ complexes are reported. Examples are $[Co(Hdmg)_2(H_2O)_2]NO_3$ (ref. 105), $Co(Hdmg)_2(H_2O)(Cl)$ (ref. 106) and $Co(Hdmg)_2(PPh_3)(hal)$ (ref. 107). In each of these cases the complex occurs in two isomeric forms which are speculated to have *cis* and *trans* octahedral geometries. However, convincing experimental evidence is lacking. Interestingly $Co(Hdmg)_2(PPh_3)(NO_2)$ also occurs in two forms which (on the basis of indirect PMR data) are believed to be nitrito and nitro isomers of the *trans* complex[108].

Lastly, we note a few minor variants of the $Co(Hvdo)_2(A)(B)^{m\pm}$ complexes. The dimeric organometallic complexes of the type $[Co(Hdmg)_2(R)]_2$ have been assigned a $[Cu(Hdmg)_2]_2$-like structure (Table 2) on the basis of PMR data[109]. The sixth coordination position around each cobalt(III) is occupied by the R group[109]. The $Co(Hvdo)_2(A)(B)^{m\pm}$ complexes can be readily protonated and deprotonated to yield structural types XIII and XIV respectively (charges not shown). Examples are $Co(Hdmg)(H_2dmg)Cl_2$ (ref. 103) (type XIII) and



XIII



XIV

Co(Hdmg) (dmg) $(py)_2$ (refs. 110–112) (type XIV).

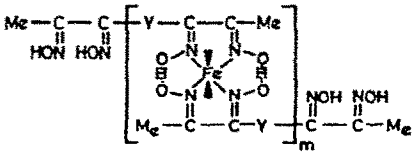
(*v*) *Iron complexes*

Both iron(II) and iron(III) form[113] complexes with H_2vdo but the diamagnetic iron(II) chelates of the type $Fe(Hvdo)_2(D)_2$ are the best characterised. The neutral donor D is usually an amine. In two cases the *trans* octahedral structure for such complexes has been proven from X-ray data (Table 2). These complexes are red in colour due to the occurrence of metal → ligand charge-transfer transitions[114]. Mössbauer spectral[115] and theoretical[116,117] studies on bonding are reported.

Two *vic*-dioximes bridged as in XV give rise to a tetraoxime. Tetraoximes yield polymeric metal chelates[118,119] with iron(II) and other metal ions. When Y in XV is $-(CH_2)_6-$ or $-(CH_2)_{10}-$, the polymers are proposed[118] to have the structure XVI with $m \sim 5$. The axial positions are occupied by amines such as pyridine, and the complexes are diamagnetic. On the other hand, when Y = biphenylyl or some other aromatic bridges, the solid complexes do not have amines in axial positions[119]. These are paramagnetic (~ 2 B.M. per iron atom) and may contain grossly planar iron(II). In pyridine solution these become diamagnetic, presumably due to axial coordination. Because of the lack of proper solubility nothing is known about their molecular complexity.

$$[H_3C-C(=NOH)-C(=NOH)]_2Y$$

XV

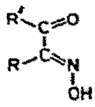


XVI

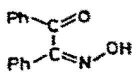
Ruthenium and osmium complexes of H_2dmg do not appear to have been studied with any degree of thoroughness.

F. CARBONYL-OXIMES

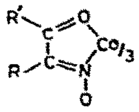
The *vic*-dioximes are oximes of carbonyl-oximes such as XVII. Familiar examples of XVII are diacetylmonoxime (R = R′ = Me) and α-benzilmonoxime (R = R′ = Ph). The β-isomer of the latter has[120] the structure XVIII. It fails to yield metal chelates. Unlike the *vic*-dioximes, XVII is a poor coordinating agent for nickel(II). The greyish complexes[121,122] are usually amorphous and unstable. Their composition is believed[122] to correspond to Ni(L) (LH) (OH) where LH stands for XVII. An attempted synthesis of the palladium(II) complex of diacetylmonoxime has failed[123]. The copper(II) complexes[121,122] of XVII are of the composition Cu(L) (OH). Although speculations have been made[122], nothing definite is known about the structure of these nickel(II) and copper(II) complexes. There is considerable confusion in the literature[124] about the nickel(II) complexes of XVII. Thus diacetylmonoxime and α-benzilmonoxime were described as forming red nickel(II) complexes. These are actually complexes of the *vic*-dioximes present as contaminants in the ligand or formed by the disproportionation reaction[122]



XVII



XVIII

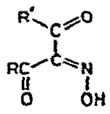


XIX

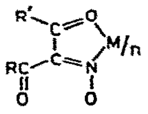
$$2\,-\mathrm{C(O)}-\mathrm{C(=NOH)}- \rightarrow -\mathrm{C(O)}-\mathrm{C(O)}- + -\mathrm{C(=NOH)}-\mathrm{C(=NOH)}- \qquad (4)$$

In the reactions of XVII with cobalt(II), the metal is rapidly oxidised (cf. similar reactions of nitrosophenols and arylazooximes (Section G and J) and crystalline complexes of the type CoL_3 are readily isolated[121,122,125,126]. These are probably pseudooctahedral tris chelates of type XIX. Octahedral blue iron(II) complexes $FeL_2(H_2O)_2$ and $FeL_2(py)_2$ are readily[127,128] obtained and so are the unsolvated species FeL_2. The hydrated and anhydrous complexes are described[129,130] as being paramagnetic ($\mu_{eff} \sim 3.4$ B.M. at room temperature). A collection of magnetic data on various iron(II) complexes containing carbonyl-oxime functions is available[131]. Potentially interesting from the point of view of magnetic exchange interaction is a trinuclear complex of isonitroso malonamide formulated[129,131] as $K_2[Fe_3\{(NH_2CO)_2C=NO\}_8]$.

Isonitrosoacetylacetone, i.e. 3-hydroxyiminopentane-2,4-dione (Hinaa) is a common example of ligands of the type XX. Such ligands are not good coordinating agents for nickel(II). Copper(II) is reported to yield Cu(L) (OH) in a few cases. On the other hand, the crystalline, grossly planar



XX



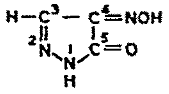
XXI

palladium(II) complex, Pd(inaa)$_2$, belonging to the structural type XXI is readily obtained either by reacting the ligand with palladium(II) salts[132] or by nitrosation[123] of Pd(acac)$_2$ with nitric oxide (acac = acetylacetonate anion). In the latter synthesis the intermediate complex Pd(acac) (inaa), in which the acac ring is six-membered while the inaa ring is five-membered (as in XXI), can also be isolated. The nitrosation reaction presumably proceeds by initial attack at the γ-carbon atom of the acac ring with subsequent reorganisation of chelation sites[123]. Further examples of similar nitrosation reactions are described in Section H.

Pd(inaa)$_2$ occurs[123,132] in two modifications, green and orange-red. In the synthesis using Hinaa, the green form is first formed and on heating is converted to the orange-red form. The synthesis from Pd(acac)$_2$ yields the orange-red form directly. It is speculated[132] without any substantial supporting evidence that the two forms are *cis* and *trans* isomers. The platinum(II) complex[123], Pt(inaa)$_2$, also occurs in green and brown forms which are isomorphous respectively with palladium(II) complexes of similar colours.

Pd(inaa)$_2$ is reactive towards various reagents[123]. The imine-oxime complexes (Section H) are directly obtained from reactions with primary amines. In the adducts Pd(inaa)$_2$D$_2$ (D = PPh$_3$, AsPh$_3$, etc.) the metal atom is believed to be four-coordinated; monodentate inaa units are bonded only via nitrogen centres. Reaction with HBF$_4$ plus AsPh$_3$ yields [(AsPh$_3$)$_2$Pd(inaa)] BF$_4$, in which inaa is bidentate.

The neutral cobalt(III) tris chelates[121] of XX belong to the structural type XXI ($n = 3$) as is evident from spectroscopic data[133,134]. The diamagnetic iron(II) complexes[130] of XX were recently reinvestigated[135]. These belong to two types: M[Fe(inaa)$_3$] (M = Na, Ca/2, etc.), in which the complex anion is octahedral



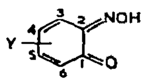
XXII

(type XXI) and Fe(inaa)$_2$(py)$_2$, in which the py molecules probably occupy axial positions of the Fe(inaa)$_2$ plane.

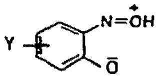
Lastly we mention the 4-isonitrosopyralozone (LH; XXII) complexes of copper (II) (ref. 136), nickel(II) (refs. 137, 138) and manganese(II) (refs. 137, 138). These are usually of the type ML$_2$D$_2$ in which D is py, NH$_3$, H$_2$O, etc. Copper(II) complexes of the type Cu(L) (OH) are also known. NiL$_2$D$_2$ and MnL$_2$D$_2$ are high-spin and ochtahedral. The species NiL$_2$ and MnL$_2$ are also known. They are believed to be polymeric.

G. NITROSOPHENOLS

2-Nitrosophenols have a pronounced tendency to tautomerise to the corresponding quinonemonoximes. For example, infrared data[139,140] suggest that 1-nitroso-2-naphthol (abbreviated as Honn) and 2-nitroso-1-naphthol (Htnn) exist in the respective oxime forms in the solid state. In simple oximes the N—O stretching frequency lies[141] in the range 930—960 cm^{-1}. In quinonemonoximes the frequency shifts[139,140] to 980—1080 cm^{-1} probably due to resonance between XXIII and XXIV. The known X-ray structures of α and β forms of 5-propoxy-2-nitrosophenol are in accord with such a description[142,143]. In view of these results the *ortho*-nitrosophenols find a natural place in



XXIII

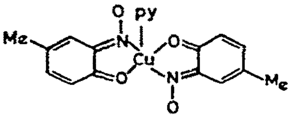


XXIV

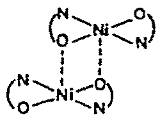
the family of oximes. In view of structure XXIII it is only appropriate that they are classed close to the carbonyl-oximes. With this understanding we shall continue to call this class of compounds as nitrosophenols.

Feigl has made the following observation in his well known treatise[9]: "If organic reagents that form coloured precipitates with metal ions are arranged in the chronological order of their discovery, the list will be headed by 1-nitroso-2-naphthol". This ligand and its reactions with cobalt(II) salts — a reaction that produces a characteristic red brown precipitate which is often used for qualitative detection of cobalt — was reported by Ilniski and Knorre in 1885. The nature of the reaction between cobalt(II) salts and Honn or its sulphonated derivatives is complicated[144–146]. The bis and tris chelates of cobalt(II) are first formed[145,146]. The tris complex is then rapidly oxidised by oxygen and/or excess ligand to the stable Co(onn)$_3$ complex.

2-Nitrosophenol (XXIII, Y = H) and some of its metallic salts were first described by Baudisch[147]. Systematic physicochemical studies on the copper(II) and nickel(II) complexes of XXIII (HYnp) were recently reported[148–151]. The



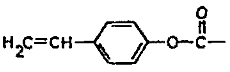
XXV



XXVI

complex Cu(4-Menp) (py) is described as having the square pyramidal structure XXV on the basis of X-ray data[152]. The ligand is in the quinoneoxime form and the chelate rings are five-membered, i.e. binding occurs via oxime nitrogen. The probable structures of some other HYnp complexes were derived on the basis of indirect evidence[149 - 151] such as mass spectrometry, infrared and electronic spectra and magnetic susceptibility. Some results are collected in Table 3. Most interesting among these are the dimeric $Ni_2(Ynp)_4$ complexes, for which the structural type XXVI is suggested.

Apart from XXV, another complex of definitely known structure is ferroverdin, the green diamagnetic iron(II) pigment produced by a species of *Streptomyces*[153]. The metal is very strongly held in this complex and is not removed by strong coordinating agents such as ethylenediaminetetraacetic acid. Depending on the conditions of crystallisation, ferroverdin can be obtained in polymorphic forms which usually contain solvent of crystallisation[154]. Ignoring solvent molecules, ferroverdin is $Na[Fe(Ynp)_3]$, where Y is XXVII attached to the 4-position of the np ring. Honn gives[155] a similar green iron(II) complex $Na[Fe(onn)_3]$. In ferroverdin



XXVII

iron(II) is *cis*-octahedral, XXVIII, with five-membered chelate rings (XXIX); the sodium ion is also grossly octahedral with six oxygen neighbours coming partly from the complex anion and partly from solvent of crystallisation[154]. The average bond distances (in Å) shown in XXIX, when compared with some other results (refs. 142, 143), suggest considerable contribution from the true nitrosophenol structure. The neutral cobalt(III) analogue of ferroverdin is known[156].

