Coordination Chemistry Reviews, 23 (1977) 31—117

TRANSITION METAL COMPLEXES WITH BINUCLEATING LIGANDS

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(Received 28 July 1976)

CONTENTS

A. INTRODUCTION

Metal chelation is involved in many important biological processes [1] where the coordination can occur between a variety of metal ions and a wide range of ligands. Generally the chelating ligand is a polyfunctional molecule which can encase the metal in an organic sphere.

Many types of ligands are known and the properties of their derived metal chelates have been investigated [2,3]; however there is a need for the synthesis of new ligands of specific design which could lead to metal complexes with special and predictable properties.

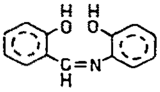
The aim of this review is a critical investigation of ligands which can coordinate more than one metal in their coordination sites. The design of such ligands must take into account the factors influencing the stability and the molecular geometry of the metal complexes.

The discussion is restricted to the more common binucleating ligands containing nitrogen, oxygen and sulphur as donor atoms. Emphasis is placed on the preparative routes to the ligands and the complexes and on their physicochemical properties and structures. Many of the structures proposed are drawn in a way which emphasises the donor atom sites and the type of coordination involved in the complexes; such structures do not necessarily reflect the exact geometry of the ligand itself.

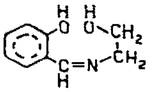
B. COMPLEXES WITH POTENTIALLY TERDENTATE SCHIFF BASES

The ligands, derived by condensation of a primary amine and an active carbonyl group, contain the azomethine group —C=N—. They form stable complexes with metal ions especially if the amine and/or the carbonyl compounds contain a second functional group sufficiently near the site of condensation to form a five- or six-membered chelate ring upon chelation [4]. There are many publications dealing with metal chelates formed by Schiff bases [5], however, at this time, there is a lack of information concerning binucleating Schiff base ligands.

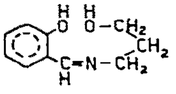
Most of the binuclear complexes have been prepared from tridentate Schiff bases containing ONO or ONS donor atoms; they are derived from the condensation of salicylaldehyde or acetylacetone with *o*-aminophenols, aminoalcohols, *α*-aminoacids, *o*-aminothiophenols and aminothiols. The structural formulae for a series of tridentate ligands, depicted in their Schiff base form, are [6]



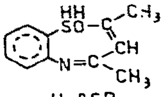
H_2SAP



H_2SAE



H_2SPA



H_2ASP

Their characteristic IR absorption bands and ^1H NMR data are given in Tables 1 and 2.

The IR spectrum of H_2SAP in DMSO shows several bands in the hydroxyl stretching frequency region and their weakening and shift to lower energy in the solid state is compatible with extensive intramolecular H-bonding. Some of the strong IR bands near 1600 cm^{-1} are doubtless associated with C=N stretching frequencies but any assignment to uncoupled ν(C=N) is unwise in view of the recent isotopic labelling study indicating an extensive vibrational coupling in Schiff bases derived from salicylaldehyde [7]. In the ^1H NMR spectra, the resonance peaks at 13.75δ disappear on addition of D_2O. This substantiates the IR assignment of the presence of intramolecularly-bonded hydroxyl groups. The single proton, which does not exchange with D_2O, giving a singlet at 8.95δ, has been assigned to the azomethine proton.

Similarly, the ligands H_2SAE and H_2SPA involve a C=N linkage strongly hydrogen-bonded to the hydroxyl hydrogen atoms. The band at 1638 and 1635 cm^{-1} in the IR spectra of H_2SAE and H_2SPA, respectively, have a strong ν(C=N) component because they shift to higher frequencies in DMSO where the intramolecular hydrogen bond is weakened. The single proton resonance in the ^1H NMR spectra of these ligands occurring near 8.2δ in $CDCl_3$

TABLE 1

Characteristic IR bands of some Schiff base ligands (cm^{-1})

Compound	Solvent	3600–2500 cm^{-1}	1700–1500 cm^{-1}
H_2SAP	CCl_4	3050w, 2925w, 2620w, 2580w	1638s, 1620m, 1600m, 1542sh, 1532s, 1510w
	dmso	3530s, 3200s, b, 2880s, b	1630vs, 1605s, 1585sh, 1504w
H_2SAE	CCl_4	3370s, b, 2940s, 2890s	1638vs, 1616s, 1585m, 1532m, 1500s
	dmso	3350vs, b, 2750vs, b	1655sh, 1610vs, b, 1510vs, 1502vs
H_2SPA	CCl_4	3400s, b, 2940s, 2870s	1635vs, 1615sh, 1582m, 1530m, 1498s
	dmso	3430vs, b, 2900m, b	1650vs, b, 1605sh, 1520s
H_2AAP	CCl_4	3140–2980b, 2880sh, 2740m, 2630m	1613vs, 1560vs, 1515m, sh
	dmso	3510m, 3430m, 3190vs, 2850s, b, 2740s, b, 2620m	1625vs, 1605vs, 1578vs, 1520s, 1503sh
H_2ASP	CCl_4	3340s	1715vs, 1588vs
	dmso	3500vs, b, 3270vs, b	1725vs, 1675sh, 1592vs, 1485vs

s = strong, m = medium, b = broad, v = very, sh = shoulder, w = weak.

TABLE 2

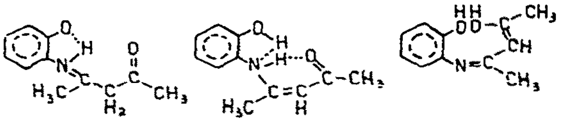
^{1}H NMR data for some Schiff bases (p.p.m.)

Compound	—N=CH—	—OH and/or NH	Other resonance peaks
H_2SAP	8.95	13.75, 9.64	—
H_2SAE	8.57 (8.19)	ca. 7.1	3.68
H_2SPA	6.59 (8.25)	ca. 7.1	3.50, 1.78
H_2AAP	—	12.22, 9.90 (12.08, 8.10)	5.24, 1.97
H_2ASP	—	6.43 (4.97)	3.20, 2.14, 1.63

In dmso-d_6 or $CDCl_3$ (in parentheses), TMS as internal standard. Broad multiplets centered at ca. 7.1 p.p.m., due to the phenyl proton, are omitted.

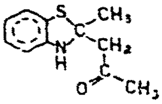
and 8.6δ in DMSO-d_6 has been assigned to the azomethine. The hydroxyl proton resonance signals are masked by phenyl proton resonance peaks. This upfield shift of the hydroxyl proton chemical shifts for these compounds compared to H_2SAP was attributed to the greater shielding of the hydroxyl protons by the more basic nitrogen atoms of the two compounds derived from aliphatic amines.

Although the structure of the condensation product of acetylacetone with *o*-aminophenol (H_2AAP) is depicted in the Schiff base form, it can be formulated also in the ketoimine or ketoamine forms



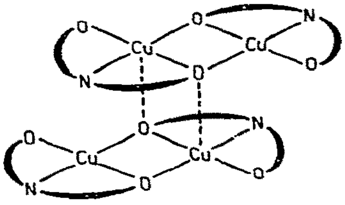
H_2AAP

The ligand derived from acetylacetone and *o*-aminothiophenol (H_2ASP) seems to have the heterocyclic benzothiazoline form



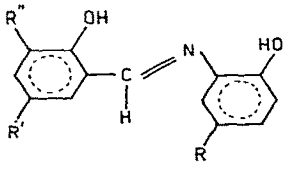
The physico-chemical data agree well with such a formulation. When these ligands react with metal ions, their tridentate character causes polymerisation and polynuclear complexes with anomalous magnetic properties can be obtained. It was presumed that the copper(II) atoms of these chelates would have an unusual coordination number of three [8—11]. These complexes show magnetic moments considerably smaller than the theoretical value predicted from the presence of one odd electron. A possible explanation for these subnormal moments was afforded by the formation of binuclear complexes with a possible copper—copper interaction [8]. The binuclear nature has been confirmed by an X-ray structural analysis of acetylacetone-mono-(*o*-hydroxyanil)copper(II) [12,13]. The dimeric molecules are arranged in layers parallel to the (110) plane separated by a 3.50 Å distance. The two copper atoms in the unit are bridged together by the phenolic oxygen atoms of the ligands, the copper—copper distance being 2.99 Å. Each copper atom is surrounded by four oxygens at the corners of a very distorted square and, although each copper of the dimeric unit has an identical arrangement, they have different environments. One copper atom forms a distorted square pyramid with an oxygen from another dimeric molecule, the other has square planar coordination. It was suggested that the ligand is coordinated in its ketoamine form (Fig. 1).

More recently the magnetic properties of the complex acetylacetone-mono-(*o*-hydroxy-5-nitroanil) copper(II) have been described using a four-centre exchange-coupled model [14]. The agreement between the experimental and calculated susceptibility values being in satisfactory agreement with the tetrameric model structure

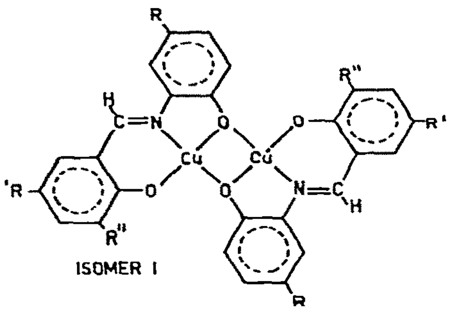


It should also be noted that a small concentration of paramagnetic impurities would bring the binuclear structure model to still closer agreement with experimental data [15].

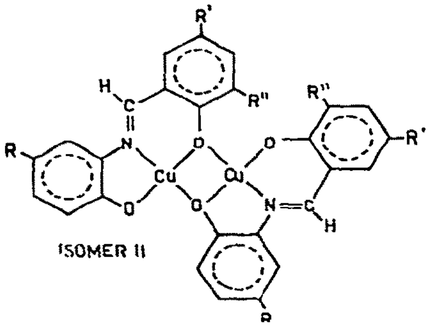
The interaction of the Schiff bases, derived from 5-substituted salicylaldehyde and substituted and unsubstituted *o*-aminophenol, of the type



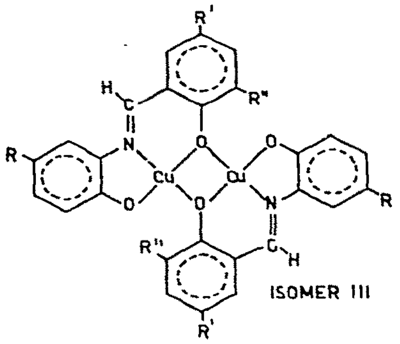
with transition metal ions have been investigated [10,16—19]. The copper complexes have a magnetic moment lower than the spin-only value per copper(II). This has been attributed to dimerization in the solid state, leading to a copper—copper interaction [17]. Three isomers can be depicted for these complexes



ISOMER I



ISOMER II



Isomer I has the bridging oxygens from the aminophenol moieties. In isomer II, one bridging oxygen comes from the aminophenol and the other from the salicylaldehyde moiety. The third isomer (III) could have both bridging oxygens from salicylaldehydes [18]. Even if evidence for the existence of isomers has been obtained, it was impossible to separate them. For the compound where $R''=NO_2$ the isomers II and III can be rejected on the grounds of steric interaction [18]. The electronic spectra of these complexes are very similar and show a multicomponent band system covering the spectral range from 350 to 500 nm. The spectra appear quite simple, perhaps due to the overlapping of a number of the bands in the chromophore region; *d—d* transitions have been found at about 450 nm. There are no features in the spectra which would serve to differentiate them from the mononuclear complexes obtained by dissolving the binuclear species in pyridine.

The magnetic properties of these binuclear complexes have been investigated over a temperature range of approximately 280°. The behaviour of χ_M against T is as expected for an antiferromagnetic exchange in the pres-

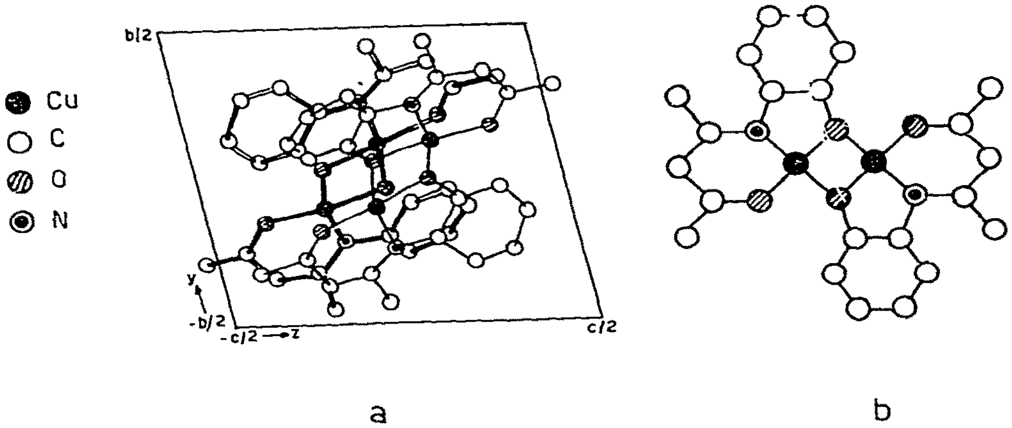
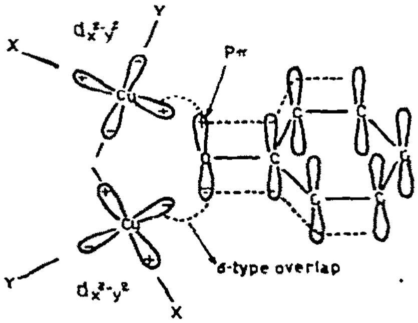


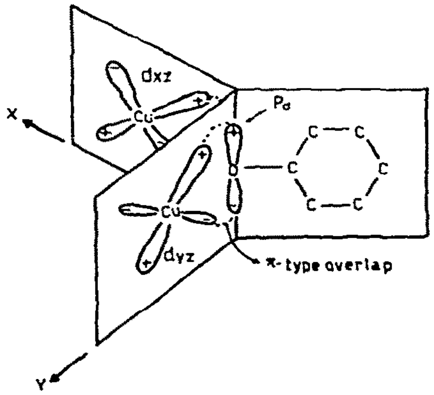
Fig. 1. a, The arrangement of the atoms in the unit cell of acetylacetone-mono-(o-hydroxyanil)copper(II). b, View in the plane perpendicular to $\mathrm{Cu}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\lozenge}}\mathrm{Cu}$ ring.

ence of a small amount of a paramagnetic impurity. It has been observed that the magnetic properties are markedly affected by the nature and the position of the substituent on the chelate ring; electron-withdrawing groups increase the exchange interaction if they are introduced into the salicylaldehyde but decrease it if they are introduced into the *o*-aminophenol. The following order for $|J|$ (R,R′) has been found [19]

$J(\text{H, Cl}) \sim J(\text{H, Br}) > J(\text{NO}_2, \text{NO}_2) > J(\text{H, H}) > J(\text{H, CH}_3) > J(\text{NO}_2, \text{H}) > J(\text{Cl, H}) \sim J(\text{Cl, Cl})$

From the structure in Fig. 1, it appears that a direct metal—metal interaction is not possible; spin coupling must therefore take place by a superexchange interaction using the following two pathways

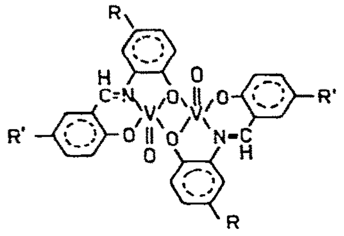




The σ-type is considered more effective for electron migration and the bond angle Cu—O—Cu is the most important factor in determining the electron exchange. In these complexes the ligands differ only by the substituent in the aromatic rings, the bond angles are about the same and the π-pathway should be the main factor.

This factor is reflected in the variation of J, the coupling constant, with the electron density on the bridging oxygen atoms. Substituents on the chelate rings which remove the electron density from the p_z orbitals of the bridging oxygen atoms give rise to lower singlet—triplet splitting energies. Similarly, electron-donor substituents in the chelate rings stabilize the singlet state and give rise to higher J values. The analogous vanadyl(IV) complexes have been prepared by the reaction of vanadyl(IV) chloride with the tridentate ligands [20,21]. On the basis of elemental analyses of the vanadium and nitrogen, it was previously suggested that these complexes contain a water molecule strongly held to vanadyl ion [20,21].

Ginsberg et al. [22] have proposed that these complexes are anhydrous with the exception of $[(5\text{NO}_2\text{—N(2-hydroxy-4NO}_2\text{-phenyl)salicylideneimine)VO}]_2$ which has a band at 3300 cm^{-1} attributed to ν_{OH} of water or ethanol. Their low magnetic moments at room temperature suggest the structure



The complexes with R = Cl, R′ = H and R = R′ = Cl show two V=O stretching bands [22], separated by about 10 cm^{-1}; this separation was attributed to the unit cell group or to a crystal packing effect which causes the two vanadium atoms to be inequivalent. In the complex with R = NO_2 and R′ = H the separation is 110 cm^{-1}. This suggests an interaction of the vanadyl oxygen in each dimer molecule with a vanadium atom in a second molecule to form a tetranuclear or highly polymeric unit.

In the electronic spectra of all these complexes the band around 700 nm was assigned to the d_{xy}—d_{xz} transition and the band around 527 nm was assigned to the d_{xy}—$d_{x^2-y^2}$ transition. The magnetic moments of these complexes except for R=R′=NO_2 decrease as the temperatue is lowered; their $|J|$(R,R′) values are in the order

$$J(\mathrm{H, NO_2}) > J(\mathrm{Cl, Cl}) \sim J(\mathrm{H, H}) \sim J(\mathrm{Cl, H}) \sim J(\mathrm{H, Br}) > J(\mathrm{H, Cl})$$

The substituents in the ligands at R and R′ positions influence the J values in the vanadyl(IV) and copper(II) complexes in different ways.

