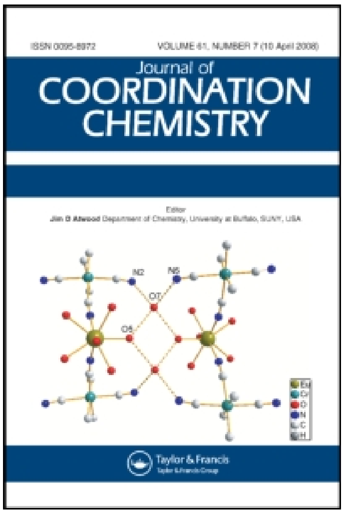

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RECENT DEVELOPMENTS IN THE METALLOSUPRAMOLECULAR AND MOLECULAR STRUCTURES OF THE COBALT, IRON AND VANADIUM COMPLEXES OF THE DIANIONIC TETRADENTATE SCHIFF BASE LIGANDS OF SALICYLIDENEIMINE AND ACETYLACETONEIMINE

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REVIEW:

RECENT DEVELOPMENTS IN THE METALLOSUPRAMOLECULAR AND MOLECULAR STRUCTURES OF THE COBALT, IRON AND VANADIUM COMPLEXES OF THE DIANIONIC TETRADENTATE SCHIFF BASE LIGANDS OF SALICYLIDENEIMINE AND ACETYLACETONEIMINE

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Four different types of metallosupramolecular structures are distinguishable for the title complexes. These types are described as: (a) The metal complex could react with other metal ions as a ligand, (b) Dimerization occurs through Lewis acid and Lewis base interactions of the metal ion and the coordinated oxygen atom of the ligand with those of an adjacent molecule, (c) Dimerization and chain formation occur using the donor-acceptor behaviour of the oxovanadium (IV) ion, and (d) Molecular association occurs through the bridged fluoride. Types (b), (c) and (d) are self-assembly. Chemical understanding of those types could lead to designing, and establishing procedures for, the preparation of new metallosupramolecular structures of homo- and heterobinuclear (as well as polynuclear) metal complexes with similar or mixed ligands.

Keywords: metallosupramolecular structures, cobalt, iron and vanadium complexes, metal complexes of salicylideneimine and acetylacetoneimine, transition metal complexes of Schiff bases, review

CONTENTS

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*Author for correspondence

ABBREVIATIONS

H_2 salen = N,N′-ethylenebis(salicylideneimine)
H_2 acen = N,N′-ethylenebis(acetylacetoneimine)
H_2 salpeen = N,N′-[2-(2′-pyridyl)ethyl] ethylenebis(salicylideneimine)
H_2 salphen = N,N′-*o*-phenylenebis(salicylideneimine)
H_2 salpen = N,N′-propane-1,3-diylbis(salicylideneimine)
H_2 salben = N,N′-butane-1,4-diylbis(salicylideneimine)
H_2 salnptn = N,N′-2,2-dimethyltrimethylenebis(salicylideneimine)
$dhbq^{2-}$ = dianion of 2,5-dihydroxy-1,4-benzoquinone
sq^{2-} = dianion of 3,4-dihydroxy-3-cyclobutene-1,2-dione
H_2 cat = catechol
Hacac = acetylacetone
Hbzac = benzoylacetone
Hsal = salicylaldehyde
ox^{2-} = oxalate dianion

INTRODUCTION

The chemistry of coordination compounds of Schiff-base ligands has been the subject of extensive and continuous studies since the work of Pfeiffer[1] over sixty years ago. Several reviews2 have summarized the developments as they appeared. The continuous and unfading interest in the coordination chemistry of Schiff-base ligands in general (and particularly those of the dianionic tetradentate Schiff bases derived from condensation of two molecules of either salicylaldehyde or a β-diketone with an aliphatic or aromatic diamine) was ascribed to the following factors:2,3 (1) metal complexes could serve as models for the reactivity of vitamin B_{12}, (2) the tendency of the coordinated sites (*e.g.*, oxygen atoms) for side-coordination and bridging of metal centers, (3) the possibility of isolating a suitable system for studying metal exchange interactions and magnetic cross-over systems and (4) the applications of the metal complexes, particularly those of divalent cobalt as oxygen carriers.

Our interest4 in transition metal complexes of the tetradentate Schiff-base ligand, N,N′-ethylenebis(isonitrosoacetylacetoneimine), was related to: (a) the chelate isomerism behaviour whereby five- or six-membered chelate rings were characterized (N- and O-coordination by the oximato group, respectively) and (b) the types of metal complexes produced from related vicinal oxime-imine ligands.

This review is limited to the cobalt, iron and vanadium complexes of the dianionic tetradentate Schiff bases derived from condensation of two molecules of either salicylaldehyde or acetylacetone with one molecule of aliphatic or aromatic diamine (Figure 1). It is aimed at elucidating the importance of metallosupramolecular and molecular structures of the metal complexes under consideration and to the inter-related coordination chemistry of the metal ions. Supramolecular chemistry was defined as that chemistry of the intermolecular bond concerning the structures and functions of the entities formed by association of two or more chemical species.5 Types of intermolecular interactions include electrostatic and ion-pairing interactions, hydrogen bonding between complementary substituents and other donor-acceptor interactions.5 When the intermolecular interaction involves coordination of the appropriate ligand to a metal center then the structure was termed a metallosupramolecular structure.6 This structure has not been previously reviewed for coordination compounds of cobalt, iron and vanadium ions and the ligands in Figure 1. The coordinated oxygen atoms of the N_2O_2 chromophore are known for their tendency for side coordination.2,3 Furthermore, the Lewis acid characteristics of the coordinated metal ions enhance the intermolecular interactions. This behavior prompted us to write this review article in order to characterize the metallosupramolecular chemistry6 which comprises the concepts of molecular recognition and self-assembly.7,8

COBALT COMPLEXES

Several reports9-12 have dealt with the dioxygen binding ability of the Fe(II), Cu(II), Ni(II) and Mn(II) complexes of tetradentate Schiff bases. The Co(II) complexes were subjected to enormous investigation owing to the wide range of stabilities of the cobalt-dioxygen complexes and the associated structures. It was concluded that the Co(II) complexes do not by themselves bind oxygen strongly, but their adducts with suitable monodentate Lewis bases readily bind oxygen under certain conditions of temperature and oxygen pressure.13-15 The axial base increased the electron density at the metal center which led to a stable metal-dioxygen bond (Figure 2).