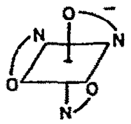
Even though $Co(onn)_3$ was discovered so many years ago, the chelate ring size in this complex has been repeatedly debated[9]. In view of the results described in

TABLE 3
Nitrosophenol complexes

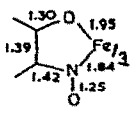
Compound type	Probable structure	Ref.
$Cu(Ynp)_2$, where Y = 4-Cl, 4-Br, 4-Me, 5-OMe; $Cu(onn)_2$; $Cu(tnn)_2$	Polymeric in the solid state with pseudooctahedral copper(II) environment; may be dimeric in solution; mass spectra (i.e. gaseous state) show the occurrence of monomer and monomer-2(oxygen), probably due to loss of two oxime oxygen atoms; this suggests five-membered chelate rings	149, 151
$Cu(Ynp)_2(py)$; $Cu(onn)_2(py)$; $Cu(tnn)_2(py)$	Monomeric in chloroform solution; square pyramidal (vide structure XXV)	149
$Ni(Ynp)_2$, where Y = 4-Cl, 4-Br, 4-Me, 4-*t*-Bu	Dimeric in chloroform solution and in solid state with structure XXVI; magnetic interaction of the two metal atoms occurs with an exchange integral of 40 cm^{-1}; square pyramidal metal environment from electronic spectra; dimers together with dimer-4(oxygen) persist in the gaseous phase (mass spectra)	150, 151
$Ni(Ynp)_2(py)_2$, where Y = 4-Cl, 4-Br, 4-Me, 4-*t*-Bu	Monomeric, *trans*-octahedral with axial py	150

the preceding paragraphs, we strongly suggest that the five-membered (coordination through oxime nitrogen) ring structure with CoN_3O_3 coordination sphere be accepted as most probable. Infrared spectra of the complexes of Honn and Htnn including $Co(onn)_3$ and $Co(tnn)_3$ were recently interpreted[140] in terms of six-membered chelate rings (coordination through oxime oxygen). Careful examination of the reported data[140] convinces us that these in no way prove the six-membered formulation. A five-membered ring structure can be used to interpret the results equally well.

The polymeric metal complexes of 2,4-dinitrosoresorcinol were recently described[157].



XXVIII

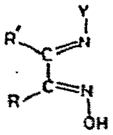


XXIX

H. IMINE-OXIMES

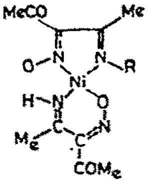
(i) Bidentate ligands

The imine-oximes are Schiff bases of carbonyl-oximes described in Section F. The bidentate imine-oximes (XXX) are abbreviated as HYio (Y = alkyl, aryl or NH_2). On complex formation the oxime proton may or may not dissociate. Probable structures of some complexes[135,158–164] are shown in Table 4. In each case bonding is believed[158] to occur via the oxime and imine nitrogen atoms (but see below).

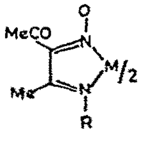


XXX

The reaction of isonitrosoacetylacetone with ammoniacal nickel(II) solution yields a red complex[121]. The same material is obtained[165,166] by nitrosating bis (acetylacetonato)nickel(II) with potassium nitrite in the presence of ammonium acetate at neutral pH. Various structures[166] have been suggested for the red complex on the basis of fragmentary evidence. Careful PMR, IR and mass spectrometric data[166] now make it certain that the correct structure is XXXI (R = H). The final proof has come from X-ray work[167] on the homologous complex XXXI(R = CH_3). The most unusual feature of this grossly planar structure is the occurrence of a six-membered chelate ring in which the oxime oxygen is bound to the metal. The N–O distance (in the five-membered ring) in XXXI(R = CH_3) is much shorter (1.26 Å) than the N–O distances met so far. The N–H proton is probably hydrogen



XXXI



XXXII

TABLE 4
Probable structures of the complexes of bidentate imine-oximes

Compound[a]	Probable structure	Ref.
$Ni(Hio)_2$	*Trans*-planar	135, 158
$Ni(Meio)_2$ ($R = Me$, $R' = Et$)	*Trans*-planar	158
$Cu(Phio)_2$ ($R = R' = Ph$)	*Trans*-planar	159
$Co(Phio)_3$	Octahedral with three phenyl rings meridionally disposed	160
$Co(Phio)_2(X)(py)$	*Trans*-octahedral ($X = Cl, SCN, Ph$)	160
$Co(HPhio)(Phio)hal_2$	*Trans*-octahedral	160
$[Co(HPhio)(Phio)(D)]_2(ClO_4)_2$ and $[Co(HPio)(Phio)]_2(ClO_4)_2$	Dimeric cation with weak Co–Co bond; cobalt environment pseudooctahedral or pentacoordinated; subnormal magnetic moment (3.2–3.6 B.M.)	161
$[Fe(Meio)_3]I_2$	Octahedral	162, 163
$Ni(HNH_2io)_2hal_2$	*Trans*-octahedral	164
$Ni(NH_2io)_2$	*Trans*-planar with intramolecular $O\cdots H\cdots N$ bridges.	164

[a] Unless otherwise stated $R = R' = Me$.

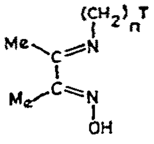
bonded to the nearby N–O oxygen. The Ni–N distance (1.81 Å) of the six-membered ring is significantly shorter than that (average, 1.89 Å) of the five-membered ring. As expected, XXXI($R = H$) gives rise to four distinct methyl PMR signals. Strong $C=N$ and N–O stretches occur at 1596 and 1201 cm^{-1} respectively[166]. The conversion XXXI($R = H$)→XXXI(R = alkyl) can be carried out by transamination reactions[168].

When the two –COMe groups in XXXI are replaced by $-CO_2Et$, the hybrid ring structure is retained[166]. The palladium(II) analogues of XXXI($R = H$), α-branched alkyl, Ph, etc., are known to have the same hybrid ring structure. On the other hand, when R = straight chain alkyl, the palladium(II) complexes are believed[123,169] to have the symmetrical *trans* structure XXXII, which will be abbreviated as M(N-Rinaa)$_2$. Reaction of Pt(inaa)$_2$ with ethylamine yields Pt(N-Etinaa)$_2$, which probably has the structure XXXII[123]. The Cu(N-Hinaa)$_2$ and Cu(N-Meinaa)$_2$ complexes are also reported to belong to the structural type XXXII, though the experimental evidence[135] is not very convincing.

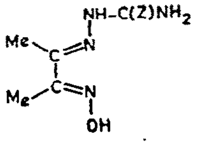
The structure XXXII is analogous to the structure suggested[158] for the simple imine-oxime complexes of the type Ni(YiO)$_2$. The results described in the last two paragraphs raise the interesting possibility that these imine-oxime complexes, particularly those with Y = H (Table 4), may actually belong to the structural type XXXI in which –COMe is replaced by R. Factors which determine the relative stability of structural types XXXI and XXXII are not properly understood at present. Steric factors[169] appear to play some role.

(ii) Tridentate ligands

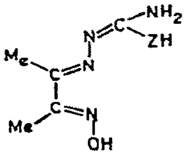
Most of the work in this area centres around two types of ligands, XXXIII and XXXIV, abbreviated as HTio and H$_2$Zio respectively. In XXXIII T contains a coordination site such as pyridyl nitrogen or a hydroxyl oxygen. The ligands of the type XXXIV (Z = O, S or Se) include semicarbazone, thiosemicarbazone and selenosemicarbazone of diacetylmonoxime. In the semicarbazone complexes, bonding to metal occurs as usual at the nitrogen atoms of the oxime and imine functions; a third bonding site is then provided by the terminal amino nitrogen. This conclusion is based on IR data[170]. On the other hand in the thiosemicarbazone and selenosemicarbazone chelates, the third coordination position is most probably the chalcogen atom[171]. In complex formation the oxime protons of XXXIII and XXXIV may or may not dissociate. In several cases two protons dissociate from XXXIV (Z = S or Se). In such instances the ligand may be thought to react in the tautomeric form XXXV (Z = S, Se).



XXXIII

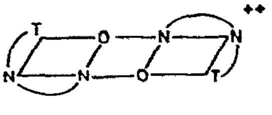


XXXIV



XXXV

Among complexes of XXXIII are octahedral chelates[172] such as [Fe(HTio)$_2$]I$_2$ (low spin) and [Co(HTio)$_2$]I$_3$, both having n = 1, T = α-pyridyl. The complexes [Ni(HTio)$_2$]X$_2$, [Ni(HTio)$_2$(NCS)] (NCS) (one HTio is probably bidentate) and polymeric Ni(HTio)(SCN)$_2$ having n = 2, T = α-pyridyl all contain pseudooctahedral nickel(II)[173], as does [Ni(HTio)$_2$] X$_2$, having[174] n = 2 and T = OH. An example[175] of octahedral cobalt(III) is [Co(Tio)$_2$] X, n = 2, T = α-pyridyl. The chelates of composition Cu(Tio)X, $n = 2$, T = α-pyridyl[173] or OH[174] have subnormal magnetic moments. They may be dimeric, one probable structure[173] of the cation being XXXVI.



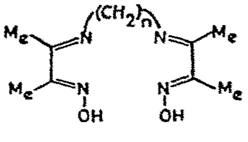
XXXVI

Important stereochemical types among the complexes of XXXIV are again the octahedron and the square plane. Octahedral geometry is present in $[M(H_2Zio)_2]X_2$, Z = O (ref. 176), M = Co, Ni, Cu; Z = S (ref. 177) or Se (refs. 178, 179), M = Fe, Co, Ni; in $M(HZio)_2$, Z = S (refs. 177, 180), M = Fe, Co; Z = Se (ref. 179), M = Fe; in $[Co(HZio)_2]X$, Z = Se (ref. 179) and in M(HZio)(Zio), Z = S (refs. 179, 180), M = Fe; Z = Se (ref. 179) M = Fe, Co. Spectral and magnetic data are sparse, but where available[176,178,179] such data do suggest that the iron(II) and iron(III) species are low-spin whereas cobalt(II) is high-spin. Grossly planar stereochemistry is present in diamagnetic Ni(Zio).$\frac{1}{2}H_2O$ (probably dimeric with H_2O bridge), Z = S (ref. 181), Se (ref. 178); Cu(Zio).$\frac{1}{2}H_2O$, Z = S (ref. 182), Se (ref. 183) and in diamagnetic Ni(Zio)(D), Z = S (ref. 181), Se (ref. 178), D = amine, e.g. py.

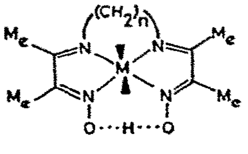
In the octahedral complexes of XXXIV, the tridentate ligands probably span meridionally rather than facially because of the limited length of the chain emanating from the imine nitrogen. This may not be true for the complexes of XXXIII when $n = 2$ and T = α-pyridyl.