In the vanadyl complexes the J values are not sensitive to the substitution of R and R′; this is attributed to the difference in the exchange mechanism

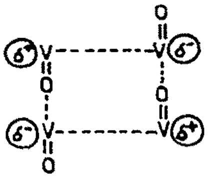
TABLE 3

Exchange integral values (cm^{-1}) for vanadyl(IV) and copper(II) Schiff base complexes and related V=O stretching frequencies (cm^{-1}) [22,19]

Complex		$\nu_{V=O}$	$-J$	
R	R′		VO(IV)	Cu(II)
H	H	990s	125	289
H	CH_3	993s	118	245
H	Cl	992s	90	371
H	Br	901s	115	341
H	NO_2	1010m—900vs	218	—
Cl	H	1000s—989s	120	—
Cl	Cl	983s—993s	132	—
NO_2	NO_2	999s	—	307
H	Cl monopyridinate	978s	—	—

operating in the vanadyl(IV) and copper(II) dimeric complexes. In the vanadyl complexes the coordination around the metal atom has been assumed to be a distorted square pyramid. For this configuration the unpaired vanadium electron is expected to be in the $3d_{xy}$ orbital [23,24]. In the bridging atoms both the $2p_x$ and $2p_y$ orbitals are involved in strong bonding and therefore do not donate to the vanadium $3d_{xy}$ orbital. The $3d_{xy}$ orbital is therefore lowered in energy with respect to the $3d_{xz}$ and $3d_{yz}$ orbitals. In the binuclear complexes the $3d_{xy}$ orbital has the appropriate symmetry for an overlap with the $3d_{xy}$ orbital of another vanadium atom. It is believed that the magnetic exchange in the oxovanadium(IV) complexes is mainly due to this metal—metal interaction [20]. J is then relatively independent from the substituent R and R′ in the benzene ring.

The fact that $J(\mathrm{H}, \mathrm{NO_2})$ is considerably higher than the other exchange integrals may be explained with a tetranuclear structure of the type



where V=O · · · · V=O interactions are operating.

As a consequence the effective charge of one vanadium atom in each pair increases and that of its partner decreases resulting in an increase of the magnetic interaction of two adjacent vanadium atoms. Copper(II) and oxovanadium(IV) complexes of the Schiff bases, derived from 2-hydroxynaphthaldehyde and 4-substituted *o*-aminophenol (4 R = H, Cl, NO_2), have been prepared [25—27].

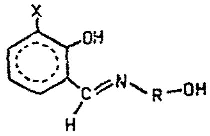
The magnetic moment at room temperature of the (2-hydroxynaphthylidene-*o*-aminophenol)Cu(II) is 1.39 BM, this is abnormally small and consistent with a dimeric structure. The vanadyl(IV) complexes show magnetic properties very similar to the complexes derived from salicylaldehyde and *o*-aminophenol [22]. The J values of these compounds are in the order

$$J(4\text{-}\mathrm{NO_2}, \mathrm{H}) > J(4\text{-}\mathrm{Cl}, \mathrm{H}) > J(4\text{-}\mathrm{H}, \mathrm{H}).$$

However, the data indicate that J is relatively unaffected by the substituents in the benzene ring.

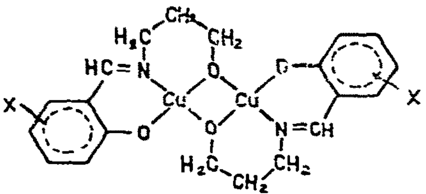
The coordination around the vanadium atom is assumed to be distorted square pyramidal. On treatment of the complex (R = R′ = H) with a strong chelating agent, such as *o*-phenanthroline, the dimer is broken, with the formation of a mononuclear complex VO(2-hydroxy-*o*-aminophenol) (*o*-phenanthroline) [27]. Similar complexes have been independently prepared by other authors [25,26] by the reaction of these Schiff bases with vanadyl(IV) chloride in water.

The synthesis and properties of binuclear copper(II) complexes derived from salicylaldehyde and aminoalcohol

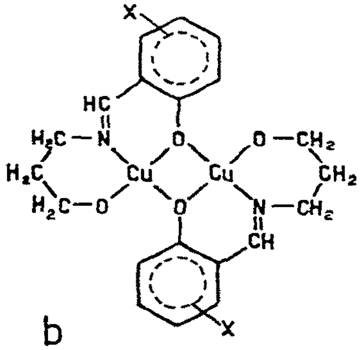


have been described [28—31].

The molecular weight data for one of the compounds, $[Cu(salN(CH_2)_3O]_2$ in $CHCl_3$, are in accordance with a binuclear structure. For these complexes two dimeric configurations are possible, one with bridging alcoholic oxygen atoms (a) and the other with bridging phenolic oxygen atoms (b)

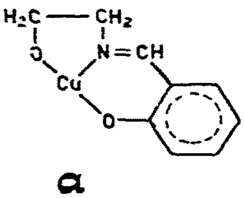


a

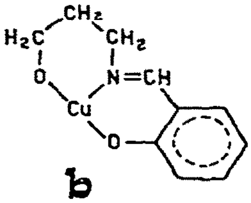


b

The experimental data seem to indicate that the configuration (a) is preferred [29]. The stability of these dimeric complexes would be essentially determined by the nature of the bridging groups and the electronic atmosphere of its neighbours in the chelate ring. If the phenolic oxygen atoms bridge between the two copper(II) ions, the stability of the complexes would be about the same. On the other hand, if the alcohol oxygens are the bridging atoms in the complexes



a



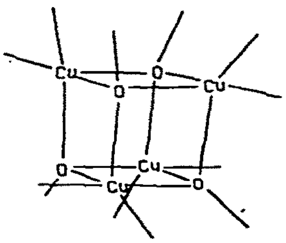
b

the stability should be quite different owing to the different size of the chelate rings involving the bridging oxygens. The preparation of the monomeric complexes of the type (a) with a water molecule was reported [32]; the same complex cannot be prepared for the ligand in (b). In contrast, the dimeric complex can be prepared only with the ligand in (b).

Comparative magnetic studies of the dimeric copper(II) compounds indicate that the magnetic moments for the complexes with bridging phenolic oxygens are usually greater than those of the complexes with bridging alcoholic oxygen atoms [33,34]. The observed magnetic moments for the complexes in Table 4 of about 0.5 BM per copper(II) ion are much smaller than those observed in the complexes containing phenolic oxygen bridges. These results indicate that the dimeric structure with alcoholic oxygen is most probable for these complexes.

When the hydroxypropyl group is shortened to hydroxyethyl or substituted hydroxyethyl, the magnetic moments of the complexes at room temperature are in the range 1.77—2.09 BM (Table 4). All these complexes involve a five-membered ring. In all cases the susceptibility curves are linear in the temperature range 80—300 K. The extrapolated linear portion of each curve intercepts the temperature axis at a positive value, indicating the existence of ferromagnetic interaction. Their structures consist of a tetrameric molecule in which the four copper ions are bridged tetrahedrally (Fig. 2) in accordance with the molecular weight determinations on the complex $[Cu(salN(CH_2)_2O]_4$. Their normal magnetic moments have been attributed to a negligible π-type superexchange interaction among the four copper(II) ions via the bridging oxygen atoms. The ferromagnetic interaction has been explained by a σ-type superexchange resulting when three sp^3 orbitals of a bridged atom form a σ-bond with the $d_{x^2-y^2}$ orbitals of three copper(II) ions. Recently the crystal and molecular structures of $[Cu(5NO_2\text{-}salN(CH_2)_3\text{-}O)]_2$ and $[Cu(5Me\text{-}salN(CH_2)_3O]_2$ have been studied [35].

The first complex contains dimeric molecules with an intramolecular Cu · · · Cu separation of 3.0 Å. In the intermolecular Cu · · · Cu separations



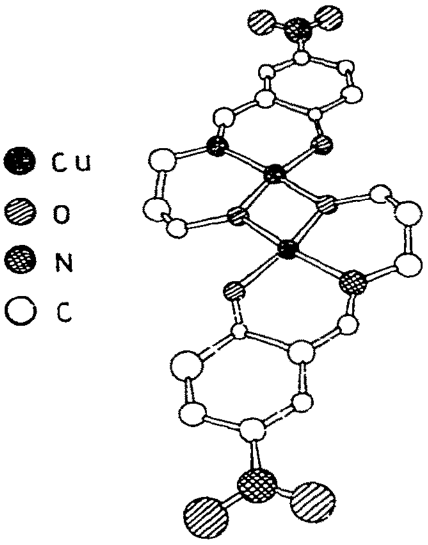


Fig. 2. Tetrameric skeleton of $[Cu(salNCH_2CH_2O)]_4$ molecule.

Fig. 3. The molecular structure of $[Cu(5NO_2\text{-}salN(CH_2)_3O)]_2$.

TABLE 4

Magnetic moments (BM) at various temperatures (K) for salicylaldimine-alcohol copper(II) complexes

Cu(salNCH$_2$CH$_2$O)	2.09 (76.4)	1.94 (140.3)	1.92 (180.6)	1.87 (288.0)
Cu(salNCH$_2$CH$_2$O)H$_2$O	2.04 (76.2)	1.95 (155.7)	1.93 (189.6)	1.89 (283.1)
Cu(salNCH$_2$CH(CH$_3$)O)	2.00 (76.4)	1.91 (147.1)	1.89 (177.0)	1.84 (286.2)
Cu(salNC(CH$_3$)$_2$CH$_2$O)	2.41 (76.4)	2.19 (160.7)	2.14 (190.6)	2.09 (286.1)
Cu(salNCH$_2$CH$_2$CH$_2$O)	— (76.2)	0.07 (150.1)	0.13 (193.0)	0.37 (276.7)
Cu(5 NO$_2$salNCH$_2$CH$_2$O)	1.87 (76.4)	1.82 (140.7)	1.81 (180.0)	1.77 (286.5)

$N\alpha = 60 \cdot 10^{-6}$ cgsu.

TABLE 5

Magnetic moments (BM) at various temperatures (K) for salicylaldimine-alcohol copper(II) complexes [31]

Cu(salNCH$_2$CH$_2$OH)NO$_3$	1.81 (81.0)	1.80 (142.7)	1.81 (185.3)	1.80 (300.5)
Cu(salNCH$_2$CH(CH$_3$)OH)NO$_3$	1.80 (76.4)	1.83 (143.6)	1.82 (183.2)	1.83 (289.1)
Cu(salNCH$_2$CH$_2$CH$_2$OH)NO$_3$	1.80 (76.4)	1.80 (141.2)	1.79 (178.8)	1.81 (301.0)
Cu(salNCH$_2$CH$_2$OH)ClO$_4$H$_2$O	0.16 (76.4)	0.37 (144.7)	0.85 (173.0)	1.27 (292.0)
Cu(salNCH$_2$CH$_2$OH)ClO$_4$ · 2 dmf	1.86 (76.2)	1.85 (159.6)	1.85 (199.8)	1.86 (290.5)
Cu(salNCH$_2$CH(CH$_3$)OH)ClO$_4$ · C$_2$H$_5$OH *	0.07 (76.2)	0.47 (143.2)	0.79 (197.3)	1.18 (294.8)
Cu(salNCH$_2$CH(CH$_3$)OH)ClO$_4$ · 2 dmf	1.82 (76.2)	1.81 (157.6)	1.81 (193.3)	1.81 (291.2)
Cu(salNCH$_2$CH$_2$OH)Cl	1.00 (76.4)	1.43 (145.1)	1.53 (179.8)	1.65 (289.7)
Cu(5 NO$_2$salNCH$_2$CH$_2$OH)Cl	1.79 (76.2)	1.82 (152.6)	1.79 (172.4)	1.80 (291.8)
Cu(salNCH$_2$CH(CH$_3$)OH)Cl · H$_2$O	1.82 (76.2)	1.81 (159.1)	1.82 (206.4)	1.83 (299.7)
Cu(salNCH$_2$CH$_2$CH$_2$OH)Cl **	— (76.1)	0.26 (140.3)	0.49 (180.0)	1.01 (300.0)

$N\alpha = 60 \cdot 10^{-6}$ cgsu; * $N\alpha = 40 \cdot 10^{-6}$ cgsu; ** $N\alpha = 50 \cdot 10^{-6}$ cgsu.

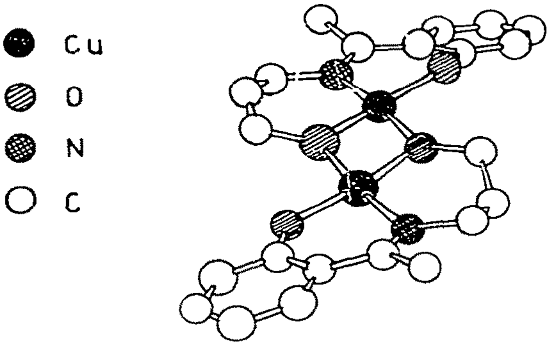


Fig. 4. The molecular structure of $[Cu(2CH_3\text{-}salN(CH_2)_3O)]_2$.

of 3.6 Å are too long for bonding interactions and the complex cannot be considered polymeric. The second complex contains well separated dimers.

The magnetic moments of these complexes show little temperature dependence: 0.30 BM the first and 0.26 BM the second at 273 K, 0.31 and 0.33 BM, respectively at 305 K. Thus the complexes are almost diamagnetic, owing to very strong antiferromagnetic coupling between the adjacent copper atoms with a singlet—triplet separation of the order of 1000 cm^{-1}. The structures and the magnetic properties of both complexes support a general correlation between decreasing strength of antiferromagnetic interaction and increasing distortion towards tetrahedral metal environment in binuclear copper(II) complexes [35]. Complexes of the type $Cu_2(RsalN(R)OH)X$ (R = $—CH_2CH_2—$, $—CH_2CH_2CH_2—$, $—CH_2CH(CH_3)—$, $—C(CH_3)_2CH_2—$; X = Cl^-, NO_3^-, ClO_4^-) have been prepared [30,31]. Their magnetic properties are significantly dependent upon the nature of the anion X [31]. The chloro complexes exibit normal paramagnetism in the temperature range 76—290 K; only $Cu(salN(CH_2)_2OH)Cl$ and $Cu(salN(CH_2)_3OH)Cl$ show antiferromagnetism. On the basis of the magnetic data the first complex probably has a binuclear structure with phenolic oxygen bridges. The electronic spectra of the complexes indicate a four coordination environment closer to planar than tetrahedral around the copper except $Cu(salN(CH_2)_3OH)Cl$ which shows pentacoordination with trigonal bipyramid configuration (Table 6). The structure of this pentacoordinated complex has been reported [36]

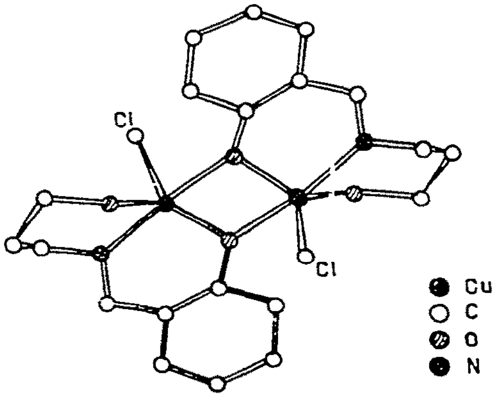


TABLE 6

Reflectance spectral bands in 340—1500 nm region of salicylaldimine-alcohol copper(II) complexes

Complex	Electronic spectral band maxima
$Cu(salNCH_2CH_2OH)_2$	390vs, sh 470s, sh (610, 680)s,
$Cu(salNCH_2CH_2OH)Cl$	380vs, sh 470s, sh 710s, br
$Cu(salNCH_2CH_2OH)NO_3$	360vs, sh 430s, sh 654s, br
$Cu(salNCH_2CH_2OH)ClO_4 \cdot H_2O$	425s 700s, br 880m, sh
$Cu(salNCH_2CH_2OH)ClO_4 \cdot 2\ dmf$	360vs, sh 430s, sh 594s, br 940m, sh
$Cu(salNCH_2CH_2O)$	390vs, sh 650s, sh
$Cu(salNCH_2CH_2O)H_2O$	355vs, sh 390s, sh 644s, br
$Cu(5\text{-}NO_2salNCH_2CH_2OH)_2$	410vs 600s, br 740m, sh
$Cu(5\text{-}NO_2salNCH_2CH_2OH)Cl$	410vs, sh 470m, sh 690s, br
$Cu(5\text{-}NO_2salNCH_2CH_2O)$	405vs 664s, br
$Cu(salNCH_2CH(CH_3)OH)_2$	390vs, sh 430s, sh 600s, br
$Cu(salNCH_2CH(CH_3)OH)Cl \cdot H_2O$	440s, sh 680s, br
$Cu(salNCH_2CH(CH_3)OH)NO_3$	360vs, sh 430s, sh 638s, br
$Cu(salNCH_2CH(CH_3)OH)ClO_4 \cdot C_2H_5OH$	420vs, sh 664s, br
$Cu(salNCH_2CH(CH_3)OH)ClO_4 \cdot 2\ dmf$	370vs, sh 410s, sh
$Cu(salNCH_2CH(CH_3)O)$	380vs, sh 650s, br
$Cu(salNC(CH_3)_2CH_2O)$	385s, sh 634s, br
$Cu(salNCH_2CH_2CH_2OH)_2$	390vs, sh (610, 650)s, br
$Cu(salNCH_2CH_2CH_2OH)NO_3$	488s, br 690s, br
$Cu(salNCH_2CH_2CH_2OH)Cl$	470s, sh (845, 950)vs, br,
$Cu(salNCH_2CH_2CH_2O)$	380vs, sh 570s, br 650m, sh
$Cu(salNCH_2CH_2CH_2OCH_3)Cl$	420vs, sh 470s, sh (840, 900)vs,

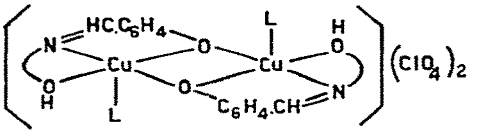
It consists of dimeric units of the complex with the phenolic oxygens bridging the copper(II) ions. The long copper—copper distance (3.29 Å) and the low magnetic moment found (1.01 BM at 300 K) suggest that direct interaction between the metal ions is not responsible for the subnormal magnetic moment. The four membered copper—oxygen ring, essentially planar, is unsymmetrical with a short copper—oxygen distance (1.78 Å) to the oxygen of the ligand chelated to the copper and a long copper—oxygen distance (2.22 Å) to the oxygen of the other ligand. The copper atom is five coordinated and the coordination approaches a trigonal bipyramid with the nitrogen and the oxygen in the axial positions.