The axial base may be an aliphatic or aromatic amine; pyridine and substituted pyridines were most frequently employed. The gas volumetric apparatus used for oxygen uptake measurements was described.[15,16] The most preferred solvent medium was diethylene glycol methyl ether (diglyme) because of its wide liquid

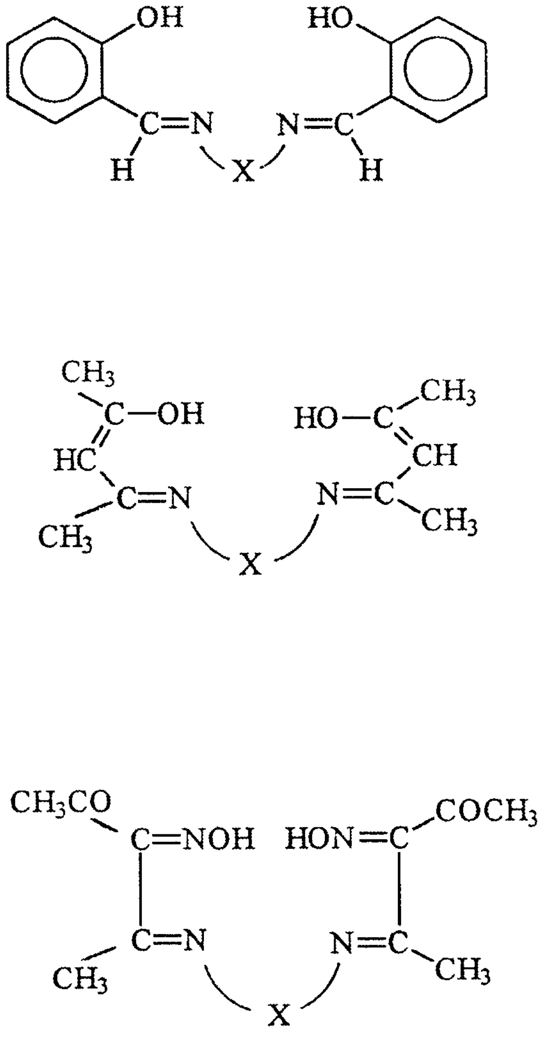


FIGURE 1 General representation for the dianionic tetradentate Schiff bases; X = aliphatic or aromatic diamine moiety.

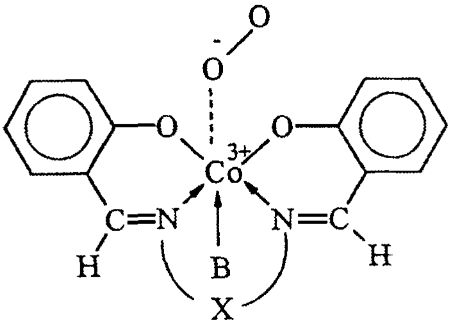


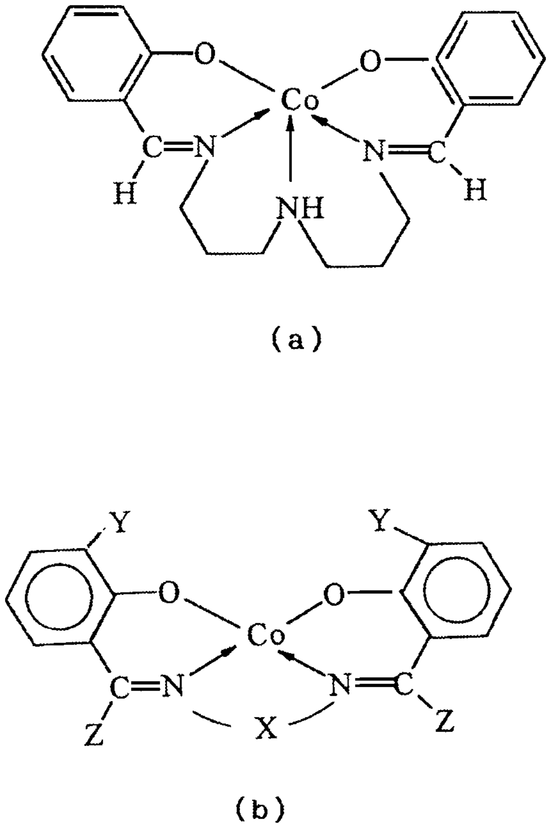
FIGURE 2 Dioxygen complex of Co(salen); X = $-(CH_2)_2$.

range (>200° C) as well as for its solvating properties, thus simplifying the adjustment of dioxygen affinities through temperature variation.15

The stability of the oxygen adducts was found to increase with increasing: (a) the strength of the metal-ligand binding, (b) electron-donating chelate ring substituents and (c) axial interactions which involve strong Lewis bases capable of π-bonding.17,18 The dioxygen complexes were most conveniently formulated as $\mathrm{Co^{III}} - \breve{\mathrm{O}}_2$ species. The degree of electron transfer from Co(II) to O_2 varies with the localized metal ion bonding conditions.19 Replacement of the oxygen atom in the N_2O_2 chromophore by sulfur led to stabilization of the cobalt ion in the lower oxidation state.20

ESR and IR spectroscopic studies revealed21-23 an angular geometry for the cobalt-dioxygen moiety in the 1:1 dioxygen adduct shown in Figure 2. The polarized species $\mathrm{Co^{III}} - \breve{\mathrm{O}}_2$ was suggested whereby the electron transferred from the metal ion resides24,25 essentially in a π^* (O_2) orbital. Some variation in the amount of electron transfer ($\mathrm{Co} \rightarrow O_2$) between the complexes [Co(salen)Py(O_2)] and [Co(salpeen)(O_2)] indicated that complete electron transfer was not valid for all cases.24,26

The crystal structure of the dioxygen adduct of N,N′-ethylenebis(3-tert-butylsalicylideniminato)cobalt(II) with pyridine as the axial base gave the O-O distance of 1.350 Å and the Co-O-O angle of 116.4°; both values were compatible with the $\mathrm{Co^{III}} - \breve{\mathrm{O}}_2$ formulation,27 known as a superoxo complex. The alternative μ-peroxo-complexes of formulation Co_2O_2 were also realized.28 Instead of adding the base at the axial position of the tetradentate Schiff base, the five-coordinated Co(II) complex in Figure (3-a) was used to form the dioxygen complex.28 ESR spectral measurements of the dioxygen complexes of $[\mathrm{CoL}]O_2$ (L = salen or substituted derivatives, Figure 3-b) in frozen chloroform solutions containing pyridine or 2,6-dimethylpyridine led to the conclusion29 that the Co-O-O angle lies within the range 115-120°.