(iii) Tetradentate ligands

The best examples are the ligands of type XXXVII which will be called H_2enio when $n = 2$ and H_2pnio when $n = 3$. The complexes[72,184] of XXXVII usually have the moiety XXXVIII which has an O · · · H · · · O bridge like those present in dioximates,



XXXVII

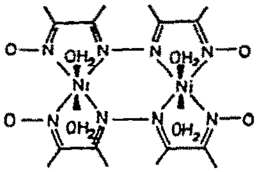


XXXVIII

amine-oximates, etc. Apart from $-(CH_2)_n-$, other groups[185] have also been used as a bridge for the two halves of XXXVII. The nickel(II) species Ni(Henio)X and Ni(Hpnio)X are described[184] as being either five-coordinate (X = halogen) with axially bound X or planar ($X = ClO_4$) with ionic X. More interesting are the cobalt (III) complexes[186–190] of the general type $[Co(Hpnio)(A)(B)]^{n+}$, in which A and B occupy axial positions of the Co(Hpnio) plane. The ligands A and B can be a variety of species, either neutral or anionic. The chemistry of these complexes is in many ways similar to that of the $[Co(Hdmg)_2(A)(B)]^{n+}$ complexes described earlier. Organometallic species in which either or both of A and B are bonded to the metal through carbon can be readily obtained. For example, the reaction of $Co(Hpnio)I_2$ with excess Grignard reagent yields[187] $Co(Hpnio)R_2$ (R = Me, CH_2Ph). Like the *vic*-dioximates the Hpnio chelates are also reducible[186] to deep blue, highly reactive cobalt(I) nucleophiles. The sodium amalgam reduction of Co(Hpnio) (Ph) (I) followed by the addition of MeBr affords[187] Co(Hpnio) (Ph) (Me). The cobalt(I) complex Co(Hpnio) (PPh_3) can be isolated in the crystalline state[186]. The cobalt (II) chelate $[Co(Hpnio)(H_2O)_2](BPh_4)$ is also known[186].

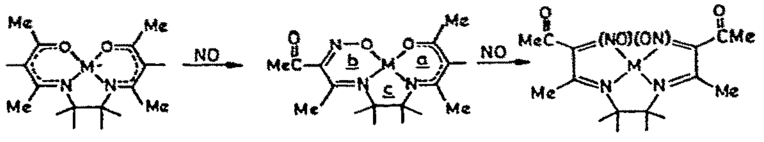
The three-dimensional X-ray structure of $[Co(Hpnio)(CH_3)(H_2O)](ClO_4)$ has been reported[191]. The occurrence of the grossly planar moiety XXXVIII is confirmed. The O · · · H · · · O bridge is 2.39 Å long. The Co—C distance of 1.99 Å compares favourably with those in $Co(Hdmg)_2(CH_2C(O)OMe)(py)$ (Table 2) and other organometallic cobalt(III) species[192]. The average Co—N, C = N and N—O distances in the Hpnio complex are 1.90, 1.29 and 1.42 Å respectively[191].

A ligand which formally belongs to the same class as XXXVII is diacetylazine-oxime (XXXVII, $n = 0$), abbreviated as H_2azio. The copper(II)[193] and the nickel (II)[193,194] chelates are respectively of the formula types Cu(azio) and Ni(azio) $(H_2O)_2$. The nickel(II) complex may have[193,194] the structure XXXIX in which the nickel(II) environment is grossly octahedral. In the copper(II) complex the water molecules are absent. These complexes show clear evidence[193] of antiferromagnetic superexchange interaction.



XXXIX

The reaction sequence[134]



XL XLI XLII

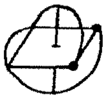
produces the grossly planar complexes XLI (M = Cu, Ni) and XLII (Cu, Ni, Pd). The chelates XLII can also be obtained by reacting metal(II) salts with isonitrosoacetylacetone and ethylenediamine[123,195]. The molecular and crystal structure of XLI (M = Cu) is known[196]. The chelate ring a is planar. The other two chelate rings show significant deviation from planarity. In ring b, the average C = N, N—O and C—C distances are 1.29, 1.31 and 1.50 Å respectively. The coordination around the metal is planar. The complex is similar to XXXI in that binding through oxime oxygen is involved. The structural status of XLII is not known at present. The symbol (NO) (in XLII) is meant to indicate that it is not known whether the nitrogen or oxygen atom binds to the metal.

(iv) Hexadentate ligands

The Schiff base XLIII of diacetylmonoxime and triethylenetetramine will be designated simply as H_2L. The ligand is hexadentate and forms[197] complexes with cobalt(III) of composition $[Co(H_2L)]X_3$ and $[CoL]X$. These are believed to have the coordination sphere XLIV.

$[HON{=}C(Me){-}C(Me){=}N{-}(CH_2)_2{-}NHCH_2]_2$

XLIII

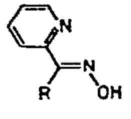


XLIV

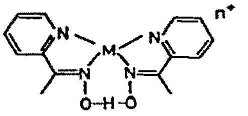
We wish to note that the Schiff base of diacetyl monoxime and *cis, cis*-1, 3, 5-triaminocyclohexane does not appear to have been investigated. This ligand may be expected to yield trigonal prismatic complexes via encapsulation reactions (BF_n capping).

I. PYRIDINE-OXIME AND RELATED LIGANDS

The best known examples in this class are the complexes of 2-pyridinaldoxime (abbreviated as Hpao) and its substituted derivatives, particularly phenyl-2-pyridylketoxime (Hppk). These react with metal ions in the *syn* form XLV, and can also be considered as imine-oximes in which the imine fragment is part of a heteroaromatic ring. The iron(II), cobalt(II) and nickel(II) complexes given by the pyridine-oximes were briefly reviewed some time ago[198]. Some compound types[199–210] (an interesting type being XLVI) and their probable structures derived from indirect evidence such as bulk susceptibility, IR, electronic spectra, etc., are set out in Table 5. These will not be discussed any further.

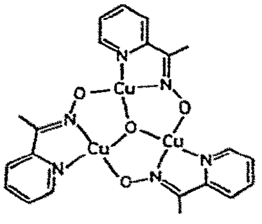


XLV

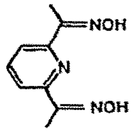


XLVI

The composition of the species obtained from solutions of copper(II) ions and Hpao depend on the pH of the solution and the metal-to-ligand ratio. The system is characterised by 1 : 1 and 1 : 2 complexes, as can be seen from Table 5. More interesting are the trinuclear species of the type[211,212] $Cu_3(pao)_3(OH)X_2 \cdot nH_2O$ ($X^- = \frac{1}{2}SO_4^{2-}, I^-, NO_3^-, ClO_4^-, OH^-$). These have anomalously low[212–214] magnetic moments. In the temperature range 100–400°K, the susceptibility obeys Curie's law with μ_{eff} of ~ 1.0 B.M. per copper(II) atom. This suggests[214] the occurrence of a trinuclear Cu_3 core in which strong exchange interactions have caused pairing of two of the three unpaired electrons associated with the three copper(II) atoms. Both linear and triangular arrangements of the copper(II) atoms are compatible with the magnetic data. In practice the triangular arrangement occurs, as has been substantiated by three-dimensional X-ray work[213] on $Cu_3(pao)_3(OH)SO_4 \cdot 16.3H_2O$. Each pao unit functions as a bidentate ligand to one of the copper(II) atoms through its two nitrogen atoms and as a bridging ligand using oximato oxygen (compare with the structure VII of Section D), shown as structure XLVII. The planar $Cu_3(pao)_3$ fragment has a threefold symmetry axis. The oxygen atom of the hydroxo group situated on this axis is 1.98 Å from each of the copper (II) atoms and is 0.7 Å above the $Cu_3(pao)_3$ plane. The sulphato group (not shown in XLVII) lies on the threefold axis below the trinuclear plane and acts as a tripod bridge bonding to the three copper(II) atoms. The coordination environment of each copper(II) is roughly square pyramidal. Adjacent copper(II) atoms are too far away (3.21 Å) from one another for direct exchange interaction. Indirect interaction can occur through the OH group. The Cu_3OH cluster can be described[214] as having multicentre bonding.



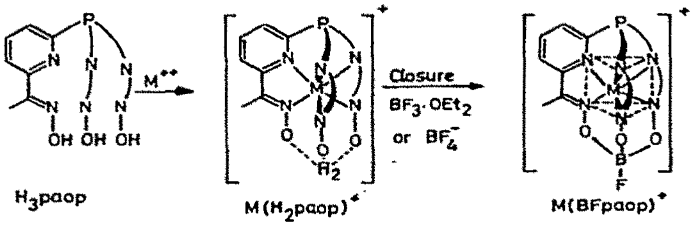
XLVII



XLVIII

Hppk and benzyl-2-pyridylketoxime can be used[215] to stabilise trivalent nickel. For example, oxidation of nickel(II) salts in the presence of Hppk by persulphate in alkaline medium yields a crystalline complex of composition $Ni(ppk)_3$. This is paramagnetic (1.75 B.M.) and shows ESR signals ($g_1 = 2.08$; $g_2 = 2.10$; $g_3 = 2.14$). This presumably octahedral complex is believed[215] to contain nickel(III) and three ppk$^-$ anions rather than nickel(II) plus one ppk$^\cdot$ radical and two ppk$^-$ anions. The dioxime ligand XLVIII (H_2dapd) is tridentate and readily yields pseudooctahedral iron(II) and nickel(II) complexes[216,217]. The latter[216] are of the types $[Ni(H_2dapd)_2](ClO_4)_2$ and $Na_2[Ni(dapd)_2]$ and can be readily oxidised to the diamagnetic neutral complex $Ni(dapd)_2$ believed[216] to contain nickel(IV). It is argued[215,216] that the higher oxidation states of nickel are favoured by two factors, viz. high concentration of negative charge on donor atoms and strong metal–ligand σ-bond formation.

The sexadentate ligand tris(2-aldoximo-6-pyridyl)phosphine XLIX was recently synthesised and used[81] to encapsulate metal ions in trigonal prismatic geometry using the reaction sequence



H_3paop
XLIX

$M(H_2paop)^+$
L

$M(BFpaop)^+$
LI

TABLE 5
Probable structures of some pyridine-oxime complexes

Compound	Probable structure and other observations	Ref.
$Ni(Hpao)_3X_2$	Contains paramagnetic octahedral $Ni(Hpao)_3^{2+}$; similar low-spin iron(II) complexes and their acid dissociation constants are known; similar Hppk complexes of both nickel(II) and cobalt(II) are known	199–203
$Ni(Hpao)_2X_2$	X = Cl, Br, oac; all fully paramagnetic and pseudooctahedral; probably dimeric, in which the two metal atoms are bridged by X yielding *cis*-NiN_4X_2 coordination sphere for each nickel(II); similar Hppk, 2-quinolinaldoxime and 2-isoquinolinaldoxime complexes are known	199, 201 204, 205
Ni(Hpao) (pao) X	Paramagnetic with pseudooctahedral nickel(II); may contain planar intramolecularly hydrogen-bonded cations $Ni(Hpao)(pao)^+$ of type XLVI linked to one another through axially coordinated X^-, resulting in an NiN_4X_2 coordination sphere for each nickel(II); $[Ni(Hpao)(pao)(py)_2]I$ is known; similar Hppk complexes are known	199–201
Cu(Hpao) (pao)X	Structure similar to the nickel(II) analogue but with very weak axial coordination	206–208
Pd(Hpao) (pao) X	Contains planar intramolecularly hydrogen-bonded $Pd(Hpao)(pao)^+$; a similar platinum complex is known	209, 210
$Ni(pao)_2$	Paramagnetic in both solid and solution phases; polymeric	199, 200
$Pd(pao)_2.2H_2O$	*Trans*-planar arrangement of two pao ligands	209
$Pt(pao)_2.2H_2O$	Known in two forms believed to be *cis*-planar and *trans*-planar	210
$Cu(Hpao)X_2$	Distorted octahedral; polymeric	208
$Cu(Hpao)_2SO_4.2\frac{1}{2}H_2O$	Octahedral $[Cu(Hpao)_2SO_4(H_2O)].1\frac{1}{2}H_2O$ with monodentate sulphate	208

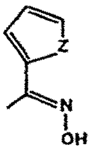
TABLE 6
Twist angles in [M(BFpaop)] BF_4

M	μ_{eff} (B.M.)	Twist	angles	(°)	Ref.
Fe	0.4	21	22	22	219
Co	4.91	0.4	1.0	3.2	82
Ni	3.11	1.1	1.8	1.8	218
Zn	Diamagnetic	1.1	2.3	2.3	82

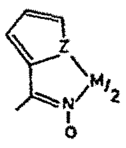
The species L (M = Co, Ni, Cu, Zn) are hexacoordinate but specific geometries are not known; three oximato oxygens and two oximato hydrogens are believed to be involved in hydrogen bonding. The complex L can be isolated as a crystalline perchlorate[81]. The clathro chelate LI (M = Fe, Co, Ni, Zn) can be crystallised as a fluoborate[81]. The three-dimensional X-ray structures of the fluoborates are being systematically determined[218,219]. The results for the nickel(II)[218] and iron(II)[219] complexes are already available and those of cobalt(II) and zinc(II) are briefly quoted elsewhere[82]. These have gross trigonal prismatic structures. The twist angles are collected in Table 6. The twist is unsymmetrical and the three twist angles are not the same. Only in the iron(II) complex (low-spin d^6) is there a substantial distortion from the trigonal prismatic geometry (compare with Section E(iii)).