The possibility of the interconversion reaction

$$[Cu(salN(CH_2)_3O)]_2 + HX \rightleftharpoons [Cu(salN(CH_2)_3OH)(X)]_2$$

has been studied [30]. When the complex $[Cu(salN(CH_2)_3O)]_2$ was treated with HCl in methanol, deep brown crystals have been obtained with identical physico-chemical properties to $[Cu(salN(CH_2)_3OH)(X)]_2$. The reverse conversion was effected by boiling this last complex in pyridine. In each case the reaction appeared to be complete in a few minutes. The interconversion reaction has not been found possible using hydroxyethyl in place of 3-hydroxypropyl. The nitrato complexes exhibit normal magnetic moments and their electronic spectra are characteristic of a four coordination environment with a slight distortion from the planarity.

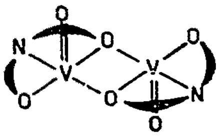
The IR spectra confirm that the nitrate group is coordinated but it is impossible to distinguish between mono- or bidentate coordination. The perchlorate complexes were obtained only as solvate adducts; their magnetic moments at room temperature are unusually low and their χ_A versus T data agree well with a binuclear structure of the type



$L = H_2O$ or C_2H_5OH

This square pyramidal configuration is in accordance with the IR and electronic spectroscopic data.

Oxovanadium(IV) complexes with the ligand $RsalN(CH_2)_nOH$ (R = H, 5-Cl, 5-Br, 5-NO_2, 5-MeO, 3-NO_2, 3-MeO; $n = 2, 3$) have been described [37—40] and were formulated as VO(ligand). The room temperature magnetic moments of the complexes with the ligands $RsalN(CH_2)_2OH$ are lower (0.89—1.41 BM) than the complexes with $RsalN(CH_2)_3OH$. It was inferred, on the basis of the magnetic data, that the alcoholic oxygens are bridging rather than the phenolic oxygen and in the absence of structural data the prediction of the structure was made on the basis of the magnetic data. The magnetic moments of these complexes decreased considerably as the temperature was lowered in accordance with an antiferromagnetic exchange interaction in binuclear structures. The IR spectra show characteristic $\nu V{=}O$ absorption bands in the range 880—998 cm^{-1}. These bands are usually very strong and broad and in some cases they split into two bands. Their electronic spectra show four bands around 714, 625, 526 and 400 nm; the last band is due to a charge transfer and/or to intraligand transition; the others were assigned to *d—d* transitions. For these complexes the structure



was assigned in which the ligands behave as tridentate dibasic species. Mononuclear, binuclear and trinuclear nickel(II) complexes of *N*-hydroxyethylsalicylaldimines (H_2L_a) and *N*-hydroxypropylsalicylaldimines (H_2L_b) have been reported [41]. In ethanol solution the ligands gave with NiX_2 (X = ClO^-_4, Cl^-, Br^-, NO_3^-) the mononuclear complexes [NiLX]. Only when strong bases were added to the reaction solution have the complexes $[NiLS]_2$ (S = 2-methoxyethanol, the solvent from which the complexes were

TABLE 7

Magnetic moments (BM) and exchange integral $-J$ (cm^{-1}) of VO(X—salN—R—O) complexes

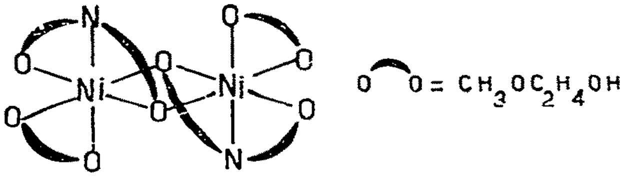
Complex	T (K)							
	78	120	152	189	228	265	Room temp.	
VO(salNCH$_2$CH$_2$O)	0.49	0.89	1.14	1.20	1.31	1.37	1.41(296)	215
VO(5 Cl-salNCH$_2$CH$_2$O)	—	0.42	0.67	0.88	1.04	1.16	1.26(295)	330
VO(5 Br-salNCH$_2$CH$_2$O)	—	0.44	0.69	0.90	1.04	1.18	1.27(294)	321
VO(5 NO$_2$-salNCH$_2$CH$_2$O)	—	0.48	0.69	0.86	0.98	1.11	1.19(294)	339
VO(3 NO$_2$-salNCH$_2$CH$_2$O)	—	—	0.37	0.52	0.66	0.84	0.97(293)	486
VO(5 MeO-salNCH$_2$CH$_2$O)	—	0.32	0.50	0.68	0.84	1.04	1.17(295)	398
VO(3 MeO-salNCH$_2$CH$_2$O)	—	—	0.35	0.43	0.59	0.78	0.89(297)	519
VO(salNCH$_2$CH$_2$CH$_2$O)	0.98	1.22	1.34	1.41	1.46	1.51	1.53(296)	141
VO(5 Cl-salNCH$_2$CH$_2$CH$_2$O)	0.87	1.14	1.29	1.38	1.44	1.49	1.52(294)	153
VO(5 Br-salNCH$_2$CH$_2$CH$_2$O)	0.86	1.12	1.26	1.34	1.40	1.45	1.48(293)	166
VO(5 NO$_2$-salNCH$_2$CH$_2$CH$_2$O)	—	0.54	0.77	0.94	1.10	1.25	1.34(293)	294
VO(3 NO$_2$-salNCH$_2$CH$_2$CH$_2$O)	0.86	1.14	1.31	1.40	1.46	1.51	1.54(293)	147
VO(5 MeO-salNCH$_2$CH$_2$CH$_2$O)	1.08	1.30	1.42	1.47	1.52	1.56	1.58(294)	117
VO(3 MeO-salNCH$_2$CH$_2$CH$_2$O)	0.92	1.17	1.33	1.42	1.47	1.51	1.54(294)	137

TABLE 8

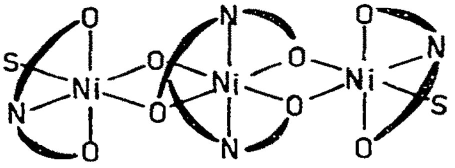
Magnetic moments (BM) and IR data (cm^{-1}) for *n*-hydroxypropylsalicylaldimine nickel(II) complexes

Complex	μ_{eff} (298 K)	ν(C=N)	ν(C—O)	Molecular weight	
				Found	Calcd
[Ni(salNCH$_2$CH$_2$CH$_2$O)(CH$_3$OCH$_2$CH$_2$OH)]$_2$	3.25	1627m	1542m	626	627
[Ni(3 Me-salNCH$_2$CH$_2$CH$_2$O)(H$_2$O)]$_2$	3.40	—	—	646	508
[Ni(4 Me-salNCH$_2$CH$_2$CH$_2$O)(CH$_3$OCH$_2$CH$_2$OH)]$_2$	3.35	—	—	606	655
[Ni(5 Me-salNCH$_2$CH$_2$CH$_2$O)(CH$_3$OCH$_2$CH$_2$OH)]$_2$	3.56	—	—	571	655
Ni$_3$(salNCH$_2$CH$_2$CH$_2$O)$_2$(salNCH$_2$CH$_2$CH$_2$OH)$_2$	3.36	1647, 1627	1567, 1542	969	946
Ni$_3$(5 Cl-salNCH$_2$CH$_2$CH$_2$O)$_2$(5 Cl-salNCH$_2$CH$_2$CH$_2$OH)$_2$(H$_2$O)$_3$	—	—	—	1240	1088

recrystallized) been obtained. The trinuclear complexes were prepared only with *N*-hydroxypropylsalicylaldimine in acetonitrile. In the binuclear complexes the magnetic data and the electronic spectra are typical of nickel(II) in an octahedral environment. The IR spectra do not indicate any phenolic oxo bridging, the strong basic conditions used in the preparation of the complexes favouring alkoxy bridging [42]. A structure consistent with these physico-chemical data is

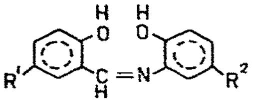


The IR spectra indicate the presence of two different coordination modes for the phenolic oxygens in the trinuclear complexes, one is consistent with a bridging oxygen and the other with a terminal one. The electronic spectra and the magnetic data indicate the presence of nickel(II) in two different octahedral ligand fields, consistent with the structure

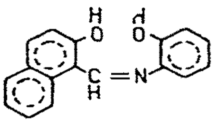


S = solvent

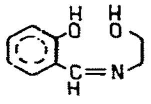
The magnetic properties and the probable structure of the iron(III) compounds with the tridentate Schiff base ligands (H_2L)



I



II



III

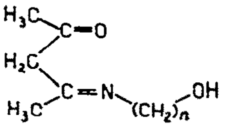
have been studied [43]. FeX_3 ($X = Cl^-$, Br^-) reacts in ethanol or acetone with these ligands to yield the microcrystalline complexes FeLX which are soluble only in coordinating solvents such as pyridine or dimethylformamide. Their far-IR spectra suggest the presence of iron—halogen bridging. The reduced values of the magnetic moments at room temperature (4.9—

5.15 BM) indicate polynuclear structures and have been interpreted by the use of the spin—spin exchange theory assuming both binuclear and long-chain models. The binuclear configuration leads to the best fit of the data.

In all the complexes the variation of the halogen atom X does not have a significant effect on the magnitude of $|J|$. There is, however, a distinct difference between the complexes with a chlorine atom substituted in either or both of the benzene rings of the Schiff base I. These show J values of about -7 cm^{-1} compared with the other complexes which display slightly higher values ($J = -10$ cm^{-1}).

The Mössbauer spectra of some of these complexes have been measured at 298, 78 and 4.2 K and compared with those of the binuclear complex [Fe(salen)Cl]$_2$. The spectra suggest that some of the complexes might possess a similar binuclear structure whereas others probably contain iron atoms in non equivalent sites.

The synthesis of copper(II) complexes of the Schiff bases derived from acetylacetone and aminoalcohol have been reported [44].



HL_A $n = 2$

HL_B $n = 3$

Although the formulae differ only by one methylene group, the room temperature magnetic moments of CuL_A and CuL_B differ markedly (1.87 and 0.41 BM, respectively). The magnetic moment of CuL_A, although normal for an isolated copper(II) atom, has been found to be similar to that in some μ-oxocomplexes [45,46] in dimers of bis chelate [47] and in the dimeric complexes of Cu(salen) [48]. An X-ray structural study has been carried out to help explain the difference in magnetic properties [44] and the molecular geometries are shown in Fig. 5. CuL_B is dimeric with an exactly planar Cu_2O_2 ring; the coordination sphere of each copper ion is planar as is the

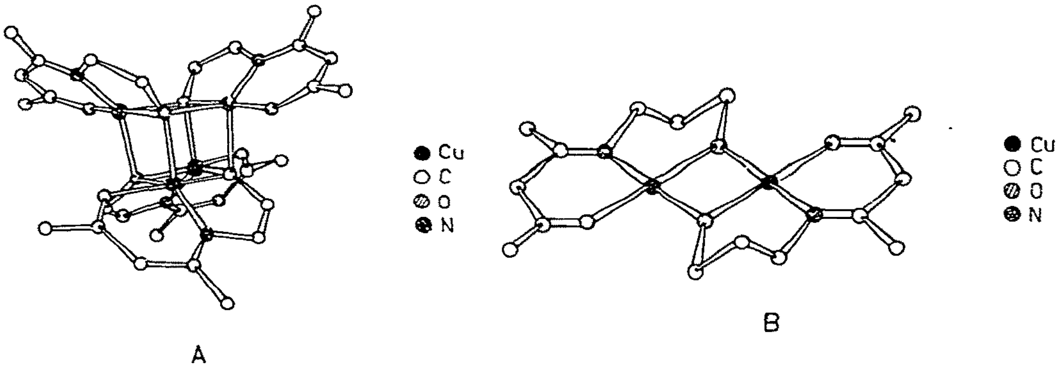


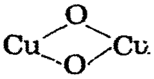
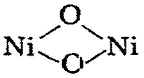
Fig. 5. The molecular structure of CuL_A (A) and CuL_B (B).

coordination around the bridging oxygen. There are two six-membered chelate rings consisting of copper, oxygen, nitrogen and three carbon atoms. The six-membered chelate rings, which contain the carbon atoms from the aminoalcohol, are considerably bent.

CuL_A is tetrameric and can be thought of as two dimers held together by Cu—O bonds; one dimer is rotated 90° with respect to the other so that there are four Cu—O interactions. The Cu—Cu distance between the dimers (3.26 Å) is longer than Cu—Cu distance within the dimer (3.01 Å). The coordination around copper is somewhat distorted but is essentially bipyramidal with the two oxygens of one chelate ligand in axial positions, the nitrogen of the same ligand and the oxygens of two other ligands of the tetramer occupy equatorial positions.

A remarkable difference in the two structures is the coordination around the bridging oxygens: this is planar in CuL_B and tetrahedral in CuL_A and may be understood in terms of chelate rings. If the coordination around bridging oxygen is planar the angle Cu—O—C must be at least 120°. In the case of CuL_B it is possible to have Cu—O—C angle of 129° and square planar coordination around the copper without any steric strain. However, the same arrangement in CuL_A would be extremely strained because of the smaller chelate ring. This strain can be removed to some extent by a change to sp^3 hybridization of the oxygen orbitals, thus decreasing the Cu—O—C angle within the chelate ring. With the change in the hybridization of the oxygen, it becomes impossible to have a planar four-membered chelate ring and a square planar coordination of the metal in CuL_A; the four-membered chelate ring is slightly bent and the coppers are five coordinated.

The diamagnetic nickel(II) complex with H_2L_A was prepared [49] and its structure determined by X-ray diffraction [50]. The molecular structure is shown in Fig. 6.

It consists of discrete oxygen bridged dimers with square planar coordination about the nickel atom. The coordination around the bridging oxygen is pyramidal. This structure differs from that found for CuL_B; the copper complex contains a four membered  planar ring, whilst in the nickel complex the  ring is bent. The nature of the 1 : 1 adduct of NiL_A with methanol has also been investigated. This adduct is formed by the addition of methanol with the

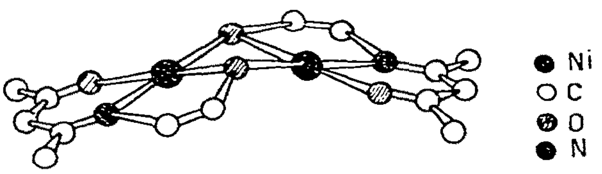
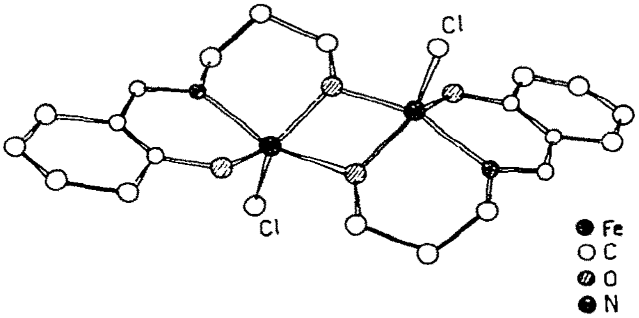


Fig. 6. A perspective view of the molecular structure of the complex NiL_A.

consequent formation of a square pyramidal configuration around the nickel atom. The complex probably retains its dimeric structure although a tetrameric one cannot be rejected.

The preparation and the properties of iron(III) complexes of Schiff bases derived from acetylacetone or salicylaldehyde and 3-aminopropanol have been described [51]. The structure of [(*N*-3-aminopropanolsalicylideneiminato)FeCl]$_2$ is

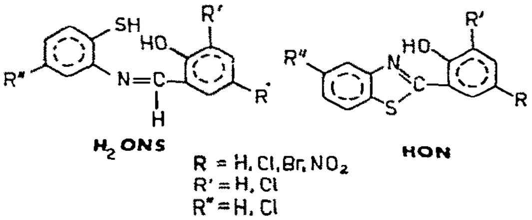


The iron ions are bridged by propoxy-oxygens, as found for the analogous copper(II) complex [184]. This is in agreement with the observed series for metal—oxygen bridging

(alkyl O^- > aryl O^- > β-diketone enolic O^- > ketonic O > alkyl OH)

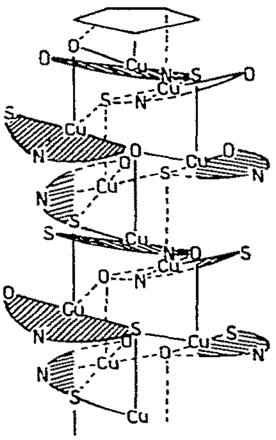
and corresponds well with the decreasing electronegativity of the bridging O [184]. The measured values of μ_{eff} are in agreement with an antiferromagnetic spin—spin exchange between high spin iron(III) ions.