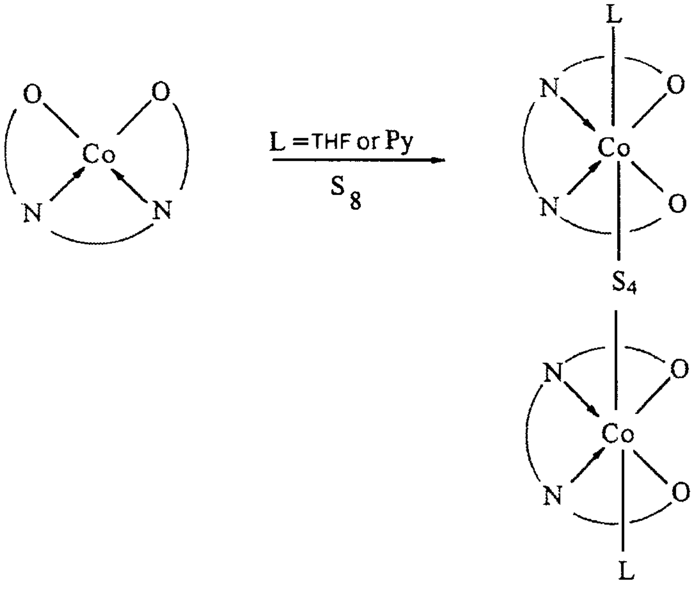
X	Y	Z
$-(CH_2)_2-$	H	H
$-(CH_2)_3-$	H	H
$-CH(Me)CH_2-$	H	H
$-(CH_2)_2-$	H	Me
$-(CH_2)_2-$	H	Et
$-(CH_2)_2-$	OMe	H

FIGURE 3 (a) Co(II) complex prepared from the 1:1 molar ratio reaction of bis(salicylaldehydato) cobaltate (II) dihydrate with bis(3-amino-propyl) amine under nitrogen. (b) [Co(salen)] and derivatives used for ESR studies

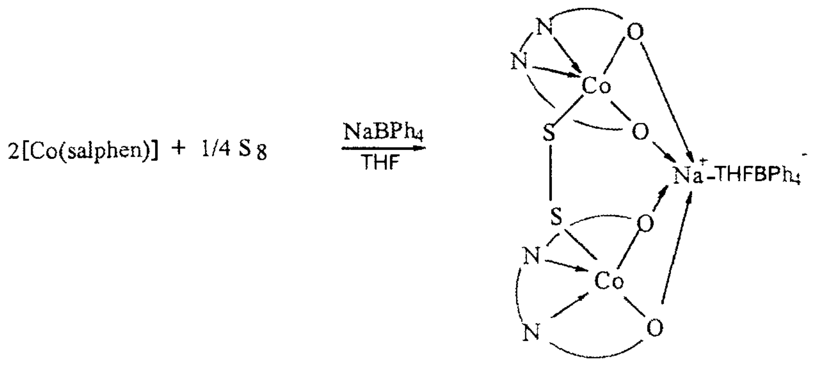
The identification of the ground state of the low-spin Co(II) complexes has been somewhat controversial.29-32 It was argued that the d_{z}^{2} ground state29,33 is most likely for the four-coordinate Co(II) complexes. However, in some cases the d_{yz} ground state is also possible. In the former state, the orbital occupied by the unpaired electron was shown to not be altered by ligation at the fifth and sixth coordination sites.34 The ^{1}H NMR spectra of [Co(salphen)] in several non- and weakly-coordinated solvents were analyzed in order to elucidate the ground electronic state.35 The reversible reaction of [Co(salen)] (as well as other related Schiff bases) with dioxygen in N,N′-dimethylformamide was investigated.36

Formation of a high-spin ground state (S = 3/2) has been investigated by ESR, NMR and magnetic susceptibility measurements for [Co(salen)] and related complexes in solutions containing N-heterocyclic bases.37 The factors which govern formation of the high-spin species were discussed. The latter species is most likely to be six coordinate where basicity of the added ligand contributed to the stability of the high-spin state.37

The reaction of elemental sulfur with either Co(salphen) or Co(salen) (as well as their derivatives) was used to compare the reactivity of the divalent cobalt complexes with the reaction with molecular oxygen.38 The reaction was carried out in coordinating solvents, (THF or py) which supplies a fifth donor atom around Co(II). The complexes formed were the μ-tetrasulfide derivatives of the binuclear diamagnetic Co(III) complexes of the type shown in reaction 1.



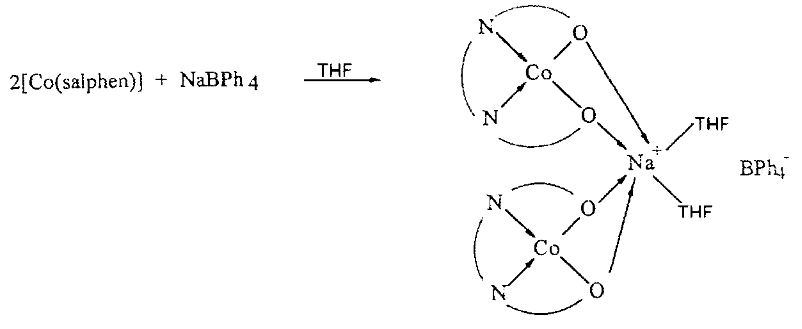
(1)



(2)

Reaction of [Co(salphen)] with elemental sulfur in THF containing $NaBPh_4$ resulted in formation38 of the diamagnetic binuclear Co(III) complex $[\{Co(salphen)\}_2S_2Na(THF)_2]BPh_4$, (reaction 2). In this complex the two Co(salphen) units are bridged by the S_2^{2-} ligand and by the Na^+ ion which is coordinated to the four oxygen atoms of the two Schiff-base ligands. The complex [Co(salphen)] reacted with $NaBPh_4$ in THF solution to produce the binuclear diamagnetic Co(III) complex $[\{Co(salphen)\}_2Na(THF)_2]BPh_4$, reaction 3. The two Co(salphen) units are arranged around the sodium ion allowing for the S_2 ligand of reaction 2 to bridge these units.

Several studies39 on the bis(pyridine)cobalt(III) complexes of (salen) homologues with substituents on the ethylene backbone revealed that the six-coordinate metal ion is characterized by pyridine molecules located at the apical sites and severe steric interactions between the pyridine molecule and the substituents.



(3)

IRON COMPLEXES

The bioinorganic chemical relationship between the iron(III) porphyrin complexes and tetradentate Schiff-base ligands was the driving force for several studies aimed at investigating the reactivity of their iron complexes. Thus, a heterodinuclear spin-crossover complex (Figure 4-a) was prepared from reaction of [Fe(salen)Cl] with a nickel(II) imidazolate chelate.40 The iron(III) complex reacted41 with an excess of L (imidazole, 1-, 2- or 4-methylimidazole) in acetone to produce the heterobis adducts [Fe(salen)L(Cl)] (Figure 4-b) in all cases and a homobis adduct [Fe(salen)L_2]Cl; L = 4-methylimidazole (Figure 4-c).

Crystal structures of the iron(III) complexes42 [Fe(acen)$(Him)_2$]BPh_4 (low-spin), [Fe(salen)$(Him)_2$]$ClO_4 \cdot H_2O$ (high-spin) and [Fe(salphen)$(Him)_2$]BPh_4 (high-spin) were determined,43 Him = imidazole. The equatorial plane in those complexes was occupied by the tetradentate ligand. The two imidazole molecules occupy the axial positions. It was concluded that the metal to imine-nitrogen bond distances were sensitive to the spin state of the metal atom which was not the case for the Fe-O bond distances. No relationship was detected between the relative orientation of the axial imidazole rings and the spin state of iron(III). The relative orientation of the imidazole rings was reported44 to be the controlling factor for the spin state in the iron(III) porphyrin complexes.