Electronic, PMR and Mössbauer spectroscopy and polarographic reduction potentials for [M(BFpaop)] BF_4 and other complexes spanning a range of geometries within the trigonal prismatic and octahedral limits were carefully examined[82] in order to establish possible correlations with coordination geometries. Some correlations do exist but they are not sufficiently well defined for unequivocal diagnosis of specific geometries.

Lastly, we include in this section the complexes[220–222] of the ligand system LII in which an oxime function is placed (as in XLV) *ortho* to a heteroatom (Z = O, S, Se). Complexes of the type ML_2 of probable structure LIII can be isolated[221] for nickel(II), palladium(II) and platinum(II). The copper(II) chelates are dimeric,



LII

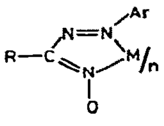


LIII

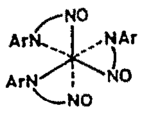
$Cu_2L_2(OH)_2$, and probably involve metal bridging via OH. The donor strengths of the ligands LII follow the order[221] Se > S > O. Thiophene-2-aldoxime (LII, Z = S) also gives complexes[222] of the type $M(LH)_2Cl_2$. When M = Co, Ni, Cu, the complexes are probably pseudooctahedral. The M = Pd complex is planar $[M(LH)_2]Cl_2$.

J. AZO-OXIMES

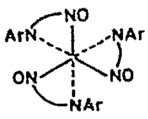
vic-Dioximes, imine-oximes and pyridine-oximes all contain the α-diimine function $-N=\overset{|}{C}-\overset{|}{C}=N-$. The isoelectronic azo-imine function $-N=N-C=N-$ is present in arylazooximes[223], ArN = N—C(= NOH)R, which will be abbreviated as HArRazox. Arylazooximes readily react[224–226] with cobalt(II) salts to give rise to tris complexes of cobalt(III), $Co(ArRazox)_3$. The oxidation of cobalt(II) to cobalt(III) occurs even when external oxidising agents (e.g. air) are excluded; the ligand itself acts as the oxidising agent[226]. On the basis of IR data[226], the $Co(ArRazox)_3$ chelates belong to the structural type LIV. PMR evidence[226] unambiguously demonstrates the exclusive population of the meridional configuration LV, the facial configuration LVI not being observed for steric reasons[226]. On the other hand, the rhodium(III) tris chelates, $Rh(ArRazox)_3$, exist in isomeric forms which have configurations LV and LVI on the basis of PMR data[227]. The difference between the cobalt(III) and rhodium(III) chelates is at least in part due to differences in the sizes of the metal atoms[227].



LIV

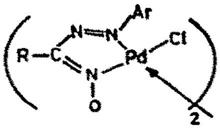


LV



LVI

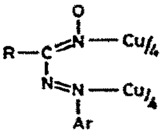
Nickel(II) complexes of arylazo-oximes are of formula $Ni(ArRazox)_2$. They are diamagnetic and evidently planar[228] (LIV, M = Ni, $n = 2$). Mixed amidoxime azooxime complexes of nickel(II) are also known[228]. The reaction of K_2PdCl_4 with HArRazox yields[227] chlorine-bridged complexes of the type LVII. The corresponding bromine-bridged species are also known[227]. Bridge-splitting reactions of LVII occur readily, e.g. reaction with RNH_2 gives $Pd(ArRazox)(RNH_2)(Cl)$. Triphenylphosphine appears to split the bridge in a reversible manner. By treating LVII with HArRazox in the presence of suspended sodium carbonate in benzene, chelates of composition $Pd(ArRazox)_2$ are obtained[227]. Unlike K_2PdCl_4, K_2PtCl_4 does not immediately react with arylazooximes. However, a slow reaction does take place[227] and eventually crystalline products of composition $Pt(ArRazox)_2$



LVII

deposit. No halogen-bridged platinum(II) chelates are isolated. The bis-chelates of palladium(II) and platinum(II) have many unusual spectral properties[227] and it is unlikely that they have simple structures of type LIV.

The copper(II) chelates[229] of arylazooximes are dimeric, $Cu_2(ArRazox)_4$. They belong to a small group of copper(II) complexes which are completely diamagnetic due to the presence of strong antiferromagnetic interactions. The $Cu_2(ArRazox)_4$ complexes are also diamagnetic in solution phase and give rise to PMR spectra which are very similar to those of the free ligands or their diamagnetic complexes with other metals such as palladium(II). The exact mode of bonding in the dimers is not known. A $Cu_2(CH_3COO)_4$-like structure[230] with bridging arylazooximes is a distinct possibility. One of the several possible modes of bridging[229] is LVIII.



LVIII

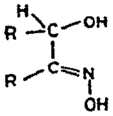
Reaction of iron(II) salts with arylazooximes followed by digestion of the product with sodium hydroxide affords[231] crystals of composition $NaFe(ArRazox)_3 . H_2O$. Electrical conductivity data for nitromethane solutions show that the sodium ion remains largely bound to the presumably octahedral diamagnetic complex cation of structural type LIV. This complex is in some ways similar[231] to ferroverdin (Section G). Acidification of $NaFe(ArRazox)_3 . H_2O$ produces $Fe(ArRazox)_2$ (HArRazox) in which one of the ligands is neutral. The complex $FeCl_2Fe(ArRazox)_3$ in which the paramagnetic $FeCl_2^+$ moiety is in some way coordinated to $Fe(ArRazox)_3^-$ is also known[231].

ω-Nitroacetaldehyde phenylhydrazone, $MeC(NO_2) = NNHPh$, reacts[226] with cobalt salts in hot ammoniacal media to yield $Co(PhMeazox)_3$. On the other hand, PhNHNHC(Me) = NOH undergoes[229] fast atmospheric oxidation in the presence of metal ions (copper(II), palladium(II), cobalt(II), etc.) to produce metal chelates of HPhMeazox.

K. HYDROXY-OXIMES

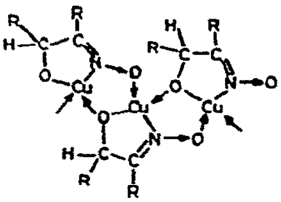
(i) α-Acyloinoximes and related ligands

α-Acyloinoximes have the general structure LIX and will be abbreviated as H_2Rayox. The best known example is α-benzoinoxime,

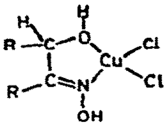


LIX

$H_2Phayox$. The most characteristic reaction of this group of ligands is the formation of green water-insoluble copper(II) complexes of composition Cu(Rayox). Infrared spectra[232], powder ESR[233] and magnetic susceptibility[234,235] data on such complexes have been reported. The most recent susceptibility work[235] has shown these complexes to have subnormal magnetic moments (0.7–0.8) B.M. at 295 °K) which decrease with decreasing temperature. Antiferromagnetic interactions in a polymeric structure (LX) with grossly planar four-coordinate copper(II) are thought to occur[235]. The same polymeric structure is proposed in order to interpret solubility data[236]. The reaction of Cu(Phayox) with hydrogen chloride



LX

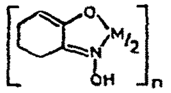


LXI

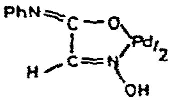
produces a green crystalline substance, $Cu(H_2Phayox)Cl_2$, of normal magnetic moment believed[235] to have the structure LXI.

Nickel(II) complexes[237] of acyloinoximes are of types: Ni(HRayox)$_2$ (paramagnetic, possibly polymeric) and K[Ni(HRayox) (Rayox)] (diamagnetic). Some lanthanide complexes[238] and the complex[239] WO$_2$(HPhayox)$_2$ are reported. The latter belongs[239] to a general class of WO$_2$(bidentate)$_2$ complexes in which the WO$_2$ group has a *cis* (C_{2v}) configuration.

The monoxime of cyclohexane-1,2-dione (H$_2$L) produces[240] polymeric copper (II), nickel(II) and cobalt(II) complexes of composition ML$_2$. Spectral and magnetic data reveal that the metal(II) environment is grossly octahedral[240]. Infrared data suggest that the ligand L in ML$_2$ has the enolate oxime structure[240] as shown in LXII. The mode of polymerisation in LXII is believed to be similar to that of metal(II) acetylacetonates[240]. Isonitrosoacetanilide also yields complexes (e.g. LXIII) in which the ligand is an enolate oxime[241].



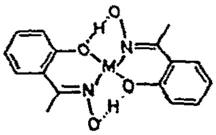
LXII



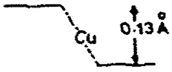
LXIII

(ii) Salicylaldoximes

The crystal and molecular structure of several bis(salicylaldoximato)metal(II) complexes are known. The copper(II)[242], nickel(II)[243,244] and palladium(II)[245] chelates have the gross centrosymmetric structure LXIV with intramolecular O · · · H · · · O bridges of a kind slightly different from those met earlier (Sections E(i), H(iii) and I). The average M–N, M–O, C = N, N–O and O· · · O distances are respectively



LXIV



LXV

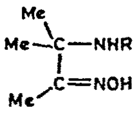
copper(II)	1.94,	1.92,	1.25,	1.45,	2.58 Å
nickel(II)	1.86,	1.84,	1.34,	1.36,	2.52 Å
palladium(II)	1.96,	1.98,	1.29,	1.42,	2.62 Å

In the copper(II) complex there are two additional contacts (Cu · · · O, 2.66 Å) with oxime oxygens of adjacent molecules. This results in a distorted octahedral geometry around copper(II). The *trans*-MN_2O_2 coordination sphere in LXIV is planar but the molecule taken as a whole often shows small but significant deviations from planarity. For example, in the copper(II) complex[242] two parallel planes can be defined by the two benzene rings, the perpendicular distance ("step") between the planes being 0.13 Å. This is schematically shown in LXV. This chelate is a typical example of a "stepped" structure. More severe "steps" (0.76 Å) occur in bis(5-chlorosalicylaldoximato)copper(II)[246]. The general question of "stepped" structures in bis-chelates of bidentate ligands is discussed elsewhere in considerable detail[247].

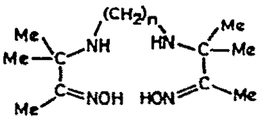
Bis(salicylaldoximato)nickel(II) is diamagnetic in the solid state but becomes partially paramagnetic in chloroform solution[248], probably due to molecular association. It readily forms[249,250] pseudooctahedral bis-adducts with amines. The cobalt(II)[251], iron(II)[252,253], iron(III)[254] and manganese(II)[255,256] complexes of salicylaldoxime and its substituted derivatives have been described.

L. AMINE-OXIMES

Bidentate 2-methyl-2-amino-2-butanoneoxime (LXVI, R = H; abbreviated as Habo) and its substituted derivatives (LXVI, R = alkyl; HRabo) readily form complexes with transition metal ions. The related tetradentate ligand system LXVII is a potent coordinating agent and will be abbreviated as H_2aboen when $n = 2$, and H_2abopn when $n = 3$. The complexes of LXVI and LXVII provide yet other examples of intramolecular O · · · H · · · O hydrogen bonding (cf. Sections E(i), H(iii), I and K(ii)).