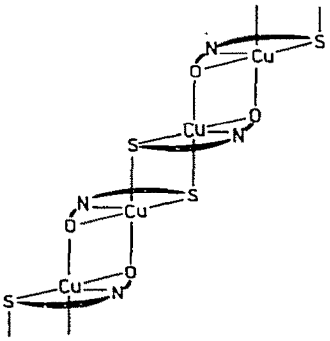
The oxovanadium(IV) complexes of the Schiff bases derived from substituted salicylaldehyde or 2-hydroxynaphthaldehyde and 2-aminothiophenol have been investigated [52]. The Schiff bases can coordinate through O, N and S as bivalent tridentate ligands

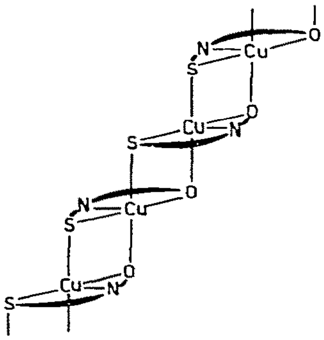


and the complexes VO(ONS) nH_2O (n = 1, 2) can be prepared by the reaction of the Schiff bases with vanadyl(IV) chloride in ethanol. The ligands are capable of cyclization when heated [53,54] and they become monovalent bidentate ligands coordinating through O and N. A series of vanadyl(IV) complexes of the type VO(ON)$_2$ was prepared. With the exception of the VO(5Cl-sal-2-aminothiophenol) (H_2O) and VO(2-hydroxynaph-2-aminothiophenol) (H_2O) the complexes do not contain any water molecules. The IR spectra of the former complexes exhibit a broad water band at about 3400 cm^{-1}. The water is coordinated to the central ion as the complexes cannot be dehydrated by heating at 150—160° C under vacuum. The V=O stretching frequencies of both the types of complexes were found in the range 895—1005 cm^{-1} and some of them exhibit a splitting of the V=O band. The electronic spectra of the two types of complexes are quite different; $VO(ON)_2$ exhibits two shoulders assigned to *d—d* transitions in the 500—840 nm region in agreement with other oxovanadium(IV) complexes [55,56]. The VO(ONS) nH_2O complexes exhibit only a broad band in the 540—750 nm region due to *d—d* transitions.

At room temperature while the $VO(ON)_2$ complexes have an effective magnetic moment in the range 1.69—1.86, the VO(ONS) nH_2O complexes exhibit a subnormal magnetic moment (μ_{eff} = 1.2—1.5 BM). Only the VO(ONS) nH_2O complexes show a temperature dependence of the magnetic susceptibilities in accordance with a dimeric structure. Copper(II) complexes with the same tridentate Schiff bases have been prepared [57,58]. *N*-(2-thiophenyl)salicylideneimine (ONS) forms Cu(ONS) with a magnetic moment at room temperature of 1.82 BM. Analogous complexes have been obtained when 5-methyl or 5-bromo-salicylaldehyde have been used; the magnetic moments at room temperature being 1.93 and 1.76 BM, respectively. The $1/\chi_M$ against T curves are not strictly linear; this was assumed to be indicative of weak magnetic exchange interaction [58]. A polymeric structure involving an infinite chain of square pyramidal copper atoms linked by sulphur and oxygen atoms was postulated.

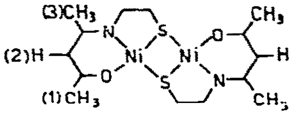




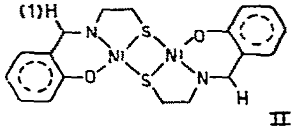


Cu(2-hydroxy-*N*-(2-thiophenyl)naphthylideneimine) shows a low magnetic moment at room temperature, indicating the presence of antiferromagnetic exchange [58]. The dimeric nature of the nickel(II) complexes with these and similar (ONS) ligands was established by molecular weight data in

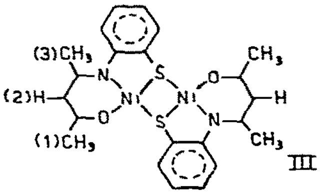
N,*N*-dimethylacetamide [59]; their configurations are



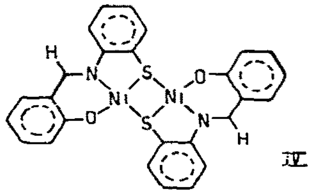
$Ni_2(AME)_2$ I



$Ni_2(SME)_2$ II



$Ni_2(AMA)_2$ III

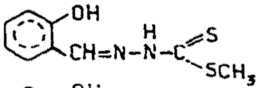


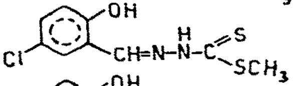
$Ni_2(SMA)_2$ IV

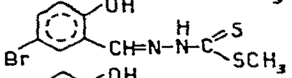
The electronic spectra are comparable with those observed in other planar sulphur-containing nickel(II) complexes. The ^1H NMR spectrum of $Ni_2(SME)_2$ shows a strong peak assignable to proton 1 at 3.64δ. In the complexes $Ni_2(AME)_2$ and $Ni_2(AMA)_2$ the methyl signals from 2,4-pentanedione residue occur at 1.78 and 1.90δ and 1.83 and 2.22δ, respectively. The methyl signal at lower field was assigned to the group adjacent to the C=O bond. The proton(2) occurs at about 5δ downfield from TMS.

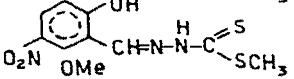
The conditions for the synthesis of Schiff bases from β-diketones or substituted or unsubstituted salicylaldehydes with β-mercaptoethylamine or 3-mercaptopropylamine were investigated; and their properties as tridentate ligands with nickel(II), cobalt(II) and copper(II) salts studied [60,61]. The Schiff bases derived from salicylaldehyde and its substituted derivatives have been isolated. 5Cl-salicylaldehyde only yields the Schiff base in equilibrium with the tautomeric 2(*p*-Cl-*o*-hydroxy)phenylthiazolidine. The β-diketones give unstable products which decompose on recrystallization. These ligands react with nickel(II) to give diamagnetic dimers of composition[Ni(ligand)]$_2$. The absorption and reflectance spectra of these complexes show three bands: a narrow intense band at 400 nm, a sharp band at 519 nm due to a charge transfer and a broad band in the range 650—730 nm due to a *d*—*d* transition corresponding to a planar structure. The absorption band at 519 nm is displaced toward higher frequencies when the 2-mercaptoethylamine group is replaced by a mercaptopropylamine group. Similar behaviour is observed when a methyl group is introduced into the benzene ring or into the chain of the diketone. Cobalt(II) forms complexes with composition $Co(HL)_2$ or Co_2L_3 even though the ligand and the metal were taken in a 1 : 1 ratio. The composition of the cobalt complexes depends strongly on the preparative method employed; thus if isolated salicylal-2-mercaptoethylamino is used, a compound of composition $Co(HL)_2$ can be isolated whereas if the crude condensation product has been used Co_2L_3 was obtained. Both types of complex contain trivalent cobalt. Copper(II) acetate gave insoluble complexes of composition $Cu(HL)_2$, the high effective magnetic moment (1.90 BM) of these chelates indicating that they are monomeric.

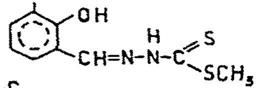
Several Schiff base ligands were prepared by the condensation of the appropriate salicylaldehyde (or acetylacetone) with *S*-methyldithiocarbazate [62]; their structural formulae are

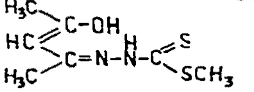

ONSH$_2$


5ClONSH$_2$

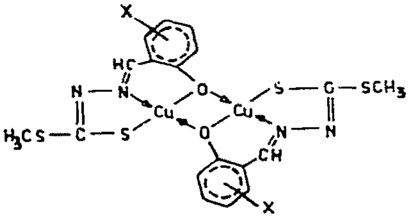

5BrONSH$_2$


5NO$_2$ONSH$_2$


3MeOONSH$_2$


acacONSH$_2$

The IR spectra show a N—H stretching at about 3080 cm^{-1}, but no νS—H at about 2570 cm^{-1}, indicating that in the solid state these ligands retain the thiono form. In solution they probably exist as equilibrium mixtures of both thiolo and thiono tautomeric forms. These Schiff bases react with copper(II) perchlorate in alcoholic medium to give complexes of the type Cu(ligand); only with H_2ONS was the hydrated complex Cu(ONS)H_2O obtained. With the exception of Cu(5NO$_2$-ONS) and Cu(acacONS), the complexes have low magnetic moments (0.6—1.0 BM) which decrease with the temperature indicating antiferromagnetic interactions between the copper atoms in an oxygen bridged structure of the type



The shift of the C—O stretching frequency in these complexes toward higher frequencies (about 25 cm^{-1}) relative to the mononuclear complexes of the salicylaldehyde Schiff base, is proof that a binuclear structure involving phenolic oxygen atoms takes place.

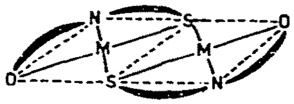
The green colour of the complex Cu(5NO$_2$—ONS), its formulation and the room temperature magnetic moment (1.99 BM) suggest a more complicated structure than a binuclear one. The IR spectrum displays νC—O at 1558 cm^{-1}, indicating the presence of bridging phenolic oxygen atoms. The mag-

TABLE 9

Magnetic moments (BM) and C—O stretching frequencies (cm^{-1}) in copper(II) complexes of the Schiff bases derived from salicylaldehyde or acetylacetone and *S*-methyldithiocarbazate

Compound	μ_{eff}	ν(C—O)	Proposed structure
Cu(ONS)H_2O	1.01	1560	Dimeric O-bridged
Cu(ONS)py	2.00	1535	Monomeric
Ni(ONS)py	Diam	1538	Monomeric
Cu(5 ClONS)	0.77	1545	Dimeric O-bridged
Cu(5 BrONS)	0.79	1560	Dimeric O-bridged
Cu(5 NO_2ONS)	2.01	1550	Tetrameric S or O-bridged
Cu(5 MeO-ONS)	0.79	1558	Dimeric O-bridged
Ni(acacONS)	Diam	—	Dimeric S-bridged
Cu(acacONS)	1.62	—	Uncertain
Pd(acacONS)	Diam	—	Dimeric S-bridged
Pt(acacONS)	Diam	—	Dimeric S-bridged

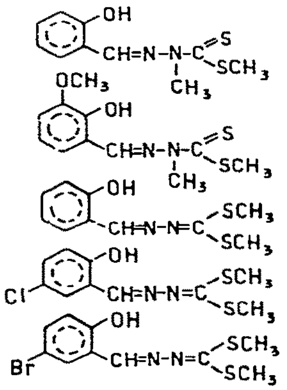
netic moment of the compound increases from 2.00 BM at 293 K to 2.43 BM at 83 K. The maximum spin only values for the magnetic moment of ferromagnetic clusters of two, three or four copper atoms are 2.00, 2.04 and 2.45 BM, respectively [63]. The magnetic data in this complex indicate that it contains four interacting copper atoms. The most likely structure appears to have pairs of oxygen bridged units [Cu(5NO_2—ONS)$]_2$ aligned to give a tetrahedral arrangement of the metal atoms as found for the copper(II) complex of the Schiff base derived from acetylacetone and 2-aminoethanol [44]. The magnetic moment of Cu(acacONS) (1.55 BM) increases with temperature, indicating the presence of ferromagnetic interaction but the reduced value of its moment could be due to the presence of antiferromagnetic interactions as well. Its structure is uncertain although an oxygen or thiolo bridge dimeric configuration seems unlikely, since this would be expected to lead to strong antiferromagnetism. A tetranuclear structure analogous to that proposed for Cu(5NO_2—ONS) is possible and this would be consistent with the observed ferromagnetic interaction. In the complexes M(acacONS) (M = Ni(II), Pd(II), Pt(II)), the metal ion has been assumed to have its usual square planar structure [62], achieved by the formation of bridged dimers; it is likely that these complexes have the thiolo-bridged structure rather than an oxygen bridged



M = Ni'', Pd'', Pt''

one as they are soft acids [64,65] and because of their strong tendency to form very stable thiolo-bridges; however a polymeric structure cannot be excluded.

The Schiff bases, listed below, have been synthesized [66]. On loss of a proton they may act as tridentate monobasic ligands. Nickel(II) forms the com-



HONMeS

3MeOHONMeS

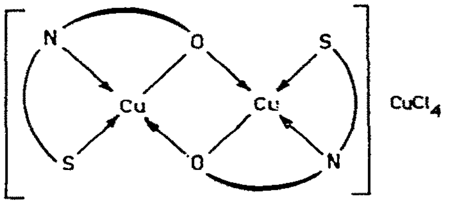
HONSMe

5ClHONSMe

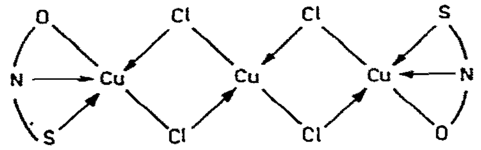
5BrHONSMe

plexes Ni(ONMeS)X (X = Cl, Br, NCS) which are diamagnetic and square planar; there is no evidence for a binuclear structure. With copper(II) fluoroborate the ligand HONMeS yields [Cu(ONMeS)] $(BF_4)_2$ with a magnetic moment (0.88 BM at 298 K) which decreases to 0.32 BM at 93 K owing to antiferromagnetic interactions in a binuclear structure. IR evidence confirms the presence of bridging phenolic oxygen atoms.

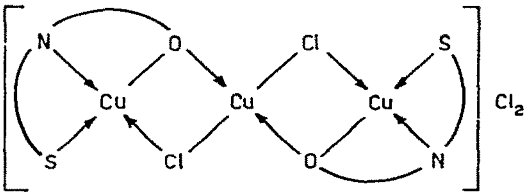
The conductivity data show that in nitromethane solution the complex exists as a mononuclear uni-univalent electrolyte, probably with a solvent molecule coordinated to the copper(II) ion. With copper(II) chloride the Schiff bases HONMeS and HONSMe yield the complexes $Cu_3(ONMeS)_2Cl_4$ and $Cu_3(ONSMe)_2Cl_4$ with the following possible configurations



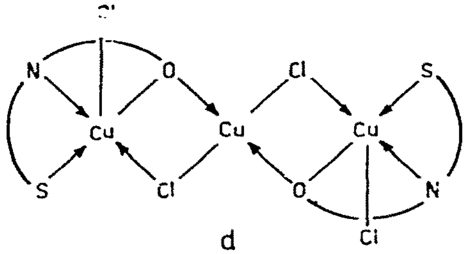
a



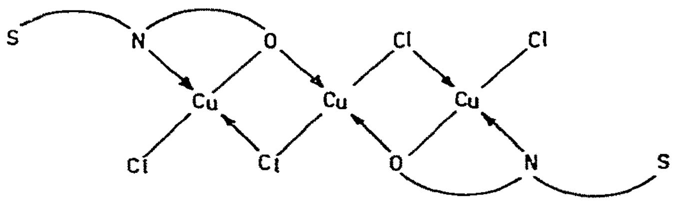
b



c



d

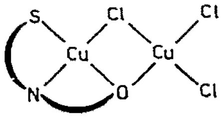


e

The magnetic moment of the $Cu_3(ONMeS)_2Cl_4$ complex varies slightly with temperature and accordingly there is no appreciable antiferromagnetic interaction between the copper ions in this complex. Therefore structure (a) can be excluded. Moreover its electronic spectrum does not show a band at 1282 nm characteristic of $CuCl_4^{2-}$ anion in a pseudotetrahedral structure.

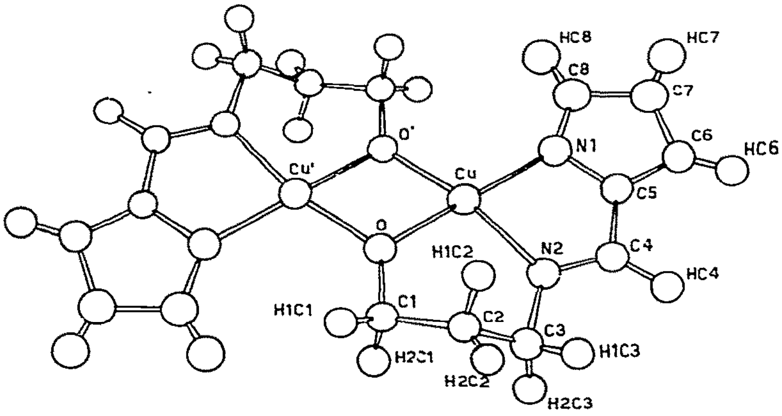
The IR spectra are indicative of bridging phenoxy groups; the conductivity (51 ohm^{-1}) is below that expected (70—80 ohm^{-1}) for a bi-univalent electrolyte in DMF and may be due to some decomposition. Therefore the ionic structure (c) is unlikely. The most probable structure for both the complexes seems to be either (d) in which the ligands are tridentate and copper atoms are five-coordinate or (e) in which the thioether group of the ligands is not coordinated and all three copper atoms have an approximately square-planar configuration.

The Schiff bases 3MeOONMeS yielded, on reaction with copper(II) chloride, the dark green $Cu_2(3MeOONMeS)Cl_3$ (μ_{eff} = 1.7 BM at 342 K and 0.89



BM at 83 K); the dimeric structure above was assigned to this complex in which oxygen and chlorine bridging atoms are present.

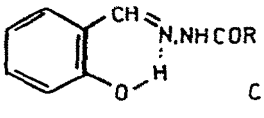
The synthesis of copper(II) complexes with the Schiff base derived from pyrrole-2-carboxaldehyde and 2-aminopropanol have been reported [67,68]. The structure consists of dimeric units



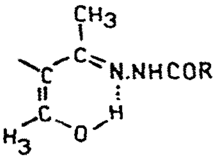
The two coppers are bridged by the oxygen of the iminoalkoxide ligands. The four membered copper—oxygen ring is exactly planar and the coordination around the bridging oxygen is essentially planar. The room temperature magnetic moment is much reduced (0.5 BM).