The iron(III) complex [Fe(salen)Cl] exists in dimeric or monomeric form in the solid state depending on the nature of the solvent used in its crystallization.45 The $[Fe^{III}(salen)]^+$ complex was isolated with catecholate ligands46-48 or other ligands such as acetylacetone or salicylaldehyde.49 The reaction of [Fe(salen)Cl] with an excess of 1,2-diaminoethane resulted50 in formation of [FeL_2Cl]$\cdot H_2O$ (L = the half unit produced by the (1 + 1) condensation of Hsal with 1,2-diaminoethane). The corresponding trivalent Cr and Co complexes of H_2salen react similarly.

The dimeric oxo-complex [{Fe$(salen)_2$O}] provides strong evidence for the continuing interest in transition metal complexes of tetradentate Schiff bases. The complex was prepared some sixty years ago,1 its magnetic properties51,52 and molecular structure were studied thirty years ago,53,54 and its solution chemistry was recently reported.55,56 It was deduced that in the case of the $[Fe(salen)(catechol)]^-$ ion that the $(salen)^{2-}$ ligand had suffered a marked structural change from the normal planar configuration to the distorted one56 shown in Figure 5.

The iron(III) complexes [Fe(salen)(O_2CMe)],57 K[Fe(salen)(cat)]57 and [Fe(salphen)(Hcat)]48 were reported. In the latter complex, X-ray diffraction studies revealed the unidentate coordination of the $(Hcat)^-$ ligand.48 X-ray diffraction studies58 for the complexes [Fe(salen)X] where X = acetylacetonate,

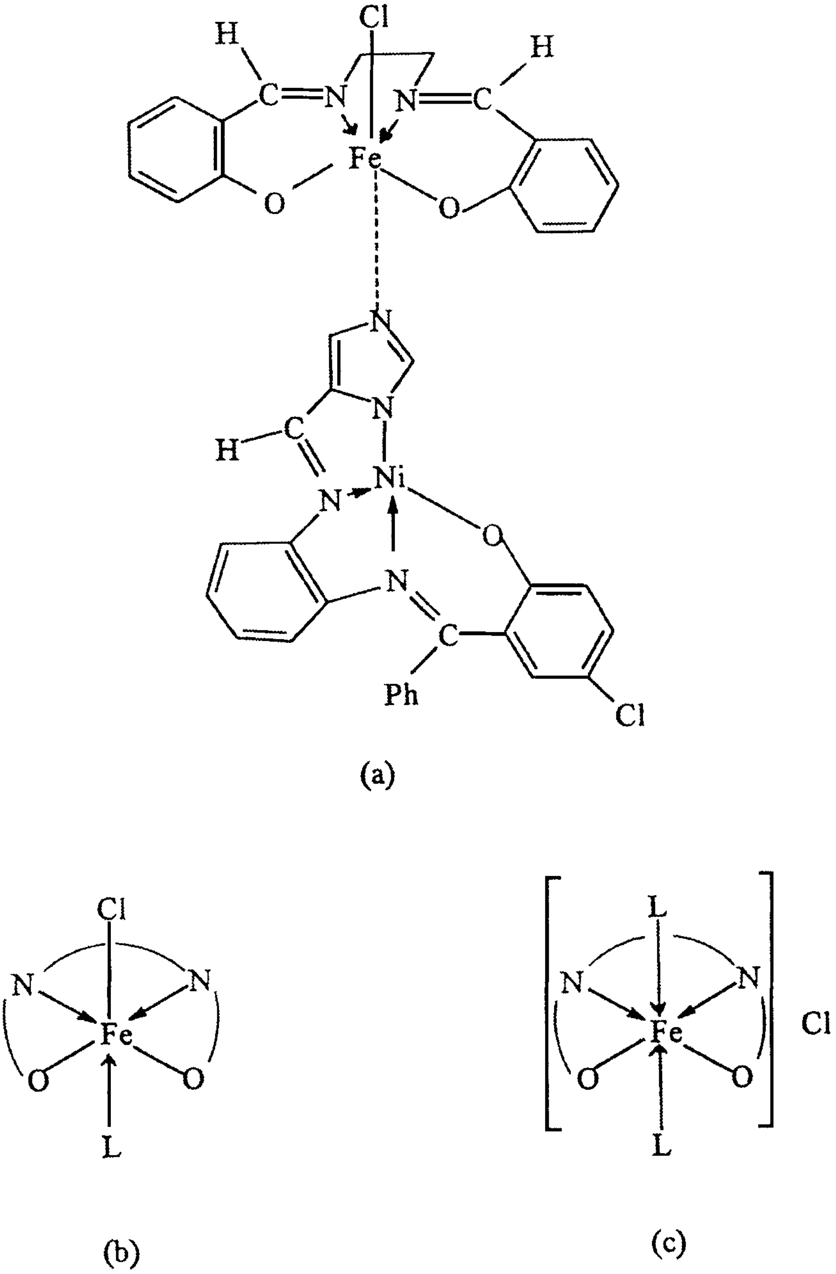


FIGURE 4 Formulation for (a) the binuclear complex; (b) the heterobisadduct with L = imidazole or 1-, 2- or 4-methylimidazole, and (c) the Homobisadduct with L = 4-methylimidazole.

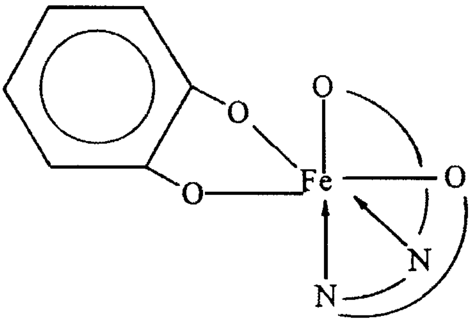


FIGURE 5 Suggested molecular structure for [Fe(salen)(cat)]$^-$

phenanthrene semiquinone and catecholate anions revealed the flexibility of the [Fe(salen)]$^+$ unit. It adopts the *cis-β* configuration in order to accommodate equatorial coordination of the bidentate ligand (X); Figure 5. A similar conclusion was observed for the Co(III) complexes [Co(salen)(acac)]59 and [Co(salen)(bzac)].60