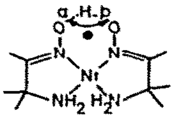
LXVI



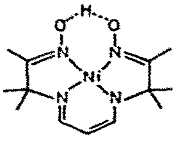
LXVII

At neutral pH, nickel(II) yields stable yellow diamagnetic cations such as Ni(Habo) (abo)$^+$, Ni(HRabo) (Rabo)$^+$, Ni(Haboen)$^+$ and Ni(Habopn)$^+$. These can be isolated as salts in the crystalline state[257–259]. In acidic solutions protonation and solvent coordination occur yielding unstable blue, presumably octahedral, paramagnetic species of the type[257,258] $Ni(Habo)_2(H_2O)_2^{2+}$. On the other hand, in alkaline solution, Ni(Habo) (abo)OH is believed to be formed[260].

The structure of [Ni(Habo) (abo)] Cl . H_2O has been carefully examined using both X-ray[261] and neutron[262] diffraction techniques. The gross structure LXVIII has a planar NiN_4 coordination sphere. The two NH_2 groups, H_2O and Cl^- are involved in a hydrogen bonding network in the crystal. Referring to LXVIII, the exact dimensions[262] of the hydrogen bridge can be judged from the parameters $a = 1.187(5)$ Å, $b = 1.242(5)$ Å and $\theta = 169.9°$. The reason for the small degree of



LXVIII



LXIX

asymmetry of the bridge is not established but the crystal surroundings of the two oxygen atoms are not the same. The analysis of thermal motions leads to the conclusion that the hydrogen atom moves in a broad single minimum potential[262]. The platinum(II) complex [Pt(Habo) (abo)] Cl . H_2O is isomorphous with the nickel analogue just described. Its accurate structure is known from X-ray work[263]. The O · · · O distance is 2.48 Å which is longer than that in the nickel(II) complex as expected. Selected bond distance data are set out in Table 7.

In basic aqueous media, $Ni(Habopn)^+$ is irreversibly oxidised[264] by O_2, IO_3^-, etc. producing the neutral complex LXIX which contains a six-membered pseudo-aromatic ring. The reaction, which is quite specific for the particular ligand and nickel(II), is to be compared with the dehydrogenation reactions of some other macrocycles[265].

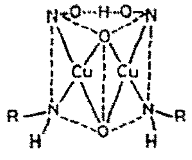
The copper(II) complexes[257,258] of Habo are like those of nickel(II). However, HRabo fails to yield mononuclear complexes with copper(II). The isolated complexes are believed to have[266,267] the composition, $[Cu_2(HRabo)(Rabo)(OH_2)]X$ (structure LXX) and have[266,267] subnormal magnetic moments (~ 1 B.M.) per copper(II) which do not vary much in the temperature range 78–400°K. The presence of copper–copper interaction is evident. In order to explain the observed magnetic behaviour, it is speculated that the exchange integral is temperature-dependent[266,267]. We wish to point out that the magnetic behaviour of these complexes is closely akin to that of some *trinuclear* complexes described in Section I.

H_2aboen complexes[257,258,268] with copper(II) yield $Cu(H_2aboen)^{2+}$ and $Cu(Haboen)^+$ both of which can be isolated as crystalline halides and perchlorates. Crystal structure work[268] on Cu(Haboen)Br has disclosed the presence of the dimeric cation $[Cu_2(Haboen)_2]^{2+}$. The coordination sphere of each copper(II) is a distorted trigonal bipyramid as shown in LXXI. The two copper(II) atoms and the two N–O groups form a six-membered ring with a boat conformation. A similar

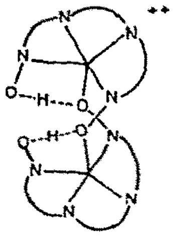
TABLE 7
Bond distance[a] data in amine-oxime complexes

Complex	Bond distances (Å)					
	M–N(oxime)	M–N(amine)	C = N	N–O	O···O	Ref.
$[Ni(Habo)(abo)]Cl\cdot H_2O$	1.86	1.91	1.30	1.36	2.38	261
	(1.86)[b]	(1.91)[b]	(1.29)[b]	(1.34)[b]	(2.42)[b]	262
$[Pt(Habo)(abo)]Cl\cdot H_2O$	1.95	2.03	1.26	1.36	2.48	263
$[Cu_2(Haboen)_2]Br_2$[c]	2.02	2.07	1.29	1.39	2.54	268
$Ni(H_2ibo)_2Cl_2\cdot H_2O$	2.08	2.12	1.28	1.42	–	270
$Cu(H_2ibo)_2Cl_2$	1.96	2.01[d]; 2.36[e]	1.29	1.42	–	270

[a] Averaged and approximated to the second decimal place.
[b] Neutron diffraction work; all others are X-ray diffraction work.
[c] Cu–O, 2.13 Å.
[d] Base of the tetragonal pyramid.
[e] Axis of the tetragonal pyramid.



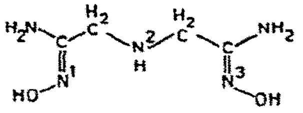
LXX



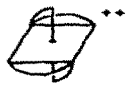
LXXI

ring but having the chair conformation occurs in $Cu_2(Hdmg)_4$, in which the metal environment is square pyramidal (Table 2). In donor solvents such as water and dimethyl sulphoxide, the dimer dissociates yielding[268] $Cu(Haboen)(solvent)_2^+$. The complexes LXVIII–LXXI show the characteristic O ··· H ··· O bending mode in the range 1750–1800 cm^{-1}.

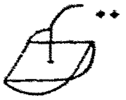
2,2'-Iminobis(acetamidoxime), LXXII, gives rise to a violet paramagnetic bis-complex[269] with nickel(II), $Ni(H_2ibo)_2Cl_2 \cdot H_2O$ where H_2ibo stands for LXXII. The complex is pseudooctahedral and centrosymmetric[270]. The chloride ions and water molecules do not occupy coordination positions. The ligand is bound to nickel(II) as shown in LXXIII via N^1, N^2 and N^3. The average Ni–N (oxime) distance (2.08 Å) is significantly longer than the corresponding distances in the grossly planar, diamagnetic complexes (Table 7), but compares favourably with the distance (2.11 Å) in octahedral $Ni(Hado)_4Cl_2$ described previously (Section D). The blue copper(II) complex, $Cu(H_2ibo)_2Cl_2$, has[270] a distorted square pyramidal structure, LXXIV, in which one ligand is tridentate while the other ligand is bidentate (coordinated at N^1 and N^2 only).



LXXII



LXXIII



LXXIV

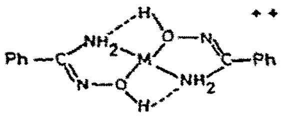
M. AMIDOXIMES

The general structural formula of amidoxime is $Y{-}C({=}\,NOH)NH_2$. The most common systems are those in which Y = R. The single ligand which has been most extensively studied is benzamidoxime, $PhC({=}\,NOH)NH_2$, abbreviated as Hbamox. Amidoximes are amphoteric substances soluble in dilute mineral acids (protonation of NH_2) as well as aqueous alkali (proton dissociation from = NOH)[271,272]. The crystal and molecular structure of formamidoxime is known (Section B). A good test for the amidoxime function is the formation of a red-brown colour with iron(III) in neutral solution. This and other chelation reactions of amidoximes were recognised in the early days of coordination chemistry[271,273,274]. The use of amidoximes as analytical reagents for the estimation of various metal ions has been reviewed[275,276]. However, little is known about the definitive structural chemistry of metal amidoximates. This is unfortunate since there are several systems begging structural work in this area, as will be evident from the discussion below.

The copper(II) complexes will be considered first. Starting with the simplest member, viz. formamidoxime, many amidoximes (LH) give rise to copper(II) complexes of composition Cu(L) (OH) . H_2O or Cu(L) (OH)[273,274,277–281]. The hydrate where formed can be readily converted to the anhydrous material..Although copper(II) complexes of other compositions[282,283] are given by some amidoximes, we shall concentrate our attention only on the Cu(L) (OH) complexes. These are unlikely to be monomeric since L can at most be bidentate towards a given metal ion. If the structure is di- or polynuclear (OH bridge?), the occurrence of magnetic exchange interaction may be anticipated. The room temperature magnetic moments reported in some cases[273,274] are indeed subnormal. Variable-temperature magnetic data are lacking.

A fresh ammoniacal solution containing nickel(II) chloride and Hbamox has a deep blue colour. On exposure to air for several hours the solution gradually turns red and eventually red needles deposit. The process can be hastened considerably by addition of hydrogen peroxide. The molecular nature of the red complex, which has oxidising power and liberates iodine from iodide solutions, remains enigmatic. Even its composition is not established beyond doubt. It was originally formulated[284] as $Ni(bamox)_3$ with nickel in the trivalent state. All subsequent measurements[274,285,286] have shown that the complex is diamagnetic and hence can not contain trivalent nickel. Several authors[274,285,286] have suggested that nickel(II) is present probably associated with some oxidised form of the ligand. But there is no agreement on the precise nature of this oxidised form. By reacting the red complex with alkali or by simply recrystallising it, other nickel(II) containing species can be obtained[274,285]. The nature of these is also obscure. Very recently it was reported[287] that nickel(II) nitrate and benzamidoxime can be oxidised in ethanolic solution by hydrogen peroxide yielding *red diamagnetic needles* of composition $Ni(bamox)_4$. The IR spectrum of this complex is not unlike that of the free ligand. It is claimed[287] that $Ni(bamox)_4$ contains *tetravalent nickel* and monodentate bamox bound to metal via oxygen. Unfortunately, however, these authors[287] do not correlate this complex with the red complex described earlier. The complete story of the "red diamagnetic needles" remains to be told. It is hoped that some structural chemist will solve this old problem with finality in the near future. Amidoximes other than benzamidoxime also give deeply coloured solutions with nickel(II) in the presence of oxygen, and crystalline complexes can be isolated from such reaction mixtures[273,288,289]. Nothing definite is known about their structures.

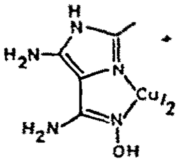
When $Ag(SCN)_2^-$ is added to a neutral reaction mixture containing benzamidoxime and Co^{2+}, the crystalline complex $[Co(Hbamox)_2]$ $[Ag(SCN)_2]_2$ can be obtained[290]. $[Ni(Hbamox)_2]$ $[Ag(SCN)_2]_2$ is similarly produced[290]. On the basis of IR data the nickel(II) and cobalt(II) species are believed to contain the ion LXXV. Unfortunately magnetic and electronic spectral data of the complexes are not reported.



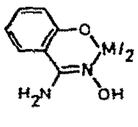
LXXV

Amidoximes such as Hbamox react with cobalt(II) solutions in alkaline pH giving a deep blue colour. However, there is no one opinion about the nature of complex formed[273,274,291]. The colour reaction between amidoximes and iron(III) was noted earlier. Brown complexes of composition Fe(bamox)X (X = NO_3, SCN, $\frac{1}{2}SO_4$) have been isolated[292]. Amidoxime complexes of chromium(III)[293], mercury(II)[271,278,279,282,294], palladium(II)[274,281], osmium(II)[279], dioxouranium (VI)[280], etc. are described in the literature. The reactions of benzanilidoxime. PhC(= NOH)NHPh, with copper(II), iron(III) and dioxouranium(VI) were examined in solution[295]. Crystalline complexes of composition CuL_2, FeL_2OH, UO_2L_2 could be isolated (HL = ligand). It is believed[295] that L is bidentate and binds metal at NHPh nitrogen and oxime oxygen.

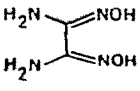
When an amidoxime ligand contains additional coordination sites, complex formation may not involve the amidoxime NH_2 group. Good examples are the H_2ibo complexes described in Section L. Similarly in the complex LXXVI, the NH_2 group is not used in binding with metal. The structure of LXXVI (isolated as the perchlorate) is accurately known from three-dimensional X-ray work[296]. The molecule is centrosymmetric with a *trans*-planar copper(II). Salicylamidoxime yields planar nickel(II), palladium(II) and copper(II) complexes which most probably have[297] the structure LXXVII. Here the ligand simply acts as a substituted salicylaldoxime. Lastly, we note that the ligands LXXVIII behaves as a dioxime and gives rise to $Ni(Hdmg)_2$-like complexes with nickel(II)[298].