Similarly, binuclear copper(II) complexes have been prepared by reaction of 1-(2-hydroxyphenyl)-3,5-diphenylformazan or 1,2-carboxyphenyl-3,5-

diphenylformazan with copper(II) chloride or acetate in ethanol solution [69]. On the basis of the low magnetic moment a dimeric structure has been suggested for the complex obtained by the first ligand. The complex with the second ligand shows normal magnetic properties and is probably tetrameric. From the reaction of aroylhydrazone, in absolute ethanol, with salicylaldehyde or acetylacetone, the tridentate Schiff bases have been obtained [70].



H_2SalR

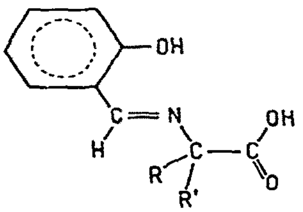


H_2AcacR

With the ligand H_2salR, copper(II) chloride forms the hydrated complexes $Cu(HsalR)Cl(H_2O)$, when R = CH_3, C_6H_5 and p-$CH_3OC_6H_4$, and the anhydrous chelate Cu(HsalR)Cl when R = o-HOC_6H_4 and p-$NO_2OC_6H_4$ [70]. A distorted square pyramidal structure was assigned for the chelate Cu(HsalR)(Cl)(H_2O) whereas the anhydrous chelates Cu(HsalR)Cl possess a square planar arrangement with the chloride ion occupying a coordination site. In both types the hydrazone molecule acts as a monobasic tridentate ligand. Their magnetic moments are normal for a spin only value and a polymeric structure cannot be ruled out.

In the IR spectra the lack of absorption due to N—H stretching, νC=O and the appearance of a very strong band at 1630 cm^{-1}, was correlated to the stretching vibration mode of the conjugate C=N—N=C system. Such behaviour is diagnostic of enolization of the hydrazone residue [71]. The low magnetic moments of Cu(salR) and Cu(acacR) strongly suggest molecular association. Their nujol electronic spectra show a multicomponent band system over the range 600—730 nm besides a strong charge transfer band at 480 nm consistent with a square planar structure. A dimeric structure with the hydrazine oxygen bridges is suggested.

In pyridine, these complexes form the monopyridine adducts Cu(salR)(py) and Cu(acacR)(py) in which the oxygen bridges are destroyed. The ligands

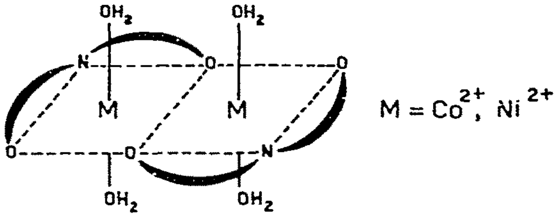


derived from salicylaldehyde and α-aminoacids were studied [72—77]. They are bivalent anions with a tridentate ONO donor set. They can be prepared, as potassium salts, by the reaction of the appropriate aminoacid with salicylaldehyde. The analysis of the IR spectra [74] indicates that these Schiff bases have the tautomeric hydroxyaldimine form A (Fig. 7).

In the IR spectrum of the *N*-salicylidenevaline the two bands at 1634 $\mathrm{cm^{-1}}$ and 1604 $\mathrm{cm^{-1}}$ have been assigned to the νC=N stretching and to a band resulting from the superimposition of the ν_{asymm} $\mathrm{COO^-}$ and the νC=C + νC=N stretching bands. The ν_{symm} $\mathrm{COO^-}$ lies at 1374 $\mathrm{cm^{-1}}$ and the strong band at 1513 $\mathrm{cm^{-1}}$ was attributed to a $\nu\mathrm{C{\overset{...}{=}}C}$ or $\nu\mathrm{C{\overset{...}{=}}N}$ stretching vibration of the conjugated amide.

Binuclear nickel(II) and cobalt(II) complexes have been obtained in quantitative yield by adding the metal acetate dropwise to a warm alcoholic solution containing stoichiometric amounts of the salicylaldehyde and the aminoacid (aminoacid = AA = glycine, L-alanine, L-valine, L-leucine, L-methionine, L-phenylalanine) [77,78]. The complexes contain two molecules of water; the presence of water is also indicated by a very broad band centered at around 3225 $\mathrm{cm^{-1}}$ for the cobalt(II) complexes and at about 3350 $\mathrm{cm^{-1}}$ for the nickel(II).

The electronic spectra and magnetic moments of these compounds are consistent with an octahedral configuration around the central ion. A molecular weight measurement carried out for the complex $[\mathrm{Ni(salgly)(H_2O)_2}]_2$ gave a value of 516 which differs by approximately 5% from the calculated molecular weight. The dimeric configuration



has been proposed for these complexes. In strong coordinating solvent such as pyridine, dimethylformamide and dimethylsulphoxide the binuclear structure is probably broken with the formation of mononuclear complexes. The assignment of the IR bands for $\mathrm{M(salgly)(H_2O)_2}$ and the dehydrated $[\mathrm{M(salgly)}]_n$ (M = cobalt(II) and nickel(II)) were based on the ^{15}N labelling of the complexes [79].

The band near 1660 $\mathrm{cm^{-1}}$ was assigned to a νC=N stretching mode and the νC=O of the carboxylic group was assigned to the broad band in the 1590—1550 $\mathrm{cm^{-1}}$ region. The shift of this νC=O on going from [M(salgly)-

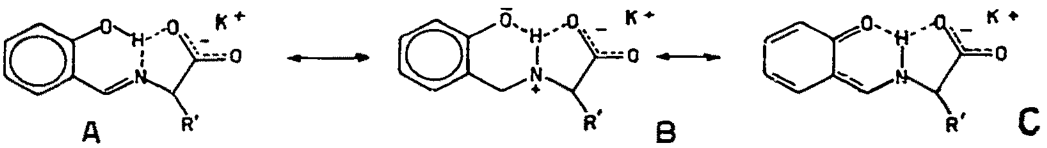


Fig. 7. The possible tautomeric forms of the salicylaldimine-α-aminoacids.

TABLE 10

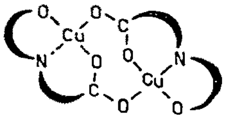
Frequencies (cm^{-1}) assignments of nickel(II) and cobalt(II) *N*-salicylidene-glycine complexes

Complex	ν(C=N)	ν(C=O)	ν(C=N) or ν(C=N) + C—H	ν(C—O)	ν(C—N)	ν(M—N)	ν(M—L)
$[Ni(salgly)(H_2O)_2]_2$	1655	1554	1452	1430	1092	484	564
			1393	1339			549
							465
							343
							234
$[Co(salgly)(H_2O)_2]_2$	1653	1555	1450	1430	1088	480	558
			1402	1335			542
							458
							341
							222
$[Ni(salgly)]_n$	1657	1576	1393	1422	1093	346	541
			1375	1331		299	469
							361
							245
$[Co(salgly)]_n$	1655	1586	1399	1430	1084	337	532
			1362	1336		269	463
							359
							242

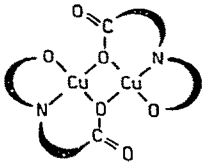
$(H_2O)_2]_2$ to $[M(salgly)]_n$ suggests that the C═O group in the first complex is bonded to the metal from an adjacent molecule; this was found in the structure of $[Cu(salgly)(H_2O)]_2$ [80]. The band near 1430 cm^{-1} was assigned to the carboxylic C—O stretching mode and the position of such a band seems to exclude the possibility that the carboxylic group may act as bridge in the dimeric structure in contrast to that proposed for $[Cu(salgly)]_2$ [81].

Copper(II) complexes with these Schiff bases have been prepared, and their structures discussed [81—84]. These complexes can be classified, using their magnetic moments at room temperature, into two groups: those belonging to group 1 have a subnormal magnetic moment and those belonging to group 2 show normal magnetic moments. The IR spectra of both the types of complexes show similar trends of bands in the 1660—1560 cm^{-1} region. The carboxylic stretching $\nu C=O$ was found to be approximately 25—30 cm^{-1} greater than those of the corresponding nickel(II) compounds.

The copper(II) complex with $5NO_2$-salicylalanthranilic acid shows a different IR spectrum; no absorption appeared on the high frequency side of the strong peak at 1589 cm^{-1} which was assigned to $\nu_{asymm}COO^-$. For the two groups of copper(II) complexes the two structures



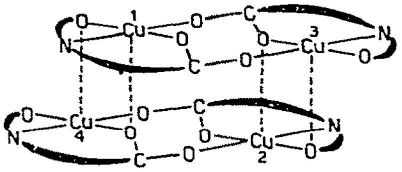
a



b

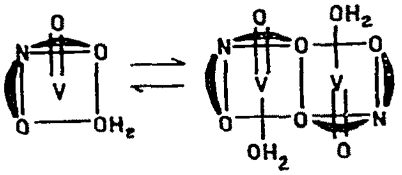
were postulated. For group 1 a binuclear structure of the type (a) or (b) can be proposed. From the data available it is difficult to make a choice between the two alternative structures. It would seem likely that the structure (b) is preferred because it forms a four membered chelate ring involving the bridging atoms. The high magnetic moments for the complexes of group 2 seem to suggest that interaction between the copper spins do not take place. The structure (a) involves an eight membered ring. Consequently, the direct spin interaction between the copper atoms is negligible, leading to a situation equivalent to the independent orientation of each spin in the external magnetic field.

Recently the *N*-salicylidene-L-valinato copper(II) complex with a normal magnetic moment at room temperature has been reinvestigated [85]. The molecular weight measurements in dilute $CHCl_3$ are in agreement with a tetrametallic species



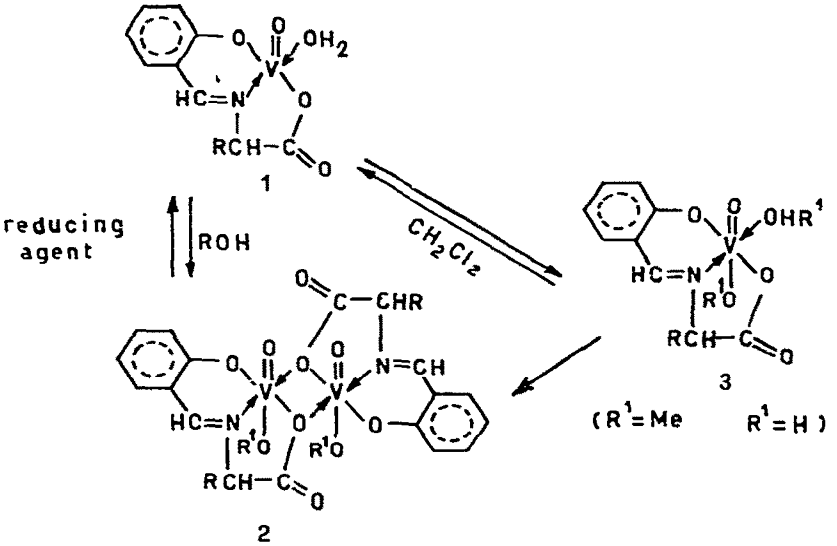
Magnetic susceptibilities, in the temperature range 77—380 K, agree well with the Van Vleck equation [86] and even though structural data are not available, a tetranuclear configuration is the most probable.

These salicylideneiminoacids (H_2salAA) react with oxovanadium(IV) to yield the complexes VO(salAA)(H_2O) having normal magnetic moments at room temperature [87,88]. In these complexes one water molecule occupies a coordination position and prevents the dimerization of the compounds. The dimers may be obtained on dissolving the monomers in absolute methanol [88] and probably in this solution the equilibrium



takes place. The dimeric nature of these complexes is supported by the marked differences in physico-chemical properties from the mononuclear complexes, by the demagnetization of the compounds and by the molecular weight determinations. The IR spectra of the binuclear complexes are characterized by a very strong band at approximately 980 cm^{-1} due to the νV=O stretching; this band is observed in the mononuclear ones at about 1000 cm^{-1}. The lowering of this band in the binuclear complexes is due to a molecule of water *trans* to the vanadyl oxygen [23].

The electronic spectra show only one broad band in the 1430—400 nm region. The *d—d* transition band was observed at 570—543 nm; the possibility of a L—M charge transfer for this band cannot be ruled out. Recently the equilibrium between mononuclear and binuclear oxovanadium compounds



has been studied [89].

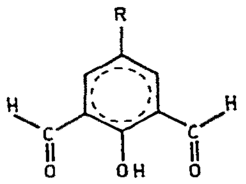
The mononuclear compound (1) dissolves in alcohol to give a red solution containing the binuclear complex as shown in the equilibrium above reported with a molecule of alcohol in the sixth coordination position of each vanadium atom. From dry methanol an orange pink product of oxovanadium(V) was obtained for which the structure 2 was assigned. With sodium bisulphite or stannous chloride this complex reduces to complex 1. The IR spectrum of the vanadium(V) complex does not contain O—H stretching vibrations but shows the bands at 2815 and 1045 cm^{-1} of a coordinated methoxy group rather than a coordinated methanol. The corresponding vanadium(V) complex containing a coordinated ethoxy group can be obtained from absolute ethanol solution. Even if no direct evidence is available, the complexes are formulated as dimers and it seems likely that the alkoxy group will coordinate *trans* to the V=O bond. From the experimental data the oxidizing agent for these complexes seems to be the oxygen molecules.

Complexes of the type $VO(L)(H_2O)$, where H_2L = 2-hydroxynaphthylideneaminoacids, react with pyridine or *o*-phenanthroline to form $VO(L)(py)_2$ or VO(L)(*o*-phenanthroline), which exhibit spin-only magnetic moments [27].

The green $VO(L)(H_2O)$ complexes gave, when dissolved in methanol, a brown solution from which the monomeric brown complexes $VO(OCH_3)(L)(CH_3OH)$ were isolated. The treatment of these brown complexes with CH_2Cl_2 followed by *n*-hexane gave green precipitates of $[VO(OH)(L)]_2$ [27].

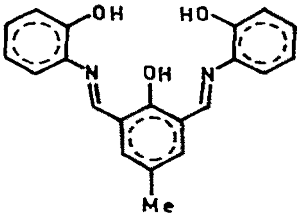
C. COMPLEXES WITH 2-HYDROXY-5-R-ISOPHTHALALDEHYDE AND ITS SCHIFF BASE DERIVATIVES

Binucleating ligands, capable of securing two metal ions at an appropriate distance to give magnetic interaction between them, were prepared by using the compound



5-R-isophthalaldehyde [90] (R = Me, Cl) and the Schiff bases derived by condensation of these ligands with aliphatic or aromatic amines. Two types of copper(II) complexes of 3-formyl-5-methylsalicylaldehyde (Hfsal) have been prepared [91].

A series of binucleating copper(II) complexes was also prepared where the ligand is a Schiff base obtained by condensation of Hfsal with alkyl amines ($R—NH_2$, R = methyl, ethyl, isopropyl, *t*-butyl or cyclohexyl group). In these complexes the organic moiety acts as tridentate chelating agent utilising the bridging phenolic oxygen, and the copper atoms are held sufficiently close to each other to give antiferromagnetic interactions. The room temperature magnetic moments for the binuclear complexes of Fig. 8(b) and (c) are 1.58 and 0.80—1.29 BM, respectively, considerably below the normal values found for copper(II) complexes. A similar result was obtained for the complex of Fig. 8(a) (1.81 BM). The binuclear structure was also confirmed by the reflectance spectra in which it was found that the *d—d* transition band (900 nm for the complex in Fig. 8(b) and 830—630 nm for the complex in Fig. 8(c)) lies at lower energy than those expected for mononuclear copper(II) complexes of similar ligands. From the reaction between Hfsal and aminophenol in boiling methanol the ligand



was obtained [H$_3$fsal(ap)$_2$], which in its trianionic form fsal(ap)$_2^{3-}$ may act as binucleating agent [92,93].

Attempts to prepare the binuclear chloro-bridge complex Cu$_2$fsal(ap)$_2$Cl were unsuccessful; the reaction between H$_3$fsal(ap)$_2$, cupric isobutyrate and tetraethylammonium chloride demonstrated that the fragment associated with Cu$_2$fsal(ap)$_2^+$ was derived from the alcoholic solvent ($^-$OR) rather than from the initial cupric salt. On using different alcohols (R = CH$_3$—, C$_2$H$_5$—, C$_2$H$_5$—CH$_2$—, CH$_3$OCH$_2$CH$_2$—), complexes with different alkoxides bridging the two metal ions were obtained. The interconversion of the alkoxides may take place by heating a suspension of an alkoxide in the appropriate alcohol. In contrast to normal alkoxides these complexes are stable in the solid form in air; however they are quite sensitive to degradation in solution in the ab-

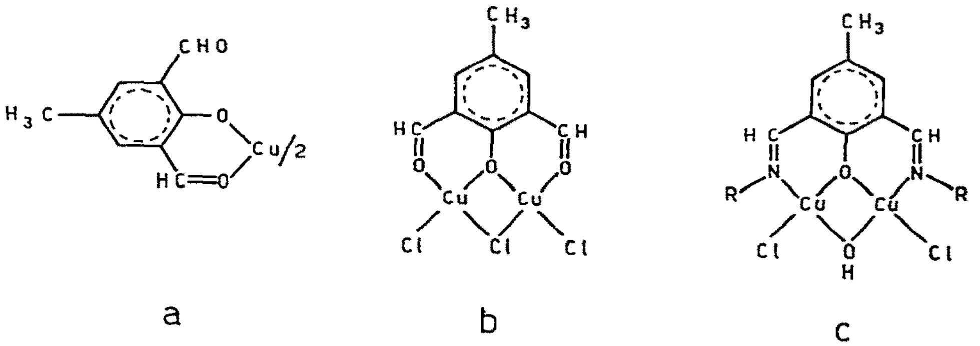
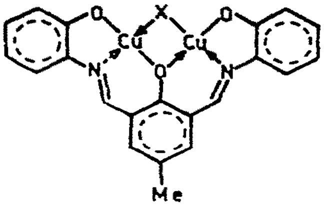


Fig. 8. The mononuclear (a) and binuclear (b) copper(II) complexes with 3-formyl-5-methylsalicylaldehyde and the binuclear (c) copper(II) complexes with the Schiff bases derived from 3-formyl-5-methylsalicylaldehyde and alkyl amines.