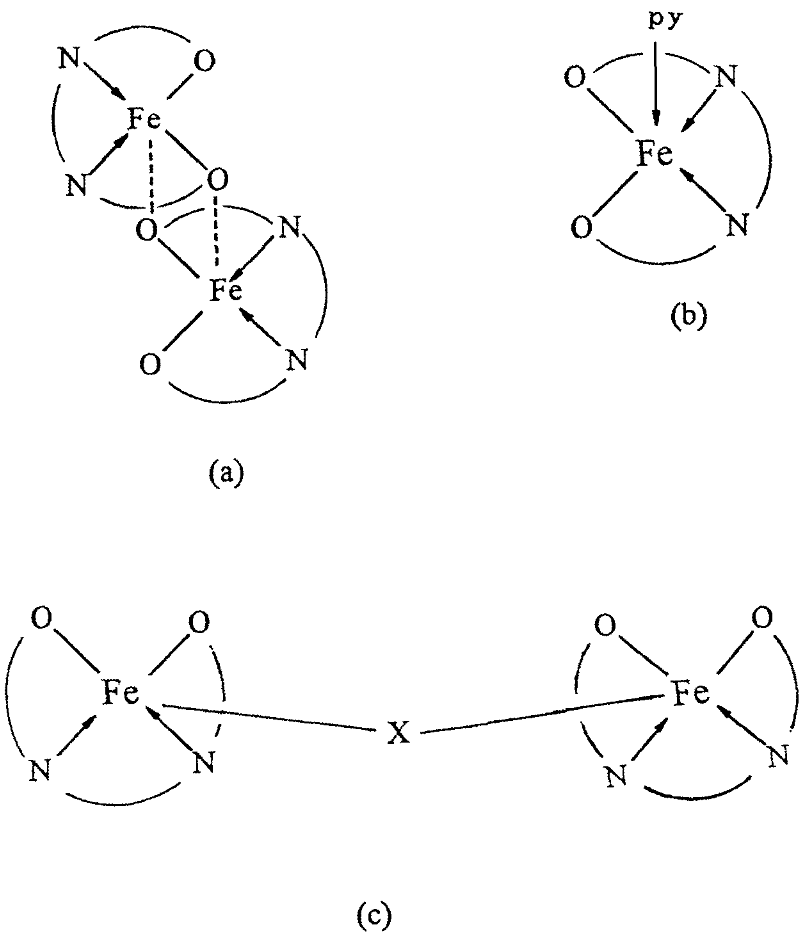
The mononuclear complexes [Hip] [M(salen)ox] (M = trivalent Fe or Cr, Hip$^+$ = piperidinium cation) and the binuclear [Fe_2(salen)$_2$(ox)]·H_2O were recently characterized.61 X-ray diffraction of the mononuclear complexes showed that the presence of the oxalate ligand in both complexes led the (salen) ligand to prefer the non-planar *cis-β* configuration. The metal ion showed distorted octahedral geometry (Figure 5) with the oxalate oxygens occupying the equatorial plane. The oxalate anion in the binuclear complex was suggested to bridge the two metal ions.

In addition to the binuclear complex discussed above, two other binuclear complexes of the type [Fe_2(salen)$_2$dhbq]·1.5H_2O and [Fe_2(salen)$_2$(CH_3OH)$_2$sq] were investigated.62 Spectroscopic, magnetic moment and X-ray studies of the latter complex indicate that the bidentate (ox), (dhbq) or (sq) ligands bridge the iron(III) ions in the three binuclear complexes.

The reaction of $FeCl_2$·1.5THF with H_2acen in the presence of NaOMe led to formation of [{Fe(acen)}$_2$]. The complex is monomeric in solution and dimeric in the solid state.63 The iron(II) ion is five coordinate in the dimer and the pyridine adduct, Figure 6-a and 6-b, respectively. The former complex is oxidized63 by molecular oxygen or elemental sulfur to produce the high-spin iron(III) complex in Figure 6-c. Both complexes are d^5 with strongly antiferromagnetic interactions (μ_{eff} = 1.80 and 2.16 BM at 293 K for the oxygen and sulfur complexes respectively).

Polymerization of the high-spin iron(II) complexes [{Fe(salpen)}$_2$], [{Fe(salben)}$_2$] and [{Fe(salphen)}$_2$] to satisfy the octahedral coordination mode of the metal was reported.64 The molybdate and oxo-bridged iron(III) complexes $[\{Fe(salen)\}_2X]$, $X = O^{2-}$ or MoO_4^{2-}, were also discussed.65

Earlier investigations on the β-diketoneimine Schiff bases were related to the ^1H NMR spectra of the ligands and their diamagnetic metal complexes.66 Studies of the salicylideneimine Schiff bases were concerned with the thermal stability67 of their metal complexes. Recently, preparations of M(salen) (M = TiO, VO, CrCl, Mn, FeCl, Co, Ni, Cu and Zn) complexes were reviewed and their mass spectra reported.68



(a) (b) (c)

FIGURE 6 (a) Structure of the dimeric $[\{Fe(acen)\}_2]$; (b) $[Fe(acen)(py)]$; (c) for X = O, $[\{Fe(acen)\}_2 (\mu\text{-}O)]$ and for X = S, $[\{Fe(acen)\}_2 (\mu\text{-}S)]$.

TABLE I Vanadium complexes of the dianionic tetradentate Schiff bases.

No.	Complex	Reference
1	[V(salphen)(THF)(Cl)]	69
2	[V(salen)(Cl)]$_2$	69
3	[V(salen)(Cl)$_2$	69
4	[V(salphen)(Cl)$_2$]	69
5	[V(NH$_2$NHPh)$_2$(salen)] I	70
6	[V(acen)CH$_2$Ph]$_2$	71
7	[V(Ph$_2$(salen)]·CH$_3$OH	72
8	[VO(salen)]	69,73,75,83
9	[VX$_2$L}, X=Cl or Br and L=salen or salphen	74, 77
10	[V(OMe)$_2$(salen)]	78
11-a	[VI$_2$(salen)]	80
11-b	[(salen)VOVO(salen)] I$_5$	76
12-a	[{V(salen)OV(salen)}$_2$O] [BF$_4$]$_2$	81
12-b	[{V[(salen)]$_2$ O}$_2$] [I$_3$]$_2$	81
13	[VO(salnptn)]	82
14	[VO(salen)] ClO$_4$	84, 85
15	[VO(OMe)(salnptn)]	82
16	[{VO(salen)}$_2$ (μ-F)] BF$_4$	85
17	[{VO(salpen)}$_2$]	88

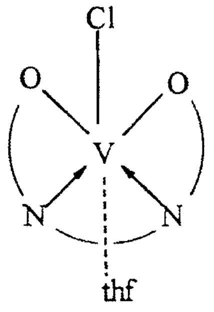
VANADIUM COMPLEXES

The compelling factor for continuing interest in vanadium ion complexes of tetradentate Schiff bases of (H_2 salen) and (H_2 acen) is that these ligands provide suitable environments for stabilization of the various oxidation states of vanadium. The formed complexes still provide active sites capable of binding other molecules. The synthetic approaches ranged from (a) displacing the halogen from VX_3 or VX_4 by the appropriate ligand or (b) investigating the reactivity of the oxygen atom in the oxovanadium(IV) complexes of the tetradentate ligands. The types of reported metal complexes are summarized in Table I.