LXXVI



LXXVII



LXXVIII

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REFERENCES

1 A. Hantzsch and A. Werner, *Chem. Ber.*, 23 (1890) 11.
2 G.B. Kauffman, *J. Chem. Educ.*, 43 (1966) 155.
3 L. Tschugaeff, *Chem. Ber.*, 38 (1905) 2520.
4 L. Tschugaeff, *J. Chem. Soc., London*, 105 (1914) 2187.
5 F.W. Atack, *J. Chem. Soc., London*, 103 (1913) 1317.
6 A.E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, Englewood Cliffs, N.J., 1952, pp. 328–333.
7 J.C. Bailar, Jr. and D.H. Busch, in J.C. Bailer, Jr. (Ed.), *The Chemistry of the Coordination Compounds*, Reinhold, New York, 1956, pp. 76–78; see also J.V. Quagliano and D.H. Wilkins, pp. 673–677.
8 F.J. Welcher, *Organic Analytical Reagents*, Vol. III, Van Nostrand, New York, 1947, pp. 157–354.
9 F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949, pp. 251–280.
10 C.V. Banks, *Rec. Chem. Progr.*, 25 (1964) 85.
11 J. Donohue, *J. Amer. Chem. Soc.*, 78 (1956) 4172.
12 W.C. Hamilton, *Acta Crystallogr.*, 14 (1961) 95.
13 D. Hall, *Acta Crystallogr.*, 18 (1965) 955.
14 T.K. Bierlein and E.C. Lingafelter, *Acta Crystallogr.*, 4 (1951) 450.
15 M. Calleri, G. Ferraris and D. Viterbo, *Acta Crystallogr.*, 20 (1966) 73.
16 L.L. Merritt and E. Lanterman, *Acta Crystallogr.*, 5 (1952) 811.
17 K. Folting, W.N. Lipscomb and B. Jerslev, *Acta Crystallogr.*, 17 (1964) 1263.
18 B. Jerslev, *Nature (London)*, 180 (1957) 1410.
19 F. Bachachi and L. Zambonelli, *Acta Crystallogr., Sect. B*, 28 (1972) 2489.
20 S.H. Simonsen, C.E. Pfluger and C.M. Thompson, *Acta Crystallogr.*, 14 (1961) 269.
21 A.N. Barrett and R.A. Palmer, *Acta Crystallogr., Sect. B*, 25 (1969) 688.
22 P. Groth, *Acta Chem. Scand.*, 22 (1968) 128.
23 I.N. Levine, *J. Chem. Phys.*, 38 (1963) 2326.
24 A. Caron, G.J. Palenik, E. Goldish and J. Donohue, *Acta Crystallogr.*, 17 (1964) 102.
25 D. Ülkü, B.P. Huddle and J.C. Morrow, *Acta Crystallogr., Sect. B*, 27 (1971) 432.
26 W. Hieber and F. Leutert, *Chem. Ber.*, 62 (1929) 1839.
27 W. Hieber and F. Leutert, *Chem. Ber.*, 60 (1927) 2296.
28 L. Cambi and C. Coriselli, *Gazz. Chim. Ital.*, 66 (1936) 81.
29 M.E. Stone, B.E. Robertson and E. Stanley, *J. Chem. Soc. A*, (1971) 3632.
30 A.A. Grinberg, A.I. Stetsenko and S.G. Strelin, *Russ. J. Inorg. Chem.*, 13 (1968) 569.
31 A.I. Stetsenko, S.G. Strelin and M.I. Gel'fman, *Russ. J. Inorg. Chem.*, 15 (1970) 68.
32 V.D. Panasyuk, N.F. Falendysh and N.A. D'yachenko, *Russ. J. Inorg. Chem.*, 16 (1971) 1452.

33 Yu. N. Kukushkin, A.I. Stetsenko, S.G. Strelin and V.G. Duibanova, *Russ. J. Inorg. Chem.*, 17 (1972) 561.
34 A. Mawby and G.E. Pringle, *J. Inorg. Nucl. Chem.*, 33 (1971) 1989.
35 J.R. Jennings and K. Wade, *J. Chem. Soc. A*, (1967) 1333.
36 M. Bartušek and A. Okáč, *Collect. Czech. Chem. Commun.*, 26 (1961) 52.
37 M. Bartušek and A. Okáč, *Collect. Czech. Chem. Commun.*, 26 (1961) 883.
38 M. Bartušek and A. Okáč, *Collect. Czech. Chem. Commun.*, 26 (1961) 2174.
39 M. Bartušek and A. Okáč, *Spisy Prirodoved. Fak. Univ. J.E. Purkyne Brne.*, No. 429 (1962) 1; *Chem. Abstr.*, 57 (1962) 9448.
40 M. Calieri, G. Ferraris and D. Viterbo, *Acta Crystallogr.*, 22 (1967) 468.
41 E.O. Schlemper and R.K. Murmann, *Acta Crystallogr.*, 23 (1967) 667.
42 M. Calleri, G. Ferraris and D. Viterbo, *Inorg. Chim. Acta*, 1 (1967) 297.
43 G. Ferraris and D. Viterbo, *Acta Crystallogr., Sect. B*, 25 (1969) 2066.
44 L.E. Godycki and R.E. Rundle, *Acta Crystallogr.*, 6 (1953) 487.
45 D.E. Williams, G. Wohlauer and R.E. Rundle, *J. Amer. Chem. Soc.*, 81 (1959) 755.
46 E. Frasson, C. Panattoni and R. Zannetti, *Acta Crystallogr.*, 12 (1959) 1027.
47 E. Frasson and C. Panattoni, *Acta Crystallogr.*, 13 (1960) 893.
48 R.H. Bowers, C.V. Banks and R.A. Jacobson, *Acta Crystallogr., Sect. B*, 28 (1972) 2318.
49 E. Frasson, R. Bardi and S. Bezzi, *Acta Crystallogr.*, 12 (1959) 201.
50 A. Vaciago and L. Zambonelli, *J. Chem. Soc. A*, (1970) 218.
51 K.S. Viswanathan and N.R. Kunchur, *Acta Crystallogr.*, 14 (1961) 675.
52 P.G. Lenhert, *Chem. Commun.*, (1967) 980.
53 F.A. Cotton and J.G. Norman, *J. Amer. Chem. Soc.*, 93 (1971) 80.
54 K.G. Caulton and F.A. Cotton, *J. Amer. Chem. Soc.*, 93 (1971) 1914.
55 C.K. Prout and T.J. Wiseman, *J. Chem. Soc., London*, (1964) 497.
56 K. Bowman, A.P. Gaughan and Z. Dori, *J. Amer. Chem. Soc.*, 94 (1972) 727.
57 R. Blinck and D. Hadži, *J. Chem. Soc., London*, (1958) 4536.
58 K. Burger, I. Ruff and F. Ruff, *J. Inorg. Nucl. Chem.*, 27 (1965) 179.
59 J.C. Canton, Jr. and C.V. Banks, *Inorg. Chem.*, 6 (1967) 1670.
60 R.D. Ellison and H.A. Levy, *Acta Crystallogr.*, 19 (1965) 260.
61 T.W. Thomas and A.E. Underhill, *Chem. Soc. Rev.*, 1 (1972) 99.
62 A. Okáč and M. Šimek, *Collect. Czech. Chem. Commun.*, 15 (1950) 977.
63 A. Okáč and M. Šimek, *Collect. Czech. Chem. Commun.*, 24 (1959) 2699.
64 J. Selbin and J.H. Junkin, *J. Amer. Chem. Soc.*, 82 (1960) 1057.
65 O.S. Ksenzhek, L.S. Burachenko, J.O. Volodina, F.E. Dinkevich and G.S. Motyagina, *Russ. J. Inorg. Chem.*, 16 (1971) 566.
66 D.J. Davis and E.A. Boudreaux, *J. Electroanal. Chem.*, 8 (1964) 434.
67 M.A. Bambenek and R.T. Pflaum, *Inorg. Chem.*, 2 (1963) 289.
68 M.K. Boreiko, E.I. Kazantsev and I.I. Kalinichenko, *Russ. J. Inorg. Chem.*, 12 (1967) 137.
69 I.I. Kalinichenko and M.K. Boreiko, *Russ. J. Inorg. Chem.*, 14 (1969) 401.
70 M. Šimek, *Collect. Czech. Chem. Commun.*, 27 (1962) 461.
71 M. Šimek, *Collect. Czech. Chem. Commun.*, 27 (1962) 220.
72 L.E. Edelman, *J. Amer. Chem. Soc.*, 72 (1950) 5765.
73 M. Šimek, *Collect. Czech. Chem. Commun.*, 27 (1962) 337.
74 A.S. Foust and R.H. Soderberg, *J. Amer. Chem. Soc.*, 89 (1967) 5507.
75 H.J. Keller and K. Seibold, *J. Amer. Chem. Soc.*, 93 (1971) 1309.
76 G.N. Schrauzer, *Chem. Ber.*, 95 (1962) 1438.
77 D.R. Boston and N.J. Rose, *J. Amer. Chem. Soc.*, 90 (1968) 6859.
78 D.H. Busch, *Rec. Chem. Progr.*, 25 (1964) 107.
79 D.R. Boston and N.J. Rose, *Abstracts, 157th National Meetings of the American Chemical Society, Minneapolis, Minn., April 1969*, No. INOR-96.

80 G.A. Zakrzewski, C.A. Ghilardi and E.C. Lingafelter, *J. Amer. Chem. Soc.*, 93 (1971) 4411.
81 J.E. Parks, B.E. Wagner and R.H. Holm, *Inorg. Chem.*, 10 (1971) 2472.
82 E. Larsen, G.N. La Mar, B.E. Wagner, J.E. Parks and R.H. Holm, *Inorg. Chem.*, 11 (1972) 2652.
83 R.A.D. Wentworth, *Coord. Chem. Rev.*, 9 (1972) 171.
84 W.O. Gillum, R.A.D. Wentworth and R.F. Childers, *Inorg. Chem.*, 9 (1970) 1825.
85 G.N. Schrauzer, *Accounts Chem. Res.*, 1 (1968) 97.
86 G.N. Schrauzer, in *Bioinorganic Chemistry*, American Chemical Society, Washington, D.C., 1971, p. 1.
87 A.G. Sharpe and D.B. Wakefield, *J. Chem. Soc., London*, (1957) 281.
88 G.N. Schrauzer, *Inorg. Syn.*, 11 (1968) 61.
89 G.N. Schrauzer and R.J. Windgassen, *Chem. Ber.*, 99 (1966) 602.
90 G.N. Schrauzer and Lian-Pin Lee, *J. Amer. Chem. Soc.*, 90 (1968) 6541.
91 L.M. Engelhardt and M. Green, *J. Chem. Soc., Dalton Trans.*, (1972) 724.
92 G.N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, 91 (1969) 3341.
93 G.N. Schrauzer, J.H. Weber and T.M. Beckham, *J. Amer. Chem. Soc.*, 92 (1970) 7078.
94 G.N. Schrauzer, J.W. Sibert and R.J. Windgassen, *J. Amer. Chem. Soc.*, 90 (1968) 6681.
95 G.N. Schrauzer and R.J. Windgassen, *J. Amer. Chem. Soc.*, 89 (1967) 1999.
96 N.N. Proskina, A.V. Ablov and V.N. Shafranski, *Russ. J. Inorg. Chem.*, 14 (1969) 1599.
97 A.V. Ablov and I.D. Samus, *Dokl. Akad. Nauk SSSR*, 146 (1962) 1071.
98 H.G. Tsiang and W.K. Wilmarth, *Inorg. Chem.*, 7 (1968) 2535.
99 Z. Finta, Cs. Várhelyi and J. Zsakó, *J. Inorg. Nucl. Chem.*, 32 (1970) 3013.
100 A.V. Ablov, A.A. Papova and N.M. Samus, *Russ. J. Inorg. Chem.*, 15 (1970) 239.
101 G.N. Schrauzer and R.J. Windgassen, *J. Amer. Chem. Soc.*, 88 (1966) 3738.
102 A. Nakahara, J. Fujita and R. Tsuchida, *Bull. Chem. Soc. Jap.*, 29 (1956) 296.
103 R.D. Gillard and G. Wilkinson, *J. Chem. Soc., London*, (1963) 6041.
104 J. Zsakó, Cs. Várhelyi and E. Kékedy, *J. Inorg. Nucl. Chem.*, 32 (1970) 2999.
105 A.V. Ablov, N.M. Samus and O.A. Bologa, *Russ. J. Inorg. Chem.*, 8 (1963) 440.
106 A.V. Ablov, O.A. Bologa and N.M. Samus, *Russ. J. Inorg. Chem.*, 13 (1968) 1685.
107 A.V. Ablov, A.M. Goldman, O.A. Bologa, Yu. A. Simonov and M.M. Botoshanski, *Russ. J. Inorg. Chem.*, 16 (1971) 1167.
108 H.A.O. Hill and K.G. Morallee, *J. Chem. Soc. A*, (1969) 554.
109 A.W. Herlinger and T.L. Brown, *J. Amer. Chem. Soc.*, 94 (1972) 388.
110 A.V. Ablov and M.P. Filipov, *Russ. J. Inorg. Chem.*, 7 (1962) 525.
111 A.V. Ablov, B.A. Bovykin and V.Yu. Zemlyak, *Russ. J. Inorg. Chem.*, 15 (1970) 241.
112 Y. Yamano, I. Masuda and K. Shinra, *J. Inorg. Nucl. Chem.*, 33 (1971) 521.
113 B.A. Jillot and R.J.P. Williams, *J. Chem. Soc., London*, (1958) 462.
114 N. Sanders and P. Day, *J. Chem. Soc. A*, (1969) 2303.
115 A.V. Ablov, V.I. Goldanskii, R.A. Stukan and E.F. Makarov, *Dokl. Akad. Nauk SSSR*, 170 (1966) 128.
116 G. De Alti, V. Galasso and A. Bigotto, *Inorg. Chim. Acta*, 3 (1969) 527.
117 G. De Alti, V. Galasso, A. Bigotto and G. Costa, *Inorg. Chim. Acta*, 3 (1969) 533.
118 J. Backes, I. Masuda and K. Shinra, *Bull. Chem. Soc. Jap.*, 45 (1972) 1724.
119 J. Backes, I. Masuda and K. Shinra, *Bull. Chem. Soc. Jap.*, 45 (1972) 1061.
120 K.A. Kerr, J.M. Robertson and G.A. Sim, *Chem. Commun.*, (1967) 170.
121 T.W.J. Taylor and E.K. Ewbank, *J. Chem. Soc., London*, (1926) 2818.
122 A. Okáč and M. Šimek, *Collect. Czech. Chem. Commun.*, 15 (1950) 445.
123 D.A. White, *J. Chem. Soc. A*, (1971) 233.
124 J.V. Quagliano and D.H. Wilkins, in J.C. Bailar, Jr. (Ed.), *Chemistry of the Coordination Compounds*, Reinhold, New York, 1956, p. 672.