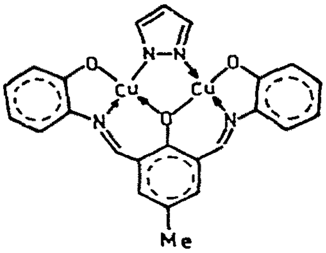
sence of added parent alcohol, especially upon heating. Upon heating in DMF, containing a small portion of water, the alkoxides give Cu_2fsal(ap)$_2$OH. The solvate Cu_2fsal(ap)$_2$OH · DMSO was obtained in crystalline form from the reaction of cupric carboxylate with the ligand in DMSO, containing a small portion of water. The alkoxy substituent in the binuclear complex can be easily replaced by the pyrazolate ion $(C_3H_3N_2)^-$ in a hot DMF—methanol solution.

For these complexes a configuration of the type illustrated was proposed



where X = OR^-, OH^-, $C_3H_3N_2^-$. Their reflectance spectra show *d—d* bands at 600—700 nm only as shoulders upon much more intense absorption centered at higher energies. This eliminates a trigonal bipyramid configuration around the copper ion, and suggests a square planar configuration with the possibility of one or two ligand atoms occupying the apical positions. The IR spectra are very similar and show a strong C=N stretching band at about 1580 cm^{-1}. Additional identifiable bands due to X^-group or solvent are present.

All these complexes showed a lower magnetic moment than normal. The plot of molar susceptibility χ_M against *T* (from 300 to 100 K) gave for Cu_2fsal(ap)$_2$($C_3H_3N_2$) a broad maximum at $T \simeq 280$ K and $\chi_M = 8.1 \cdot 10^{-4}$ cgs units per mole and for Cu_2fsal(ap)$_2$(OCH_3) a steady decrease from $4.0 \cdot 10^{-4}$ cgs at 300 K to $0.8 \cdot 10^{-4}$ cgs at 100 K in accordance with the Bleaney—Bower equation [94]. Such magnetic results are strongly indicative of binuclear complexes and an X-ray investigation on Cu_2fsal(ap)$_2$($C_3H_3N_2$) [95] indicating a near-planar structure of the type



confirms these deductions.

The reaction between H_3fsal(ap)$_2$ with copper(II) acetate or isobutyrate in anhydrous methanol yielded the complex Cu_2fsal(ap)$_2H_2O(OCH_3)$, where fsal(ap)$_2H_2O$ represents the product of the addition of a molecule of water

TABLE 11

Effective magnetic moments per Cu^{2+} (BM) for the complexes Cu_2fsal$(ap)_2$X *

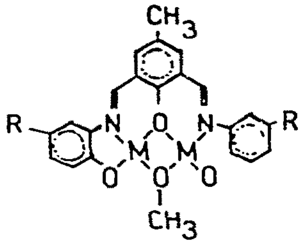
Cu_2fsal$(ap)_2(OCH_3)$	0.97	Cu_2fsal$(ap)_2(OH)$	1.17
Cu_2fsal$(ap)_2(OC_2H_5)$	0.85	Cu_2fsal$(ap)_2(OH)$ · DMSO	0.98
Cu_2fsal$(ap)_2(OCH_2CH_2OCH_3)$	0.77	Cu_2fsal$(ap)_2(C_3H_3N_2)$	1.40
Cu_2fsal$(ap)_2(OCH_2C_6H_5)$	0.60		

* At room temperature. Corrected for diamagnetism using the measured diamagnetic susceptibility of H_3fsal$(ap)_2$ ($-195 \cdot 10^{-6}$ cgs units per mole) and Pascal's constants.

across one of the Schiff base links of the ligand

$-CH{=}N- + H_2O \rightarrow -CH(OH)-NH-$

The depressed effective magnetic moment at room temperature (1.33 BM per Cu^{2+}) and the diffuse reflectance spectrum (shoulder at 620 nm) are comparable with those of the other binuclear derivatives discussed above. A study of the physico-chemical properties of a series of binuclear complexes of copper(II) and oxovanadium(IV) of the type



has been reported [96]. The complexes M_2fsal$(ap)_2(OCH_3)$ show in the IR spectra a strong band at 1600 cm^{-1} due to C=N, while no absorption bands due to the formyl groups were found in their characteristic region (1700—1620 cm^{-1}). The νV=O stretching vibration of the complexes $(VO)_2$fsal-$(ap\text{-}R)_2(OCH_3)$ lies at about 990 cm^{-1}, except $(VO)_2$fsal$(ap\text{-}NO_2)_2(OCH_3)$ for which the νV=O was observed at 900 cm^{-1}. This has been explained by assuming that $(VO)_2$fsal$(ap\text{-}NO_2)_2(OCH_3)$ has a different molecular structure from the other oxovanadium(IV) complexes.

The ESR spectra of all these complexes are comparable and show a broad strong band at about 3200 gauss and a weak band at about 1600 gauss, tentatively assigned to the $\Delta M_s = 1$ and $\Delta M_s = 2$ transitions, respectively. All these data confirm the binuclear molecular configuration proposed for the complex Cu_2fsal$(ap)_2(C_3H_3N_2)$. The magnetic susceptibility data for these binuclear oxovanadium(IV) and copper(II) complexes, show good agreement with the Bleaney—Bowers equation [94] assuming the values for J, g and $N\alpha$ reported in Table 12.

As seen in Table 12, the values of singlet—triplet energy separation ($-2J$) increase, for the vanadyl(IV) complexes, with the increasing order of elec-

TABLE 12

Magnetic parameters and effective magnetic moments (BM) of the complexes M_2fsal(ap-R)-(OCH_3)

	$-2J$ (cm^{-1})	g	$N\alpha \cdot 10^6$ cgsu	μ_{eff} (K)
$(VO)_2$fsal(ap-CH_3)$_2$(OCH_3)	180	1.87	60	1.46(291.0)
$(VO)_2$fsal(ap-H)$_2$(OCH_3)	230	1.86	40	1.37(291.2)
$(VO)_2$fsal(ap-Cl)$_2$(OCH_3)	280	1.81	45	1.25(298.0)
$(VO)_2$fsal(ap-NO_2)$_2$(OCH_3)	545	1.95	70	0.85(295.7)
Cu_2fsal(ap-CH_3)$_2$(OCH_3)	655	2.15	100	0.70(288.5)
Cu_2fsal(ap-H)$_2$(OCH_3)	570	2.15	100	0.88(298.1)
Cu_2fsal(ap-Cl)$_2$(OCH_3)	555	2.15	100	1.04(298.1)
Cu_2fsal(ap-NO_2)$_2$(OCH_3)				1.18(288.3)

tron-withdrawing abilities of the substituent R, while such a behaviour is reversed for the analogous copper(II) complexes. This is more clearly shown by Fig. 9 in which the $-2J$ values are plotted versus the Hammett's σ_p values.

As known, many oxovanadium(IV) complexes have square-pyramidal configurations, the vanadium atom being slightly lifted from the basal plane [97]. In the complexes $(VO)_2$fsal(ap-R)$_2$(OCH_3), the position of the vanadium(IV) atom is influenced by the electron density on the phenolic oxygen atom, which depends on the group R at the 4-position in 2-aminophenol. Such a deviation of the vanadium(IV) atom from the basal plane is the largest for R = CH_3 and the smallest for R = Cl.

Since direct coupling between d_{xy} orbitals would be the determining factor for the spin-exchange interaction in the binuclear vanadyl(IV) complexes, the overlapping of these orbitals increases in the order $(VO)_2$fsal(ap-

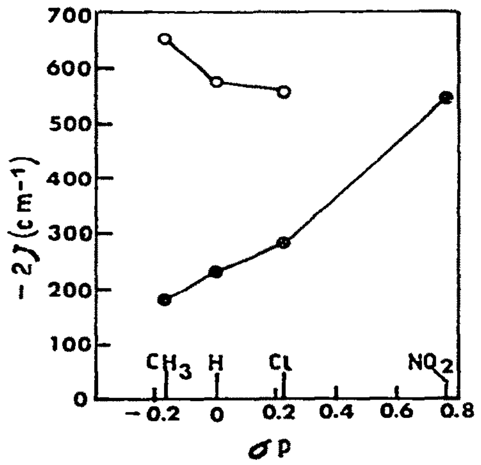
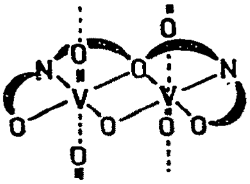


Fig. 9. The relations between the $-2J$ values and Hammett's σ_p values for $(VO)_2$fsal-(ap-R)$_2$(OCH_3) (●) and Cu_2fsal(ap-R)$_2$(OCH_3) (○).

$CH_3)_2(OCH_3) <$ $(VO)_2$fsal(ap)$_2(OCH_3) <$ $(VO)_2$fsal(ap-Cl)$_2(OCH_3)$ and the $-2J$ values increase in the same order [96—98].

In the binuclear copper(II) complexes, the spin-pairing interaction increases when the equatorial bonds are strengthened. In Table 14 $-2J$ values decrease in the order Cu_2fsal(ap-$CH_3)_2(OCH_3)$ > Cu_2fsal(ap)$_2(OCH_3)$ > Cu_2fsal(ap-Cl)$_2(OCH_3)$, because the electron density decreases in the same order; the Cu—O bond is also weakened in this order.

The complex $(VO)_2$fsal(ap-$NO_2)_2(OCH_3)$ shows a strong antiferromagnetic spin exchange ($-2J = 545$ cm^{-1}) and its V=O stretching vibration is observed at 900 cm^{-1}. The complex, probably, has the polymeric configuration



with intermolecular ···V=O···V=O··· interactions, giving a pseudo-octahedral geometry around the vanadium(IV) ion.

The anomalous magnetic value of this complex has been explained by taking into account the strong electron-withdrawing character of the $-NO_2$ group which reduces the electron density on the phenyl oxygen atom, responsible for the axial coordination to the vanadyl(IV) ion. Also for the complex Cu_2fsal(ap-$NO_2)_2(OCH_3)$ a polymeric structure, due to the high electron-withdrawing character of the NO_2 group, was proposed. Its magnetic properties can be interpreted in terms of the Ising model and the μ_{eff} expressed by the equation [99]

$$\mu^2_{eff} = \tfrac{1}{4}[\exp(4K) + (2 + K^{-1})\exp(2K) - K^{-1}\cdot\exp(-2K) + 5][\exp(2K) + \exp(-2K) + 2]^{-1}$$

where K is J/kT, are in good agreement with the experimental values ($J = -225$ cm^{-1}).

From H_3fsal(ap)$_2$ and $Co(CH_3COO)_2 \cdot 4H_2O$ in methanol under a nitrogen atmosphere, the hygroscopic red-brown compound Co_2fsal(ap)$_2(CH_3COO) \cdot xH_2O$ was obtained [101]. This complex, in methanolic solution, reacts rapidly with oxygen to yield black crystals of composition Co_2fsal(ap)$_2(OCH_3) \cdot (CH_3COO)$. The oxygen consumed in this reaction is consistent with conversion of only half the cobalt(II) to cobalt(III) with concomitant reduction of oxygen to the water (or hydroxide) level. This black complex has a magnetic moment of 3.58 BM per cobalt atom at room temperature and obeys the Curie—Weiss law from 287 to 95 K, suggesting the presence of equal numbers of diamagnetic cobalt(III) and paramagnetic cobalt(II) ions. This complex after recrystallization from aqueous ethanol yields crystals of composition Co_2fsal(ap)$_2(OH)(CH_3COO) \cdot H_2O \cdot$ EtOH which were studied by X-ray diffraction. The crystals are monoclinic of.

space group C2/c with $Z = 8$ and the molecular structure with some relevant dimensions is reported in Fig. 10.

The asymmetric unit is constituted by $[Co(II)Co(III)fsal(ap)_2(OH)(CH_3COO)]_2 \cdot 2H_2O \cdot EtOH$, where the water and ethanol molecules participate in an intricate H-bonded chain.

The most important features of the structure are:

(i) the coplanar array of four cobalt centres which fall into two distinct pairs of Co(III) ions (Co(1) and Co(1′)) and Co(II) ions (Co(2) and Co(2′)) which can be differentiated on the basis of cobalt bond lengths;

(ii) the μ_3-hydroxo-group;

(iii) the unusually long Co(2)—O(2′) distance (2.2 Å) probably due to steric hindrance between the benzene ring of the aminophenol and the chelate ring system (Co(2), O(3) and N(2)).

The reaction of $H_3fsal(ap)_2$ with $Ni(CH_3COO)_2 \cdot 4H_2O$ or $Co(CH_3COO)_2 \cdot 4H_2O$ in methanol yields $[M_2fsal(ap)_2(OH)]_2(CH_3COO)_2(H)_2$ presumed to have a tetranuclear core analogous to that in the figure above reported.

The nickel compound reacts with nitrite or pyridine to give $[Ni_2fsal(ap)_2(OH)]_2(CH_3COO)(NO_2)(H)_2$ and $[Ni_2fsal(ap)_2(OH)]_2(CH_3COO)(py)_2(H)_2$. The additional protons $[(H)_2]$, required for electrical neutrality, are observed for all four complexes of the divalent metals by potentiometric titration with lithium hydroxide in 2-methoxyethanol. The most likely basic sites for the titratable protons are the aminophenol oxygen atoms of the ligand.

Binucleating ligands, containing sulphur donor atoms, have been prepared [100,102,103] in the hope that they might show enhanced affinity for soft cations as compared with the analogous ligands containing nitrogen and oxygen donor atoms.

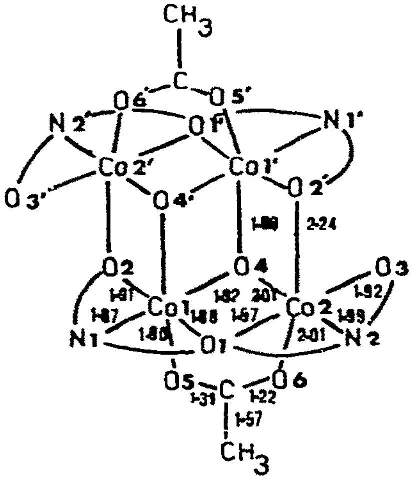
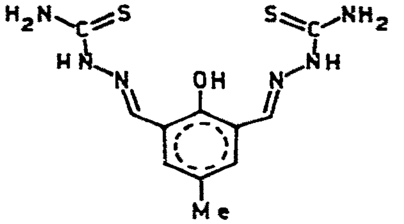
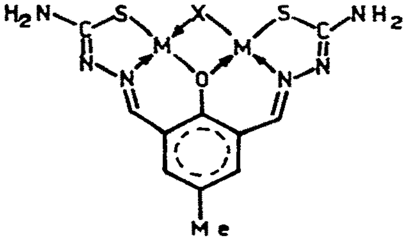


Fig. 10. The molecular structure around the tetranuclear core of $[Co^{III}Co^{II}fsal(ap)_2(OH)(CH_3COO)]_2 \cdot 2H_2O \cdot 2EtOH$.

From the reaction between 3-formyl-5-methylsalicylaldehyde with thiosemicarbazide in aqueous ethanolic solution the ligand H_3fsal(thise)$_2$ was prepared [102].



This ligand reacts with copper(II) and nickel(II) to give solvated (DMSO, DMF) binuclear complexes of the type



The following complexes have been isolated

M = Ni(II); X = CH_3O^-, $C_2H_5O^-$, $CH_3OC_2H_4O^-$, N_3^-, NH_2^-, $C_4H_9NH^-$, $C_6H_5NHNH^-$, OH^-, OCN^-, $C_3H_3N_2^-$ (the conjugate base of pyrazole).
M = Cu(II); X = CH_3O^-, $C_2H_5O^-$, $CH_3OC_2H_4O^-$, $C_6H_5CH_2O^-$, N_3^-, Cl^-, $C_3H_3N_2^-$.

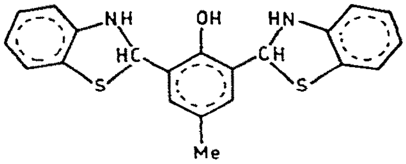
The physico-chemical data support this type of structure and it has been confirmed by X-ray structural data [102] for the complex Ni_2fsal(thise)$_2$-(OC_2H_5)(DMF)$_2$. Crystals of this complex are monoclinic with space group $P2_1/m$. All the atoms other than H in the complex are coplanar except for a carbon atom of the ethoxide fragment.

The IR spectra of all the prepared complexes are almost identical with the exception of the additional identifiable bands due to X^- groups or to the solvate molecule. In particular the νC=S band, at 829 cm^{-1} in the ligand, is absent from the spectra of all the complexes while the band at 1114 cm^{-1} is reduced in intensity, this being consistent with a coordination through the sulphur rather than the nitrogen atom of the thiosemicarbazone fragment.

All the complexes are diamagnetic except for Cu_2fsal(thise)$_2(N_3)$DMSO (μ_{eff} = 0.97 BM at 287 K), Cu_2fsal(thise)$_2$Cl · DMSO (μ_{eff} = 1.23 BM at 296 K) and Cu_2fsal(thise)$_2(C_3H_3N_2)$ (μ_{eff} = 1.30 BM at 289 K). The molar susceptibilities obey the Bleaney—Bowers equation [94].

Binuclear complexes of copper(II) and nickel(II) derived from binucleating ligands containing sulphur, 2-hydroxy-5-methyl-isophthalaldehyde-di-2′-mercaptoanil (H_3fsal(at)$_2$) and 2-hydroxy-5-methyl-isophthalaldehyde dithiosemicarbazone (H_3fsal(thise)$_2$) have the general formula M_2fsal(at)$_2$X and M_2fsal(thise)$_2$X where X represents a series of monoanionic species containing a potentially binucleating site [103].