Complex (**1**) was prepared by reductive deoxygenation of [VO(salphen)] by $TiCl_3(THF)_3$. In the former complex, the chlorine and THF are *trans* to each other in the axial position while the (salphen) ligand occupies the equatorial position.69 Complexes (**1**) and (**2**) could be prepared from the reaction of $VCl_3(THF)_3$ with the sodium salt of the corresponding Schiff base. The deoxygenation of [VO(salen)] and [VO(salphen)] by $SOCl_2$ led to the octahedral complexes (**3**) and (**4**), respectively.69 Dimerization of complexes (**3**) and (**4**) took place as shown in Figure 7.

Complex (**5**) and other V(III) complexes of (salen) were reported.70 The vanadium-carbon σ-bond was stabilized by metal coordination to tetradentate Schiff bases like H_2acen and H_2salen. Thus, the vanadium(III) complex (**6**) [V(acen)$CH_2Ph]_2$ contains a σ-bond of the benzyl group to each vanadium.71

Reaction of VCl_2(salen) with PhLi led to replacement of the chloro groups by phenyl groups.72 The formed complex was purified in methanol to produce complex (**7**), [VPh_2(salen)]·CH_3OH which contains vanadium-phenyl σ-bonds. This complex was compared with its oxo (complex (**8**)) and dichloro (complex (**9**)) analogues; VO(salen)69,73 and VCl_2(salen),74 respectively.



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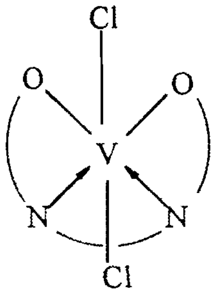
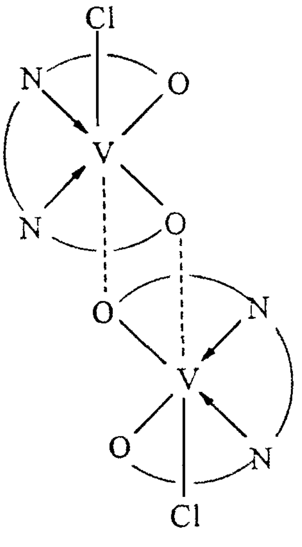


(3); L = salen
(4); L = salphen



(2)

FIGURE 7 Suggested structure of complexes (**1-4**)

Spectroscopic and magnetic moment studies were reported for the oxovanadium(IV) complexes of (salen) and its derivatives which were obtained by substitution at the methylene linkage.75 Reactions of [VO(salen)] (complex (**8**)) produced several types of complexes of the metal ion. Thus, reaction of complex (**8**) with iodine to replace the oxygen atom by I_2 and produce [VI_2(salen)] which may undergo other replacement reactions produced the mixed vanadium(IV)-vanadium(V) complex [(salen)VOVO(salen)] I_5.76 An X-ray crystal structure of this complex revealed that the cation is a discrete bimetallic with the form; shown in Figure 8.

Other complexes were also prepared76,77 from similar reactions with [VO(salpen)] and [VO(salphen)]. The complexes VX_2L (X = Cl or Br; L = salen or salphen) react78 with Li(OMe) in MeOH to yield [$V(OMe)_2L$] (complex (**10**)) which reacts with water to produce [VOL]. The phenylhydrazine complex [$V(NH_2NHPh)_2$salen] I was described70,78 and the biological significance of vanadium ions realized.79 [VI_2(salen)], complex (**11-a**), was prepared from reaction of [VO(salen)] with Me_3SiI (1:2 molar ratio) in CH_2Cl_2. The structure of this complex was determined80 by X-ray diffraction to be octahedral (Figure 9). Complex (**11-b**) was prepared as described before.

Recently, several important conclusions were reported81 regarding the reactivity of [VO(salen)], complex (**8**). First, removal of an oxide ion from complex (**8**) produces the hypothetical species $[V(salen)]^{2+}$, which reacts with complex (**8**) in the reaction mixture to form an aggregated chain of the general formulation $\{V_nO_{n-1}\}$. The value of n is determined by the molar ratio of the two species. Second, reactions of HX (X = Cl or Br) with complex (**8**) proceed as follows:

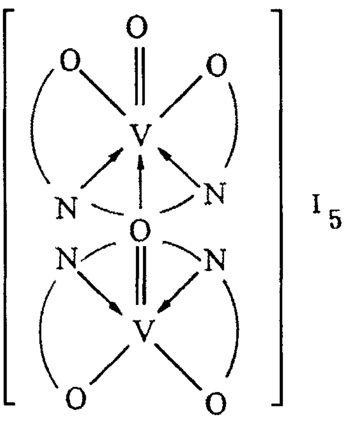


FIGURE 8 Formulation of [(salen) VOVO(salen)] I_5.

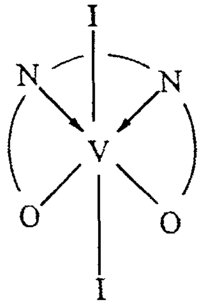


FIGURE 9 Structure of [VI_2(salen)].

$$[\mathrm{VO(salen)}] \overset{2H}{\rightleftarrows} [\mathrm{V(OH_2)(salen)}]^{2+} \overset{2X}{\longrightarrow} \mathrm{VX_2(salen)} + \mathrm{H_2O}$$

Reaction of [VO(salen)] with $HBF_4{\cdot}Et_2O$ produced complex (**12-a**), formulated as [V(salen)OV(salen)OV(salen)OV(salen)] $[BF_4]_2$, Figure 10. The basic chain in complex (**12-a**) is

$$[\mathrm{V = O \rightarrow V - O - V \leftarrow O = V}]^{2+}$$

The product of reaction between [VO(salen)] and HI was hoped to be [VI_2(salen)],81 but X-ray diffraction proved the structure to be [{[V(salen)]$_2$O}$_2$][I_3]$_2$ (complex (**12-b**)) which contains the unit ($V^{IV} - O - V^{III}$), Figure 10.