125 P. Pfeiffer and H. Buchholz, *J. Prakt. Chem.*, 124 (1930) 133.
126 C. Matsumoto and K. Shinra, *Nippon Kagaku Zasshi*, 88 (1967) 340; *Chem. Abstr.*, 67 (1967) 58963.
127 I. Masuda, *Nippon Kagaku Zasshi*, 82 (1961) 120; *Chem. Abstr.*, 56 (1962) 11182.
128 I. Masuda, *Nippon Kagaku Zasshi*, 82 (1961) 125; *Chem. Abstr.*, 56 (1962) 11182.
129 L. Cambi and A. Caganasso, *Gazz. Chim. Ital.*, 63 (1933) 767.
130 G. Jacini, *Gazz. Chim. Ital.*, 69 (1939) 714.
131 E. König, *Landolt-Börnstein*, Band 2, Volume 2, Springer-Verlag, New York, 1966, pp. 2–102 to 2–105.
132 U.B. Talwar and B.C. Halder, *J. Inorg. Nucl. Chem.*, 32 (1970) 213.
133 N.J. Patel and B.C. Halder, *J. Inorg. Nucl. Chem.*, 29 (1967) 1037.
134 I. Masuda, M. Tamaki and K. Shinra, *Bull. Chem. Soc. Jap.*, 42 (1969) 157.
135 A.V. Ablov and N.V. Zabarev, *Russ. J. Inorg. Chem.*, 13 (1968) 1563.
136 V. Hovorka and L. Šo̊cha, *Collect. Czech. Chem. Commun.*, 25 (1960) 1796.
137 V. Havorka and L. Šo̊cha, *Collect. Czech. Chem. Commun.*, 29 (1964) 983.
138 L. Šo̊cha, *Collect. Czech. Chem. Commun.*, 29 (1964) 993.
139 D. Hadži, *J. Chem. Soc., London*, (1956) 2725.
140 S. Gurrieri and G. Siracusa, *Inorg. Chim. Acta*, 5 (1971) 650.
141 A. Palm and H. Wilson, *Can. J. Chem.*, 31 (1953) 1004; A. Palm and H. Werbin, *Can. J. Chem.*, 32 (1954) 858.
142 J.W.L. van Oijen and C. Romers, *Acta Crystallogr.*, 20 (1966) 169.
143 C. Romers, *Acta Crystallogr.*, 17 (1964) 1287.
144 I.M. Kolthoff and E. Jacobsen, *J. Amer. Chem. Soc.*, 79 (1957) 3677.
145 G.C. Lalor, *J. Inorg. Nucl. Chem.*, 30 (1968) 1925.
146 G.C. Lalor, *J. Inorg. Nucl. Chem.*, 31 (1969) 1783.
147 O. Baudisch, *Science*, 92 (1940) 336.
148 H. El Khadem and W.M. Orabi, *Z. Anorg. Allg. Chem.*, 365 (1969) 315.
149 J. Charalambous, M.J. Frazer and F.B. Taylor, *J. Chem. Soc. A*, (1969) 2787.
150 J. Charalambous, M.J. Frazer and F.B. Taylor, *J. Chem. Soc. A*, (1971) 602.
151 J. Charalambous and M.J. Frazer, *J. Chem. Soc. A*, (1970) 2645.
152 E.M. McPartlin, quoted by J. Charalambous, M.J. Frazer and F.B. Taylor, *J. Chem. Soc. A*, (1971) 602.
153 J.B. Neilauds, *Struct. Bonding (Berlin)*, 7 (1966) 59.
154 S. Candeloro, D. Gardenic, N. Taylor, B. Thompson, M. Viswamitra and D.C. Hodgkin, *Nature (London)*, 224 (1969) 589.
155 K. Sone, *Bull. Chem. Soc. Jap.*, 25 (1952) 1.
156 A. Ballio, S. Bercellona, E.B. Chain, A. Tonalo and L. Verro-Bercellona, *Proc. Roy. Soc., Ser. B*, 161 (1964) 384.
157 P.W.W. Hunter and G.A. Webb, *J. Inorg. Nucl. Chem.*, 32 (1970) 1386.
158 P. Pfeiffer, *Chem. Ber.*, 63 (1930) 1811.
159 W.U. Malik, D.R. Gupta and C.L. Taploo, *Indian J. Chem.*, 7 (1969) 730.
160 E. Uhlig, E. Dinjus and M. Helbig, *Z. Anorg. Allg. Chem.*, 373 (1970) 279.
161 E. Uhlig and E. Dinjus, *Z. Anorg. Allg. Chem.*, 384 (1971) 27.
162 I. Masuda, *Nippon Kagaku Zasshi*, 82 (1961) 563; *Chem. Abstr.*, 56 (1962) 11182.
163 I. Masuda, *Nippon Kagaku Zasshi*, 82 (1961) 1350; *Chem. Abstr.*, 58 (1963) 2117.
164 A.V. Ablov and N.I. Belichuk, *Russ. J. Inorg. Chem.*, 7 (1962) 401.
165 C. Djordjevic, J. Lewis and R.S. Nyholm, *J. Chem. Soc., London*, (1962) 4778.
166 M.J. Lacey, C.G. Macdonald, J.S. Shannon and P.J. Collin, *Aust. J. Chem.*, 23 (1970) 2279.
167 M.J. Lacey, C.G. Macdonald, J.F. McConnell and J.S. Shannon, *Chem. Commun.*, (1971) 1206.

168 K.S. Bose, *J. Inorg. Nucl. Chem.*, 34 (1972) 3593.
169 B.C. Sharma, K.S. Bose and C.C. Patel, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 905.
170 A.V. Ablov, L.F. Chapurina and N.I. Belichuk, *Russ. J. Inorg. Chem.*, 10 (1965) 642.
171 R. Gronbaek and S.E. Rasmussen, *Acta Chem. Scand.*, 16 (1962) 2325.
172 F. Lions and K.V. Martin, *J. Amer. Chem. Soc.*, 79 (1957) 2733.
173 E. Uhlig and D. Schneider, *Z. Anorg. Allg. Chem.*, 333 (1964) 90.
174 A.V. Ablov, N.I. Belichuck and M.S. Pereligina, *Russ. J. Inorg. Chem.*, 17 (1972) 534.
175 E. Uhlig, D. Schneider and H. Hildebrandt, *Z. Anorg. Allg. Chem.*, 346 (1966) 173.
176 A.V. Ablov and N.I. Belichuk, *Russ. J. Inorg. Chem.*, 7 (1962) 1066.
177 A.V. Ablov and N.I. Belichuk, *Russ. J. Inorg. Chem.*, 8 (1963) 38.
178 A.V. Ablov, N.V. Gerbeleu and N.Ya. Negryatse, *Russ. J. Inorg. Chem.*, 15 (1970) 61.
179 A.V. Ablov, N.V. Gerbeleu and N.Ya. Negryatse, *Russ. J. Inorg. Chem.*, 16 (1971) 568.
180 V. Havorka and Z. Holzbecher, *Collect. Czech. Chem. Commun.*, 15 (1950) 437.
181 A.V. Ablov and N.I. Belichuk, *Russ. J. Inorg. Chem.*, 8 (1963) 592.
182 A.V. Ablov and N.I. Belichuk, *Russ. J. Inorg. Chem.*, 8 (1963) 311.
183 A.V. Ablov, N.V. Gerbeleu and N.Ya. Negryatse, *Russ. J. Inorg. Chem.*, 14 (1969) 515.
184 E. Uhlig and M. Freidrich, *Z. Anorg. Allg. Chem.*, 343 (1966) 299.
185 N. Mathur and C.K. Narang, *Talanta*, 11 (1964) 647.
186 G. Costa, G. Mestroni, E. de Savorgnani, *Inorg. Chim. Acta*, 3 (1969) 323.
187 G. Costa, G. Mestroni, T. Licari and E. Mestroni, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 561.
188 G. Gosta, G. Mestroni, G. Tauzher, D.M. Goodall, M. Green and H.A.O. Hill, *Chem. Commun.*, (1970) 34.
189 A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhoffer, L. Stefani and G. Tauzer, *Inorg. Chim. Acta Rev.*, 4 (1970) 41.
190 G. Costa, A. Puxeddu and E. Reisenhoffer, *J. Chem. Soc. Dalton Trans.*, (1972) 1519.
191 S. Brückner, M. Calligaris, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 3 (1969) 278.
192 M. Calliagaris, G. Nardin and L. Randaccio, *J. Chem. Soc. Dalton Trans.*, (1972) 1433.
193 S. Satpathy and B. Sahoo, *J. Inorg. Nucl. Chem.*, 33 (1971) 1313.
194 W.J. Stratton and P.G. Orgen, *Inorg. Chem.*, 9 (1970) 2588.
195 K.S. Bose and C.C. Patel, *J. Inorg. Nucl. Chem.*, 33 (1971) 2947.
196 M.B. Cingi, A.C. Villa, A.G. Manfredotti, C. Guastini and M. Nardelli, *Acta Crystallogr., Sect. B*, 28 (1972) 1075.
197 A.V. Ablov, N.I. Belichuck and V.N. Kaftanat, *Russ. J. Inorg. Chem.*, 17 (1972) 392.
198 L.F. Lindoy and S.E. Livingstone, *Coord. Chem. Rev.*, 2 (1967) 173.
199 R.A. Krause and D.H. Busch, *J. Amer. Chem. Soc.*, 82 (1960) 4830.
200 R.A. Krause, N.B. Colthup and D.H. Busch, *J. Phys. Chem.*, 65 (1961) 2216.
201 L.G. Ward, T.L. Meek and G.E. Cheney, *Inorg. Chem. Acta*, 4 (1970) 43.
202 B. Sen and D. Malone, B.V.M., *J. Inorg. Nucl. Chem.*, 34 (1972) 3509.
203 G.I.H. Hanania and D.H. Irving, *J. Chem. Soc., London*, (1962) 2745.
204 R.A. Krause, C. Guy and M.L. Hooker, *Inorg. Chem.*, 5 (1966) 1825.
205 G. Lees, F. Holmes, A.E. Underhill and D.B. Powell, *J. Chem. Soc. A*, (1971) 337.
206 C.H. Liu and C.F. Liu, *J. Amer. Chem. Soc.*, 83 (1961) 4167.
207 C.H. Liu and C.F. Liu, *J. Amer. Chem. Soc.*, 83 (1961) 4169.
208 F. Holmes, G. Lees and A.E. Underhill, *J. Chem. Soc. A*, (1971) 999.
209 C.F. Liu and C.H. Liu, *Inorg. Chem.*, 2 (1963) 706.
210 C.F. Liu and C.H. Liu, *J. Amer. Chem. Soc.*, 83 (1961) 2615.
211 R.W. Green and M.C.K. Svasti, *Austr., J. Chem.*, 16 (1963) 356.
212 B.F. Hoskins and D.G. Vince, *Austr., J. Chem.*, 25 (1972) 2039.
213 R. Beckett and B.F. Hoskins, *J. Chem. Soc. Dalton Trans.*, (1972) 291.
214 R. Beckett, R. Colton, B.F. Hoskins, R.L. Martin and D.G. Vince, *Austr. J. Chem.*, 22 (1969) 2527.