The ligand H_3fsal(at)$_2$, obtained by the condensation in ethanol of *o*-aminobenzenethiol with 2-hydroxy-5-methylisophthalaldehyde, has the configuration



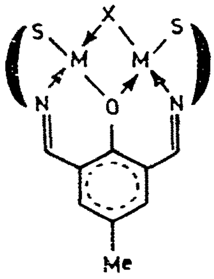
rather than the tautomeric Schiff base found for the similar condensation with *o*-aminophenol [H_3fsal(ap)$_2$].

This configuration is confirmed by the presence, in the IR spectrum, of the NH stretching bands in the range 3350—3250 cm^{-1} and by the absence of SH stretching in its characteristic region near 2600 cm^{-1}.

As already found for other benzothiazolines [104], H_3fsal(at)$_2$ can, in the presence of metal ions or bases, give rise to complexes in which the benzothiazoline acts as trianionic ligand in its tautomeric Schiff base.

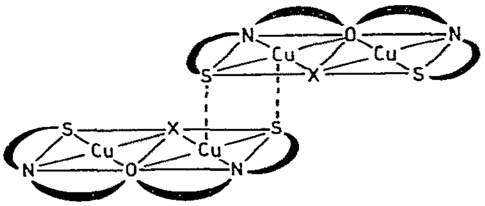
The copper(II) and nickel(II) complexes with H_3fsal(at)$_2$ and H_3fsal(thise)$_2$ have been prepared by reacting such ligands with the appropriate metal carboxylate in the presence of the X$^-$ group.

With H_3fsal(at)$_2$ the complexes crystallized without solvent molecules while with H_3fsal(thise)$_2$ solvate complexes containing DMF or DMSO molecules have been obtained. The proposed structure for these complexes



was confirmed by X-ray structural analyses for the complex Ni_2fsal(thise)$_2$-(OC_2H_5) · 2DMF [102].

Significant differences between the IR spectra of the Cu_2fsal(at)$_2$X and Ni_2fsal(at)$_2$X series have been explained by different degrees of axial interaction between a metal atom of one binuclear complex with a ligand atom (S or less likely O) of an adjacent molecule in the crystal. Such an interaction is negligible in Ni_2fsal(at)$_2$X complexes but is significant in Cu_2fsal(at)$_2$X. The splitting of the band at 1575 cm^{-1} in the Cu_2fsal(at)$_2$X complexes may arise from interactions of the type



which render the two side arms of a particular ligand no longer equivalent. This sort of tetranuclear association definitely exists in the closely related $Cu_2fsal(ap)_2(C_3H_3N_2)$ already reported [95].

The IR spectra of the complexes derived from $H_3fsal(thise)_2$ generally show much broader bands and poorer resolution than those in the complexes derived from $H_3fsal(at)_2$. Comparison of the IR spectra of the $Ni_2fsal(thise)_2X$ and $Cu_2fsal(thise)_2X$ complexes reflects more pronounced axial interactions in the copper(II) series.

The magnetic behaviour of these nickel(II) and copper(II) complexes is in accordance with the proposed binuclear structures. All the complexes, except those reported in Table 13, are diamagnetic. Exchange data for the copper(II) dimers are indicated in Table 13. The magnetic susceptibility of $Cu_2fsal(at)_2N_3$ was so low to preclude meaningful curve fitting to theoretical data, but the general behaviour (became effectively diamagnetic at 125 K) was consistent with strong antiferromagnetic coupling within pairs of cupric ions as was the effective diamagnetism of the remaining cupric complexes.

The alkoxide complexes were readily obtained by reaction of either $H_3fsal(at)_2$ and $H_3fsal(thise)_2$ with the appropriate metal carboxylate in the presence of the appropriate alcohol or by heating one alkoxy-bridged complex in presence of an excess of a different alcohol.

TABLE 13

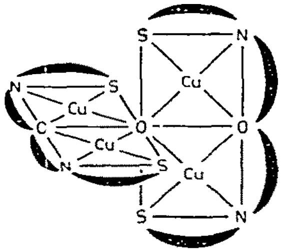
Copper(II) and nickel(II) paramagnetic complexes with the ligands $H_3fsal(at)_2$ and $H_3fsal(thise)_2$

Compound	μ_{eff} (BM)	T (K)	J * (cm^{-1})	g *	TIP * (cgs)
$Cu_2fsal(at)_2(C_3H_3N_2)$	1.2	295	−372	2.0	30
$Cu_2fsal(thise)_2(C_3H_3N_2)$	1.2	290	−414	2.2	50
$Cu_2fsal(thise)_2(N_3) \cdot DMSO$	1.0	287	−472	2.0	20
$Cu_2fsal(thise)_2Cl \cdot 2\ DMSO$	1.2	296	−430	2.3	40
$Cu_2fsal(at)_2(N_3)$	0.7	293			
$Ni_2fsal(thise)_2Cl \cdot 4\ DMSO$	2.0	295			
$Ni_2fsal(thise)_2Cl \cdot 2\ DMSO$	1.9	295			

* Values taken to yield the agreement between experimental data and data calculated on the basis of the Bleaney—Bowers equation.

The hydroxy-derivatives Cu_2fsal(at)$_2$OH and Ni_2fsal(at)$_2$OH · DMF were obtained by heating the corresponding ethoxides with undried DMF, containing a small quantity of water. The copper(II) compounds show IR bands at 3493 cm^{-1}, the nickel(II) ones at 3320 cm^{-1} due to ν_{OH}.

The oxo-derivative $[Cu_2$fsal(at)$_2]_2$(O) was obtained as brown crystalline solid from solutions of cupric isobutyrate and H_3fsal(at)$_2$ in DMSO. Its IR spectrum is almost identical with that of Cu_2fsal(at)$_2$(OH) except that the OH stretching band was totally absent. This complex very probably has the tetranuclear structure

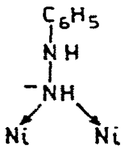


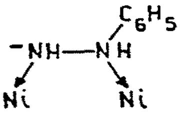
with an oxide ion bridging four cupric ions.

Hot DMF solutions containing nickel(II) acetate and H_3fsal(thise)$_2$ yielded a brown crystalline solid with elemental composition consistent with either Ni_2fsal(thise)$_2$OH · 3DMF or $[Ni_2$fsal(thise)$_2]_2$(O) · 6DMF. The IR spectra have not resolved this question.

The apparent ability of the $[M_2$fsal(at)$_2]^+$ and $[M_2$fsal(thise)$_2]^+$ units to form a stable union with highly basic bridging X^- groups is provided by the amido-bridged complexes, stable in the air as for instance Ni_2fsal(thise)$_2$-(NH-*n*-C_4H_9) and easily recrystallized from undried solvents.

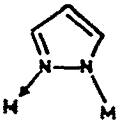
In Ni_2fsal(thise)$_2$($NHNHC_6H_5$), the amido anion may bridge in one of two possible ways





and this is the first example of the conjugate base of phenylhydrazone behaving as a bridging ligand.

The pyrazolate anion in the complexes M_2fsal(at)$_2$($C_3H_3N_2$) or M_2fsal(thise)$_2$($C_3H_3N_2$) would coordinate in one of the two ways



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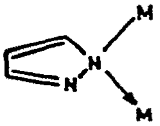
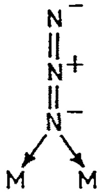


II

An X-ray crystallographic study of $Cu_2fsal(ap)_2(C_3H_3N_2)$ revealed the bridging mode (I) [105]. The IR spectra suggest that the bridging mode (II) is present also in the complexes discussed here especially $M_2fsal(thise)_2(C_3H_3N_2)$. In the case of $M_2fsal(at)_2(C_3H_3N_2)$ derivatives, the possibility of bridging through a single nitrogen atom, X, cannot be entirely discounted since the absorption in the 1600 cm^{-1} region is significantly different from that of $Cu_2fsal(ap)_2(C_3H_3N_2)$. The sulphur donor atoms, more bulky than oxygen donors in $H_3fsal(at)_2$, might have the effect of pushing the two metal ions closer together and consequently of permitting the bridging (II) mode over mode (I).

In the azido-bridged complexes, there are also two possible types of coordination of the N_3^- group



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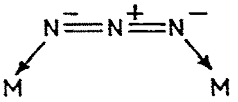


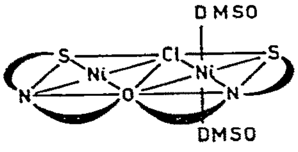
II

easily detectable on the basis of IR spectra. It was reported [106] that the appearance of a band of medium intensity near 1300 cm^{-1}, ascribed to ν_{symm} azine stretching frequency, indicates the presence of bridging azine as in I whereas for mode II, in which the azine fragment is much more symmetrically bound, ν_{symm} is IR inactive or, at best, very weak. The bands of medium intensity near 1300 cm^{-1} observed in all four azido-bridged complexes reported here, strongly support the bridging mode I. The IR spectrum of $Ni_2fsal(thise)_2(NCO) \cdot DMF$ is less useful the cyanate stretching modes being of little diagnostic value.

The chloride complexes $Ni_2fsal(thise)_2Cl \cdot 4DMSO$ and $Cu_2fsal(thise)_2Cl$ were readily obtained in pure crystalline form from DMSO solution. Repeated attempts to prepare analogous complexes of $H_3fsal(at)_2$ do not give the same complexes.

$Ni_2fsal(thise)_2Cl \cdot 4DMSO$ and $Ni_2fsal(thise)_2Cl \cdot 2DMSO$ are paramagnetic and obey the Curie—Weiss law over the temperature range 100—300 K. The room temperature magnetic moment per nickel atom of 2.0 BM together with the Curie—Weiss behaviour have been proposed to be strongly suggestive of equal number of nickel cations in the spin singlet and triplet states.

The observed magnetic susceptibility would then imply a magnetic moment for the paramagnetic centre of almost exactly the spin only value for a spin triplet. The configurations:



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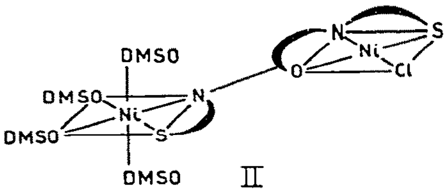
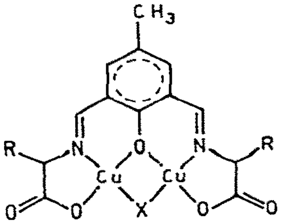


II

have been proposed in which the pseudo-square planar nickel ion is the diamagnetic centre in both cases.

Mass loss measurements under vacuum at various temperatures indicated that near 100° C two of the four DMSO molecules were rapidly lost while a temperature of 140° C was required to remove all the DMSO. In this way residues with a composition consistent with $Ni_2fsal(thise)_2Cl \cdot 2DMSO$ and $Ni_2fsal(thise)_2Cl$ could be obtained. Significantly $Ni_2fsal(thise)_2Cl$ is diamagnetic while $Ni_2fsal(thise)_2Cl \cdot 2DMSO$ has a magnetic moment of 1.9 BM per nickel atom. These results strongly suggest that the two molecules of DMSO removed at 100° C would be lost from lattice sites leaving the environment of the paramagnetic pseudo-octahedral nickel ion intact; so configuration I is the most probable. The loss of further DMSO would then yield a pseudo-square planar diamagnetic nickel(II) environment.

Copper(II) complexes of the type



have been prepared by the reaction of 2,6-diformyl-4-methylphenol with α-aminoacids [107,108]. In particular complexes of the type $Cu_2fsal(gly)_2X$ ($X = OH^-, Cl^-, Br^-$) and $Cu_2fsal(ala)_2Cl$, have been obtained where $H_3fsal(gly)_2$ and $H_3fsal(ala)_2$ are the Schiff bases derived from the aminoacids glycine or alanine, respectively.

Syntheses of binuclear copper(II) complexes of Schiff bases with other α-aminoacids such as valine, leucine, isoleucine and phenyl-alanine were unsuccessful.

The IR spectra of the four complexes above are very similar to each other, suggesting similar structures. Spectra in the range 1700—1400 cm^{-1}, resemble those of the copper(II) complex of the Schiff base derived from salicylaldehyde and glycine [109].

The complexes, except $Cu_2fsal(gly)_2OH \cdot H_2O$ which decomposes in pyridine giving bis(glycinato)copper(II), are likely to keep their binuclear structures in polar solvents such as water, methanol, pyridine.

$Cu_2fsal(gly)_2OH \cdot H_2O$ is antiferromagnetic with $-2J = 447$ cm^{-1}, $g = 2.16$, $N\alpha = 7.0 \cdot 10^{-6}$ cgs. The other three complexes prepared obey the Curie—Weiss law in the temperature range 76—290 K. The Weiss constants θ, obtained by extrapolating $1/(\chi_A - N\alpha)$ ($N\alpha = 60 \cdot 10^{-6}$ cgs) versus T, for all these complexes are negative, indicating that there is an antiferromagnetic exchange interaction between the copper(II) ions. Since the copper—copper distance (3.4 Å) excludes a direct exchange interaction between copper(II) ions, superexchange through the bridging group is most important in the magnetic interaction in the complexes.

The powder X-ray diffraction spectra of $Cu_2fsal(gly)_2X$ (X = Cl, Br) are quite similar to each other but differ from that of $Cu_2fsal(gly)_2OH \cdot H_2O$. Assuming that the spin—spin coupling through the phenolic oxygen is the same in all the complexes, the difference in the magnetic behaviour reflects the effect of the second bridging group; such an effect was found to vary in the order OH > Cl ≃ Br.

The preparation of some binuclear copper(II) complexes of the Schiff base 2,6-bis-[N-(β-dialkylaminoethyl)iminomethyl]-4-methylphenol ($Hfsal(NenNR_2)_2$) made from 2,6-diformyl-4-methylphenol and *N,N'*-dialkylethylenediamine (alkyl = methyl and ethyl) was reported [110].

The *d—d* bands of the OH-bridged complexes in the reflection spectra lie at higher energy than those of the corresponding halogen-bridged complexes; this indicates that the OH and the halogen-bridged complexes possess a molecular structure differing from each other in the solid state. The copper(II) ion in the OH-bridged complexes would be practically planar.

In the halo-complexes $[Cu_2fsal(NenNR_2)_2X]X_2$ the copper(II) ions are five coordinate in a tetragonal-pyramidal structure; one halogen ion will coordinate in an apical position. The complexes are, in methanol, five coordinate with a solvent molecule in the fifth position.

The powder ESR spectra of $[Cu_2fsal(NenNMe_2)_2X]^{2+}$ complexes (X = Cl, Br and OH) are very similar to the corresponding spectra of $—NEt_2$ derivative complexes. The Cl-bridged complex showed a broad band centered around 3500 gauss; in the spectrum of the Br-bridged complex the signal at 1700 gauss may be assigned to the $\Delta M_s = 2$ transition. Two signals at 6000 and 1600 gauss are present in the spectrum of the OH-bridged complex, tentatively assigned to the $\Delta M_s = 1$ and $\Delta M_s = 2$ transitions, respectively. The ESR spectrum of $[Cu_2fsal(NenNEt_2)_2OH](ClO_4)_2$ presents two signals at 5500 and 1600 gauss whose intensities decrease with the lowering of the temperature.

All the complexes show magnetic moments lower than expected with values of $-2J$, g and $N\alpha$ reported in Table 14. The $-2J$ data indicate that the

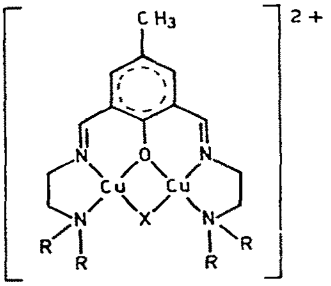


Fig. 11. The molecular geometry of the complex $[Cu_2fsal(NenNR_2)_2X]^{2+}$ ($R=CH_3$, C_2H_5; X=Cl, Br, OH).

TABLE 14

Magnetic parameters of copper(II) complexes with the ligand Hfsal(NenNR$_2$)

Complex	$-J$ (cm^{-1})	$-J'$ (cm^{-1})	g	$N\alpha \cdot 10^6$ (cgsu)
Cu$_2$fsal(NenNMe$_2$)$_2$(NCS)$_3$	105	15	2.18	43
Cu$_2$fsal(NenNEt$_2$)$_2$(NCS)$_3$	87.5	20	2.17	50
Cu$_2$fsal(pya)$_2$(NCS)$_3$	87.5	25	2.15	45

J = Exchange coupling between the two copper(II) ions in the dimeric unit. J' = Exchange coupling between two copper(II) ions between two different dimeric units.

effect of the second bridging group on the antiferromagnetic exchange interaction increases in the order X = OH >> Br > Cl. The correlation between d—d bands and the $-2J$ values of the complexes implies that the more planar the configuration around the copper(II) ion, the larger the magnetic exchange between the copper(II) ions.

Binuclear copper(II) complexes possessing a thiocyanato-bridging group have been synthesized by treating diisothiocyanatodipyridine copper(II) in acetonitrile with the ligands Hfsal(NenNMe$_2$)$_2$, Hfsal(NenNEt$_2$)$_2$, discussed above, and Hfsal(pya)$_2$ obtained from 2,6-diformyl-4-methylphenol and 2-pyridylmethylamine [111]. Infrared absorption, ligand-field and the magnetic data at room temperature are given in Table 15.