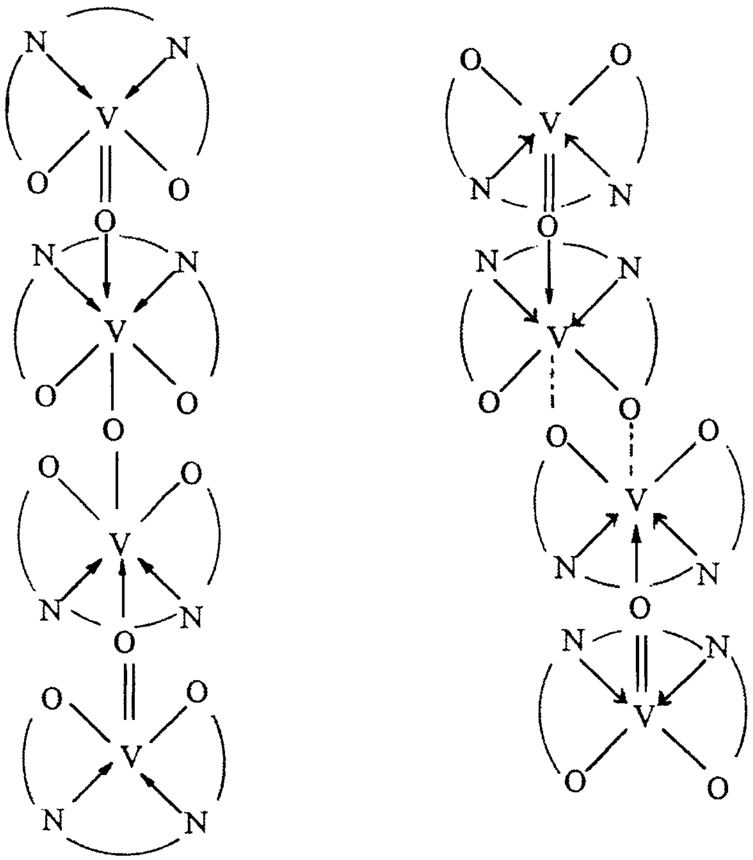
Two classes of vanadyl(IV) complexes of Schiff bases were identified.82 Both are essentially five coordinate. In the first class, the complexes are green and the oxide ion has no tendency for intermolecular interactions (ν (V = O) at *ca.* 980 cm^{-1}). In the second class, the yellow-brown complexes (ν (V = O) at *ca.* 880 cm^{-1}) polymerize in the crystal through a self-assembly metallosupramolecular structure of the type:

$$\mathrm{V = O \rightarrow V = O \rightarrow V = O \ldots}$$

The crystal structure of [VO(salnptn)] (complex (**13**)) revealed that the complex is polymeric in the solid state with the metallosupramolecular structure discussed above. The coordinated atoms of the ligand are coplanar but the ligand framework exhibits an umbrella-shaped structure; Figure 11.

The [VO(salen)] complex is unambiguously five coordinate,83 but when oxidized by perchloric acid forms84,85 the complex [VO(salen)][ClO_4] which showed a very weak V-$OClO_3$ interaction *trans* to the V = O bond (complex (**14**)). A surprising coordination mode was also reported82 for the ligand in the complex [VO(OMe)(salnptn)], complex (**15**). In this case, the (OMe) group and the vanadyl oxygen are coordinated *cis* to each other and the (salnptn) ligand occupies three equatorial and an axial coordination position.82 Reaction of [VO(salen)] with $HBF_4 \cdot Et_2O$ in air produced85 the diamagnetic [{VO(salen)}$_2$(μ-F)]BF_4 (complex (**16**)) consistent with the presence of vanadium(V). The structure of the cation is shown in Figure 12 with an almost linear OVFVO.

The magnetic moment of V(III), and V(IV) (two unpaired electrons and one unpaired electron, respectively) facilitated characterization of molecular association in the vanadium complexes.86,87 However, for [{VO(salpen)}$_2$], complex (**17**), the crystal structure showed88 infinite linear chains of molecules linked by



complex (12-a)

complex (12-b)

FIGURE 10 Structure of the cation of complexes (**12-a**), [{V(salen)OV(salen)}$_2$O] [BF_4]$_2$ and (**12-b**), [{[V(salen)]$_2$O}$_2$][I_3]$_2$

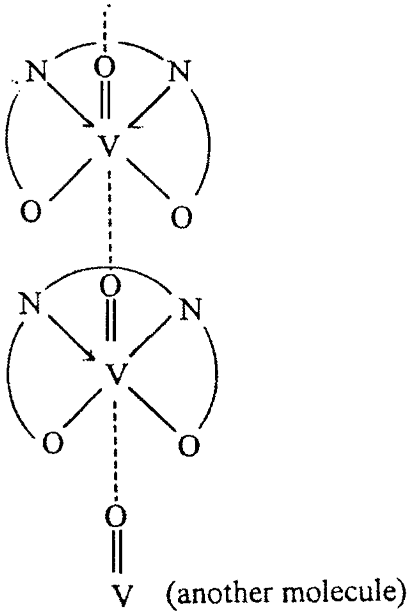


FIGURE 11 Structure of [VO(salnptn)] with the polymeric chain.

vanadyl oxygen bridges although the magnetic moment was not shifted to a significantly lower value and the complex obeys the Curie-Lewis law with Θ = −7° K. These results indicated that the vanadyl oxygen bridges did not contribute to the antiferromagnetic interaction.

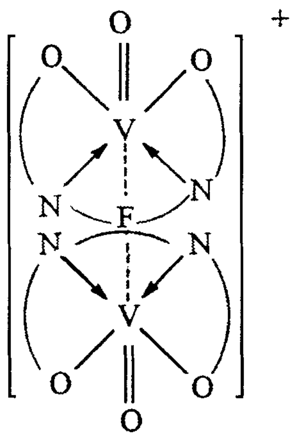
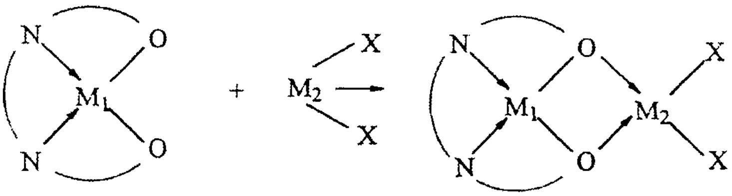


FIGURE 12 Structure of the cation of the complex [{VO(salen)}$_2$ (μ-F)]BF$_4$.

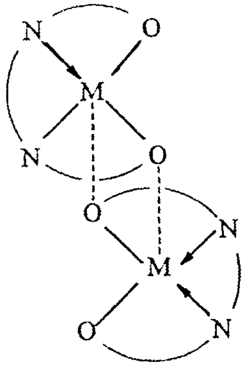
TRENDS IN THE METALLOSUPRAMOLECULAR STRUCTURES

The metallosupramolecular structure was recently5,6 defined as that structure in which intermolecular interactions involve the ligand and the metal ion. Four types of metallosupramolecular structures could be distinguished by applying this definition to the published data (Figure 13).

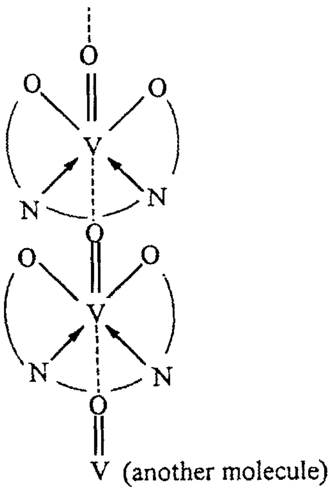
Type (a):



(a)



(b)



(c)

FIGURE 13 Types (a), (b) and (c) of metallosupramolecular structures (see Figure 12 for type (d)) M_1 and M_2 in type (a) are either similar or dissimilar metal ions.