215 R.S. Drago and E.I. Baucom, *Inorg. Chem.*, 11 (1972) 2064.
216 E.I. Baucom and R.S. Drago, *J. Amer. Chem. Soc.*, 93 (1971) 6469.
217 G.I.H. Hanania, D.H. Irving and F. Shuraya, *J. Chem. Soc., London*, (1965) 1149.
218 M.R. Churchill and A.H. Reis, Jr., *Inorg. Chem.*, 11 (1972) 1811.
219 M.R. Churchill and A.H. Reis, Jr., *Inorg. Chem.*, 11 (1972) 2299.
220 K.M.J. Al-Komser and B. Sen, *Inorg. Chem.*, 2 (1963) 1219.
221 L.S. Bark and D. Griffin, *J. Inorg. Nucl. Chem.*, 33 (1971) 3811.
222 M.P. Coakley and M.E. Casey, *J. Inorg. Nucl. Chem.*, 34 (1972) 1937.
223 A. Chakravorty and K.C. Kalia, *J. Org. Chem.*, 35 (1970) 2231.
224 L. Hunter and C.B. Roberts, *J. Chem. Soc., London*, (1941) 823.
225 A. Chakravorty and K.C. Kalia, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 319.
226 K.C. Kalia and A. Chakravorty, *Inorg. Chem.*, 7 (1968) 2016.
227 K.C. Kalia and A. Chakravorty, *Inorg. Chem.*, 8 (1969) 2586.
228 L. Malatesta and R. Pizzoti, *Gazz. Chim. Ital.*, 76 (1946) 141.
229 S. Gupta, K.C. Kalia and A. Chakravorty, *Inorg. Chem.*, 10 (1971) 1534.
230 J.M. Van Niekerk and F.K.L. Schoening, *Acta Crystallogr.*, 6 (1953) 227.
231 S. Gupta and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, 9 (1973) 109.
232 G. Duyckaerts, *Bull. Soc. Roy. Sci. Liege*, 21 (1952) 196; *Chem. Abstr.*, 47 (1953) 2601.
233 G. Schoffa, O. Ristan and B.E. Wahler, *Z. Phys. Chem. (Leipzig)*, 215 (1960) 203.
234 P. Rây and D.N. Sen, *J. Indian Chem. Soc.*, 25 (1948) 473.
235 G. Rindorf, *Acta Chem. Scand.*, 25 (1971) 774.
236 H.A. Suter and P.W. West, *Anal. Chim. Acta*, 13 (1955) 501.
237 L. Malatesta, *Gazz. Chim. Ital.*, 68 (1938) 319.
238 R.V. Rao and R.P. Murty, *Indian J. Chem.*, 6 (1968) 465.
239 B. Soptrajanov, A. Nikolovski and I. Petrov, *Spectrosc. Lett.*, 1 (1968) 117; *Chem. Abstr.*, 69 (1968) 47783.
240 J. Bassett, J. Bensted and R. Grzeskowiak, *J. Chem. Soc. A*, (1969) 2873.
241 F. Buscarons and F. Bascarons, Jr., *Anal. Chim. Acta*, 32 (1965) 568.
242 M.A. Jarski and E.C. Lingafelter, *Acta Crystallogr.*, 17 (1964) 1109.
243 R.C. Srivastava, E.C. Lingafelter and P.C. Jain, *Acta Crystallogr.*, 22 (1967) 922.
244 L.L. Merritt, C. Gaure and A.E. Lessor, *Acta Crystallogr.*, 9 (1956) 253.
245 C.E. Pfluger, R.L. Harlow and S.H. Simonsen, *Acta Crystallogr., Sect. B*, 26 (1970) 1631.
246 P.L. Orioli, E.C. Lingafelter and B.W. Brown, *Acta Crystallogr.*, 17 (1964) 1113.
247 R.H. Holm and M.J. O'Connor, *Progr. Inorg. Chem.*, 14 (1971) 241.
248 J.B. Willis and D.P. Mellor, *J. Amer. Chem. Soc.*, 69 (1947) 1237.
249 V. Romano, F. Maggio and T. Pizzino, *J. Inorg. Nucl. Chem.*, 33 (1971) 2611.
250 T.S. Kannan and A. Chakravorty, *Inorg. Chem.*, 9 (1970) 1153.
251 H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jap.*, 37 (1964) 8.
252 K. Burger, L. Korecz, I.B. Manuaba and P. Mag, *J. Inorg. Nucl. Chem.*, 28 (1966) 1673.
253 J.L.K.F. de Varies, J.M. Trooster and E. de Boer, *Chem. Commun.*, (1970) 604.
254 K.R. Monolov, *Russ. J. Inorg. Chem.*, 12 (1967) 1431.
255 M.S. Kachhawala and A.K. Bhattacharya, *Z. Anorg. Allg. Chem.*, 325 (1963) 321.
256 K.K. Ramaswamy, C.I. Jose and D.N. Sen, *Indian J. Chem.*, 5 (1967) 169.
257 R.K. Murmann, *J. Amer. Chem. Soc.*, 79 (1957) 521.
258 R.K. Murmann, *J. Amer. Chem. Soc.*, 80 (1958) 4174.
259 R.K. Murmann, *J. Amer. Chem. Soc.*, 84 (1962) 1349.
260 R.K. Murmann, *Inorg. Chem.*, 2 (1963) 116.
261 E.O. Schlemper, *Inorg. Chem.*, 7 (1968) 1130.
262 E.O. Schlemper, W.C. Hamilton and S.J. la Placa, *J. Chem. Phys.*, 54 (1971) 3990.
263 E.O. Schlemper, *Inorg. Chem.*, 8 (1969) 2740.
264 E.G. Vassian and R.K. Murmann, *Inorg. Chem.*, 6 (1967) 2043.

265 D.H. Busch, K. Farmery, V. Goedken, V. Katovic, A.C. Melnyk, C.R. Sperati and N. Tokel, in *Bioinorganic Chemistry*, American Chemical Society, Washington, D.C., 1971, p. 44.

266 J.E. Young and R.K. Murmann, *J. Phys. Chem.*, 67 (1963) 2647.

267 J.C. Wang, J.E. Bauman and R.K. Murmann, *J. Phys. Chem.*, 68 (1964) 2296.

268 J.W. Frazer, G.R. Hedwig, H.K.J. Powell and W.T. Robinson, *Aust., J. Chem.*, 25 (1972) 747.

269 L.P. Eddy, W.W. Levenhagen and S.K. McEwen, *Inorg. Syn.*, 11 (1968) 89.

270 D.L. Cullen and E.C. Lingafelter, *Inorg. Chem.*, 9 (1970) 1865.

271 F. Eloy and R. Lenaers, *Chem. Rev.*, 62 (1962) 155.

272 M.H. Millen and W.A. Waters, *J. Chem. Soc. B*, (1968) 408.

273 G.A. Pearse, Jr. and R.T. Pflaum, *J. Amer. Chem. Soc.*, 81 (1959) 6505

274 D. Bandopadhyay, *J. Indian Chem. Soc.*, 30 (1953) 119.

275 V. Stuzka, J. Kvorpil and M. Kuras, *Fresenius, Z. Anal. Chem.*, 179 (1961) 401.

276 A.I. Busev, T.N. Zholondkovskaya. L.S. Krysina and L.I. Korobkina, in I.M. Otd. (Ed.), *Sovre. Metody Anal. Mater.*, Metallurgiya, Moscow, (1969); *Chem. Abstr.*, 73 (1970) 94224.

277 M. Kuraš and E. Ružička, *Chem. Listy*, 44 (1950) 41.

278 M. Kuraš and E. Ružička, *Chem. Listy*, 44 (1950) 90.

279 M. Kuraš and E. Ružička, *Chem. Listy*, 46 (1952) 482.

280 M. Kuraš and E. Ružička, *Chem. Listy*, 47 (1953) 1870.

281 M. Kuraš and E. Ružička, *Chem. Listy*, 52 (1958) 975.

282 M. Kuraš and E. Ružička, *Chem. Listy*, 48 (1954) 1257.

283 J.V. Dubsky, M. Kuraš and J. Trtilek, *Collect. Czech. Chem. Commun.*, 7 (1935) 1.

284 J.V. Dubsky and M. Kuraš, *Chem. Listy*, 24 (1930) 464.

285 L. Malatesta and F. Monti, *Gazz. Chim. Ital.*, 70 (1940) 842; *Chem. Abstr.*, 36 (1942) 984.

286 M. Kuras, J. Bartos and J. Mollin, *Acta Univ. Palack. Olomuc., Fac. Rerum Sci.*, 3 (1960) 55; *Chem. Abstr.*, 59 (1963) 9565.

287 K.R. Monolov and B.M. Angelov, *Monatsh. Chem.*, 102 (1971) 763.

288 M. Kuraš, *Chem. Obz.*, 16 (1941) 72; *Chem. Abstr.*, 37 (1943) 3367.

289 L. Malatesta and R. Pizzoti, *Gazz. Chim. Ital.*, 72 (1942) 564.

290 K.R. Monolov, *Monatsh. Chem.*, 99 (1968) 2416.

291 K.R. Monolov, *Nauch. Tr. Vissh. Pedagog. Inst. Plovdiv, Mat. Fiz. Khim. Biol.*, 6 (1968) 81; *Chem. Abstr.*, 70 (1969) 120642.

292 K.R. Monolov, *Nauch. Tr. Vissh. Pedagog. Inst. Plovdia, Mat. Fiz. Khim. Biol.*, 5 (1967) 75; *Chem. Abstr.*, 69 (1968) 110474.

293 K.R. Monolov and N. Motechkov, *Mikrochim. Acta*, (1970) 634.

294 M. Kuraš and E. Ružička, *Chem. Listy*, 49 (1955) 1897.

295 G. Manoussakis and Th. Kouimtzis, *J. Inorg. Nucl. Chem.*, 31 (1969) 3851.

296 C.D. Stout, M. Sundaralingam and G. Hung-Yin Lin, *Acta Crystallogr., Sect. B.*, 28 (1972) 2136.

297 D. Bandpadhyay and P. Rây, *J. Indian Chem. Soc.*, 33 (1956) 21.

298 M. Kuraš and J. Mollin, *Chem. Listy*, 52 (1958) 344.