In this case the coordinated oxygen atom (*e.g.*, phenoxy oxygen of salicylideneimine) donates an electron pair to another similar or dissimilar metal ion whereby the metal complexes are ligands,89-93 Figure 13-a.

Type (b):

The self-assembly process in this case produced a dimeric (Figure 13-b) or polymeric structure.63,64 The coordinated oxygen atom of either salicylideneimine or acetylacetoneimine and the metal atom of each molecule contribute to the molecular association process. The metal complex could accept an electron pair from the Lewis base site of the ligand of another complex. In this case, the former complex behaved as a metal ion.

Type (c):

The self assembly process in this case takes place *via* the bridged oxovanadium(IV) to another metal ion to produce either polymeric complexes82 or complexes whose formulations are dependent on the reaction conditions.81 Accordingly, the donor molecule reacted as a ligand whereas the acceptor molecule reacted as a metal ion (Figure 13-c).

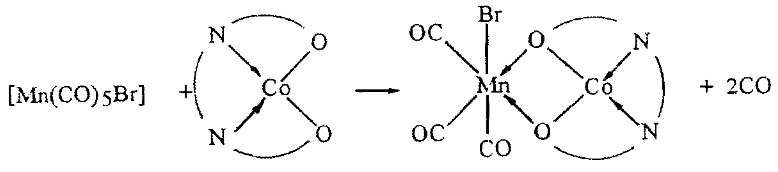
Type (d):

Dimerization of molecules is achieved in this case through a fluoride bridge between two metal ions. This is represented by complex (**16**), Figure 12.

The above mentioned types of metallosupramolecular structure should be distinguished from supramolecular structures where the intermolecular interactions involve the organic part of the associated molecules. Our recent reports94,95 of this type of interaction showed that the supramolecular structure for the Ni(II) complexes of vicinal oxime-imine ligands could induce chelate isomerism in the same molecule as a result of molecular association through the intermolecular hydrogen bonding.

Cobalt Complexes

Type (a) of the metallosupramolecular structure is shown by the product of the reaction of either [Co(salen)] or [Co(salphen)] with [Mn(CO)$_5$Br] in a variety of solvents which resulted96 in substitution of two carbonyl groups to produce complexes of general formulation [(ML)Mn(CO)$_3$Br], L = (salen) or (salphen), reaction 5.



(5)

Reaction of [Co(salen)] with pyridine is an example of metallosupramolecular interaction in which the metal complex behaved as a metal towards the Lewis base.13-29 The reaction of [Co(salphen)] with $NaBPh_4$ in THF (reaction 3) represented the formation of the metallosupramolecular structure where the cobalt(II) complex reacted as a ligand (through the phenoxy oxygen) by coordination to the sodium ion.38

Iron Complexes

Type (b) metallosupramolecular structure is exhibited by several iron(III) and iron(II) complexes. Thus, the reaction of either imidazole or its derivative40,41 with [Fe(salen)Cl] illustrated the strong tendency of the iron(III) complex to react as a metal ion (Figure 4). The latter iron(III) complex reacted similarly with the basic nitrogen of the imidazolate chelate.40

Type (b) of the self-assembly metallosupramolecular structure is also shown by dimerization of $[\{Fe(acen)\}_2]$, (to produce the five-coordinate Fe(II) ion; Figure 6-b) as well as the probable64 polymerization of $\{FeL\}_2$ (L = (salpen), (salben) or (salphen)) to form a six-coordinate Fe(II) ion.

Vanadium Complexes

The most interesting vanadium complexes are listed in Table I. Some of those complexes have a metallosupramolecular structure.

Type (b).

This type is illustrated by complexes (**2**) and (**6**); Table I (Figure 7). Dimer formation resulted through side coordination of the phenolate oxygen of the ligand with the metal atom of the adjacent molecule.

Type (c).

This type is characteristic for the oxovanadium(IV) ion and is represented by complexes (**11-b**), (**12-a**), (**12-b**) and (**17**) of Table I (Figures 8, 10 and 11). Dimerization and chain formation of the metal complexes is based upon the tendency of the oxygen of the oxovanadium(IV) ion to bridge.

Type (d).

This is represented by complex (**16**) (Figure 12) where the fluoride ion bridges two pentavalent vanadium species.

As far as we are aware these tendencies were only investigated for homonuclear metal complexes. However, it appears feasible that the donor-acceptor tendency of the oxovanadium(IV) could be combined easily with acceptor behaviour of the metal ions in the iron complexes (*e.g.*, [Fe(salen)Cl] or [Fe(acen)Cl]) or the cobalt complexes (*e.g.*, Co(salen) or Co(acen)).

Moreover, it seems that the possible formation of a metallosupramolecular structure by the metal ion is a direct consequence of the coordinative unsaturation of the metal ion. We have shown that this behaviour by the metal complex implied its reaction as a metal ion towards other ligands.97-103 This unsaturation obviously affected the geometry of the (salen) coordination with vanadium ions. Thus, in the six-coordinate environment (Figure 10, complex (**12-b**) the metal lies in the plane81 of the donor atoms of (salen) but moved by about 0.3-0.5 Å towards the oxygen of the double bond of V = O when the coordination is five. This facilitates donating an electron-pair to another coordinatively unsaturated ion of an adjacent molecule. The structure of the cation of complex (**12-b**) $[\{[V(salen)]_2O\}_2]$ indicates that types (b) and (c) of the metallosupramolecular structures are operative in this complex.

TRENDS IN THE MOLECULAR STRUCTURES

The structure of the non-associated cobalt, iron and vanadium complexes of dianionic tetradentate Schiff bases of (salen) and (acen) as well as their analogues are detailed in sections 2-4. An interesting behaviour of the imidazole adduct (and related bases) with molecular complexes of cobalt and iron is the spin-crossover. This was described in terms of two potential energy surfaces for the high- and low-spin molecules, respectively, with a very small zero point energy difference between the two states.104 Studies of this type are relevant in relation to the factors that determine the spin-state changes in axially ligated systems found in some iron proteins.104-106 Further details on this subject are beyond the scope of this review.

CONCLUSION

Metallosupramolecular structures of cobalt, iron and vanadium complexes of dianionic tetradentate Schiff bases of salicylideneimine and acetylacetoneimine are characterized and classified into four types depending on the Lewis acid—Lewis base relationship within the molecule.

Chemical understanding of the metallosupramolecular structures allows application to the preparation of homo- and hetero-binuclear (also polynuclear) metal complexes with similar or mixed ligands. This is because each molecule of the Co, Fe or V complexes contains a strong Lewis acid (the metal ion) as well as a reactive Lewis base (the coordinated oxygen atoms of the ligand). In some cases like the oxovanadium(IV) complexes, the metal ion comprises both acid and base centers. The other types (b-d) discussed above are considered self-assembly. However, their reactions with other molecules did not receive proper attention.

Acknowledgements

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