The IR spectra of Cu$_2$fsal(NenNR$_2$)$_2$(NCS)$_3$ are very similar to those of the corresponding Cu$_2$fsal(NenNR$_2$)$_2$X$_3$ (X = Cl, Br) [110]. It is likely that the present complexes have a skeleton $>\mathrm{Cu}\genfrac{<}{>}{0pt}{}{\mathrm{O}}{\mathrm{Y}}\mathrm{Cu}<$ (Y = —SCN or —NCS). Two C—N stretching vibrations of the thiocyanate group were found in the region 2080—2060 cm^{-1}, suggesting that there are two kinds of thiocyanate group with different bonding modes in the complexes. The band at 820—810 cm^{-1} may be due to the Cu—NCS bond as already found [112], while the

TABLE 15

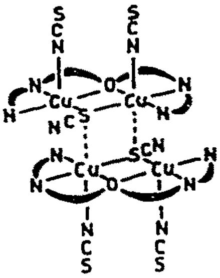
IR bands, d—d bands and effective magnetic moments of copper(II) complexes with the ligand Hfsal(NenNR$_2$)

Complex	IR (cm^{-1})			Reflectance (nm)	μ_{eff} BM, (K)
	C≡N	C=N	C—S		
Cu$_2$fsal(NenNMe$_2$)$_2$(NCS)$_3$	2080 2070	1635 1630	815 700	658	1.57(298)
Cu$_2$fsal(NenNEt$_2$)$_2$(NCS)$_3$	2080 2070	1640 1627	810 730	700	1.62(297)
Cu$_2$fsal(pya)$_2$(NCS)$_3$	2080 2060	1640	820 720	700	1.57(296)

band at 730—700 cm^{-1} was assigned to the C—S stretching vibration of the S-bonded thiocyanate group. It is very likely that the two copper(II) ions are connected by the S—C≡N group and the N-bonded thiocyanates coordinate to copper(II) ions in the apical positions.

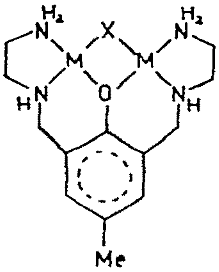
All the complexes show magnetic moments smaller than the spin-only value at room temperature and the experimental values at various temperatures are in good agreement with theory only if a tetranuclear cluster is invoked as already found for a Co(II)—Co(III) complex [101].

The most probable structure for the complexes is



A tetraamine binucleating ligand with fully saturated side arms, 2,6-bis-(*N*-2′-aminoethylaminomethyl)-*p*-cresol, Hfsal(NenN)$_2$ has been prepared [113] by reaction of 2-hydroxy-5-methylisophthalaldehyde with an excess of ethylenediamine in boiling methanol, followed by reduction of the condensation product with sodium borohydride.

By using this ligand, the series of binuclear copper(II) complexes reported in Table 16 was prepared. Their proposed configuration is



The ligand was isolated only as sodium derivative; its molecular weight suggests a 2 : 2 metal—ligand complex and an approximately octahedral ligand environment of the type

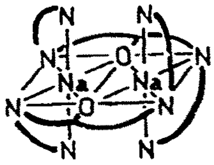


TABLE 16

Physical properties of copper(II) complexes with the ligand Hfsal(NenN)$_2$

		Reflectance * (nm)
Group 1	$Cu_2fsal(NenN)_2(OH)(ClO_4)_2$	570
	$Cu_2fsal(NenN)_2(C_3H_3N_2)(ClO_4)_2$	585
	$Cu_2fsal(NenN)_2(C_5H_5NO)(ClO_4)_3 \cdot H_2O$	590
	$Cu_2fsal(NenN)_2Cl(ClO_4)_2$	607
	$Cu_2fsal(NenN)_2Br(ClO_4)_2$	592
Group 2	$Cu_2fsal(NenN)_2Cl_2(ClO_4) \cdot MeOH$	650
	$Cu_2fsal(NenN)_2Br_2(ClO_4) \cdot MeOH$	650
	$Cu_2fsal(NenN)_2(CNS)_2(ClO_4)$	670
	$Cu_2fsal(NenN)_2(CNS)_3$	685
Group 3	$Cu_2fsal(NenN)_2Cl_3$	725
	$Cu_2fsal(NenN)_2Br_3 \cdot (H_2O)$	765
	$Cufsal(NenN)_2(ClO_4)$	615

* An additional band at 425—450 nm was observed in all cases. ** Arising from species other than the binucleating ligand. *** Aqueous solution: molarities × 10^3 in parentheses; temp. 20°. ‡ Temperatures (K) in parentheses. ‡‡ Values taken to yield the best agreement between experimental data and data calculated on the basis of the Bleaney—Bowers equation.

was supposed as already found, by X-ray crystallography, for other sodium complexes [114,115].

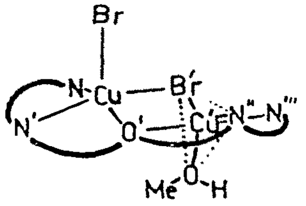
The OH stretching band of $Cu_2fsal(NenN)_2OH(ClO_4)_2$ at 3242 cm^{-1} is broadened; broadening by H bonding appears to be responsible for the lack of observable OH stretching bands in $Cu_2fsal(NenN)_2X_2(ClO_4) \cdot MeOH$ (X = Cl, Br) and in $Cu_2fsal(NenN)_2Br_3 \cdot H_2O$. The pyrazole ring vibration of $[Cu_2fsal(NenN)_2(C_3H_3N_2)](ClO_4)_2$ at 1635 cm^{-1} is consistent with bridging in which one nitrogen is attached to one copper(II) atom and the other nitrogen to the second copper(II) atom. A band at 1205 cm^{-1} assignable to the N—O stretching frequency of the pyridine N—oxide fragment in $Cu_2fsal(NenN)_2(pyN—O)(ClO_4)_3 \cdot H_2O$ appears to be characteristic of bridging through the oxygen atom.

IR bands ** (cm^{-1})	Molar conductance *** (ohm^{-1} cm^2 mol^{-1})	Magnetic properties			
		μ_{eff} ‡	$-2J$ ‡‡ (cm^{-1})	g ‡‡	$N\alpha \cdot 10^6$ ‡‡ (cgsu)
3420 (O—H str)	179(1.00)	0.66(290)			
1635 ($C_3H_3N_2$ ring vibration)	198(1.00)	0.81(292)			
1205 m (NO str), 844 (NO bend)	288(4.33)	0.58(292)			
	347(0.86)	1.61(280)			
	318(1.58)	1.69(290)			
No OH str obsd	318(1.04)	1.55(292)	195	2.05	60
No OH str obsd	316(1.48)	1.73(296)	139	2.11	80
2094 vs, 2110 sh (ν(CN)); 800 sh (ν(CS)); 473 (ν(NCS))	304(1.04)	1.47(299)	250	2.06	57
2080 vs, 2102 vs (ν(CN)); 800 sh (ν(CS)); 475 w, 469 sh (ν(NCS))		1.43(295)	250	2.02	45
	366(0.50)	1.46(291)	250	2.05	65
No OH str obsd	342(1.00)	1.54(297)	236	2.11	60
	81(0.99)	1.83(294)			

The complexes may be divided into three groups (Table 16) on the basis of their diffuse reflectance spectra and of expected different structural conformations.

The complexes having *d—d* bands of highest energy (group 1) are all of the composition $[Cu_2fsal(NenN)_2X](ClO_4)_y$ where X is a neutral or monoanionic ligand and $y = 2$ or 3. These complexes have an almost square-planar configuration although the observed energies are somewhat lower than those generally quoted for square-planar copper(II) complexes; this has been explained with the assumption either of some degree of tetrahedral distortion or of weak axial interaction within the lattice. The *d—d* bands of these complexes are all sharp consistent with both copper(II) centres of each binuclear unit having the same or not very different environments; this is not true for the complexes of the group 2 where the *d*–*d* bands are at lower energy and show distinct broadening on the lower energy side of the maxima.

One member of the group 2, $Cu_2fsal(NenN)_2Br_2(ClO_4) \cdot MeOH$ has been studied by X-ray crystallography and has been shown to contain discrete $[Cu_2fsal(NenN)_2Br_2MeOH]^+$ cations and ClO_4^- anions. One bromide in the cation



is bridging, the other is terminal and the two copper(II) environments, while both five-coordinate, are significantly different. The cupric ion with the N_2OBr_2 donor set has an environment close to square-pyramidal with a bromide ion at the apex, while the other cupric ion, Cu′, has an N_2O_2Br donor set which is intermediate between trigonal-bipyramidal and square-pyramidal with a methanol molecule at apex but approximating to the former. For the complex $Cu_2fsal(NenN)_2Cl_2(ClO_4) \cdot MeOH$ the same structure was proposed on the basis of the very similar IR and electronic spectra.

Infrared and electronic spectra of $Cu_2fsal(NenN)_2(CNS)_3$ and $Cu_2fsal(NenN)_2(CNS)_2(ClO_4)$ indicate the presence of the same cation $[Cu_2fsal(NenN)_2(CNS)_2]^+$ and five-coordinate copper(II) environments in both cases. It was proposed that the five coordination was reached with two N-bridging thiocyanate groups in a discrete binuclear species or with one intermolecular and one intramolecular N-bridging thiocyanate group in a polymeric one. The coordination of the thiocyanate groups is different from that proposed by Ichinose et al. [111] for the complex $Cu_2fsal(NenNR_2)_2(NCS)_3$ where S is the bridging atom. A distorted octahedral configuration was suggested for the complexes of group 3 of Table 16.

Aqueous conductance data indicate that the complexes $Cu_2fsal(NenN)_2OH(ClO_4)_2$ and $Cu_2fsal(NenN)_2(C_3H_3N_2)(ClO_4)_2$ are 2 : 1 electrolytes; the other complexes showed molar conductance typical of 3 : 1 electrolytes.

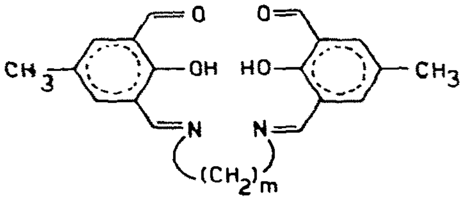
The magnetic behaviour of these complexes varies from very weak paramagnetism to only slightly depressed paramagnetism. Very strong antiferromagnetic coupling is present in the three complexes $Cu_2fsal(NenN)_2OH(ClO_4)_2$, $Cu_2fsal(NenN)_2(C_3H_3N_2)(ClO_4)_2$ and $Cu_2fsal(NenN)_2(C_5H_5N{-}O)(ClO_4)_3 \cdot H_2O$, while $Cu_2fsal(NenN)_2Cl(ClO_4)_2$ shows a smaller degree of coupling.

For almost all the complexes the experimental data could be satisfactorily fitted to the Bleaney–Bowers equation [94]. This equation could not be applied to complexes in which the two copper ions are in a different environment because they may have generally different g values; however in those complexes were χ_{Cu} changes by hundreds $\times 10^{-6}$ cgsu between 300 and 100 K it was found that this equation can be successfully applied [116,117].

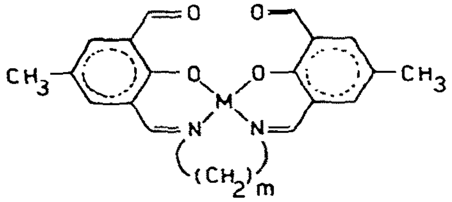
The mononuclear species Cufsal(NenN)$_2$(ClO$_4$), the last complex of Table 16, was obtained as a green crystalline solid by the reaction of Na$_2$[fsal(NenN)$_2$]$_2$ and cupric perchlorate in a 1 : 1 molar ratio in methanol. Conductance, IR, UV and molecular weight data exclude the presence of dimeric species Cu$_2$[fsal(NenN)$_2$]$_2$ also in aqueous solutions and exclude a coordination number for copper(II) ion greater than five.

Cufsal(NenN)$_2$(ClO$_4$), in contrast to all the other complexes reported in Table 16, gives a well resolved powder ESR spectrum which is in accordance with a distorted trigonal-bipyramid configuration even if molecular models indicate that a considerable strain would be involved.

The condensation of two molecules of 2,6-diformyl-4-methylphenol with one molecule of ethylenediamine or 1,3-diaminopropane affords the Schiff base



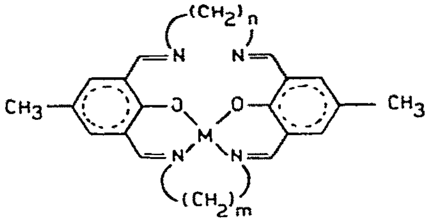
with no formation of polymer; copper(II) and nickel(II) complexes of the type



have been prepared [118,119].

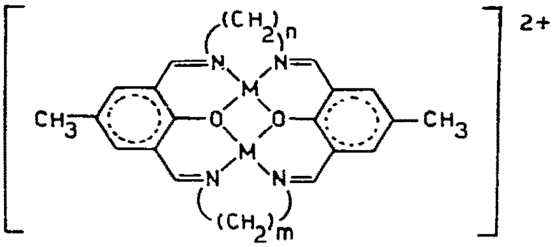
In the IR spectra the bands around 1670 and 1635—1628 cm^{-1} have been assigned to the C=O and C=N stretching vibrations, respectively. The *d—d* bands of Cufsal-3 were found at a lower energy region than that for Cufsal-2. Since it is well established that the red shift in the *d—d* bands takes place when the configuration around the copper(II) ion is distorted from planarity [120—123], Cufsal-3 is assumed to possess a slightly distorted structure and its large magnetic moment of 2.01 BM as compared with 1.81 BM for Cufsal-2 has been assumed to be an additional confirmation of the distortion from planarity toward tetrahedral configuration.

Nifsal-2 and Nifsal-3 are diamagnetic and have a planar configuration. The two formyl groups are sufficiently close to each other to allow an intramolecular cyclization by treatment with other molecules such as diamines. The complexes obtained are of the type



and their physico-chemical properties are reported in Table 17. The nickel(II) cyclic complexes are undoubtedly planar, being diamagnetic.

When Cufsal-3 and ethylenediamine were allowed to react in DMF the copper(II) migrates during the cyclization process to form a stable 6-5-6 condensed ring system. These cyclic complexes react with additional copper(II) or nickel(II) ions to form the binuclear complexes of the type



A series of binuclear complexes, by using the same ligands was prepared by other authors [124], by reaction of 5-methylisophthalaldehyde with 1,3-diaminopropane in the presence of various metal salts.

On the basis of the magnetic and spectral evidence the complexes are assigned binuclear structures in which the cations have an approximately square-pyramidal environment. These structural features have been con-

TABLE 17

Properties of Mfsal-*m*,*n* type complexes

Complex	ν(C=N)	*d*–*d* band (powder) (nm)	μ_{eff} (BM)
Cufsal-2,2 · H_2O	1645, 1635	571	1.80
Cufsal-2,3 · H_2O	1632	578	1.81
Cufsal-2(l-pn),3 · H_2O *	1635	578	1.82
Cufsal-3,3	1630, 1625	592	1.92
Nifsal-2,2 · 1/2 H_2O	1645, 1627	549	Diamagnetic
Nifsal-2,3	1628	552	Diamagnetic

* l-propylenediamine is included in the ligand instead of ethylenediamine.

firmed in the case of Cu_2fsal-3,3-$Cl_2 \cdot 6H_2O$ by an X-ray crystallographic analysis (Fig. 12) [129c]. The magnetic data of all the complexes are consistent with a binuclear arrangement within which the antiferromagnetic interactions increase on passing from manganese to nickel. This trend is continued with the copper compounds in which strong antiferromagnetic interaction is undoubtedly present.

The electronic spectra of solid Ni_2fsal-3,3-$Cl_2 \cdot 2H_2O$ both in the solid phase and in aqueous solution provide good evidence for an approximately square-pyramidal cation environment. The differences between the spectra of Ni_2fsal-3,3-$Cl_2 \cdot 6H_2O$ in the solid state and in aqueous solution indicates that upon dissolution in water the average ligand field strength is raised which is consistent with the presence of an apical chloride ligand in the solid that is displaced in aqueous solution by a water molecule with a stronger ligand field; conductance data support this interpretation.

The magnetism and spectra of Co_2fsal-3,3-$Cl_2 \cdot 3CH_3OH$ and Fe_2fsal-3,3-$Cl_2 \cdot 3CH_3OH$ are consistent with square-pyramidal cation environments, but the available evidence fails to distinguish between coordination of chloride or methanol in the apical fifth position.

In the absence of observable *d—d* spectra no direct evidence concerning the cation stereochemistry is available for Mn_2fsal-3,3-$Cl_2 \cdot 2H_2O$ and Zn_2fsal-3,3-$Cl_2 \cdot 2H_2O$ although it seems likely all the chlorides have analogous structures. The two types of macrocyclic copper(II) and nickel(II) complexes (Fig. 13) have been prepared [125] by combination of 2,6-diformyl-4-methylphenol, hydroxylamine and diamines. The properties of these complexes are reported in Table 18.

The magnetic moments at room temperature of Cu_2fsal-3(H),3(H) is subnormal (0.59 BM). Its magnetic susceptibility was measured over the temperature range 77—300 K and from the best fit of the experimental χ_A values to the Bleaney—Bowers equation, $-2J$, g and $N\alpha$ were evaluated to be 870 cm^{-1}, 2.20 and $36 \cdot 10^{-6}$ cgsu, respectively. This large $-2J$ value indicates a very strong antiferromagnetic exchange interaction between the copper(II) ions. Generally the more planar is the geometry around the

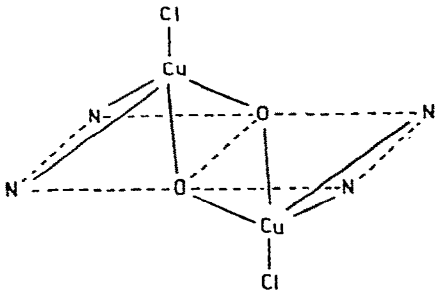


Fig. 12. Representation of the geometry around the binuclear core of the complex Cu_2fsal-3,3-$Cl_2 \cdot 6H_2O$.

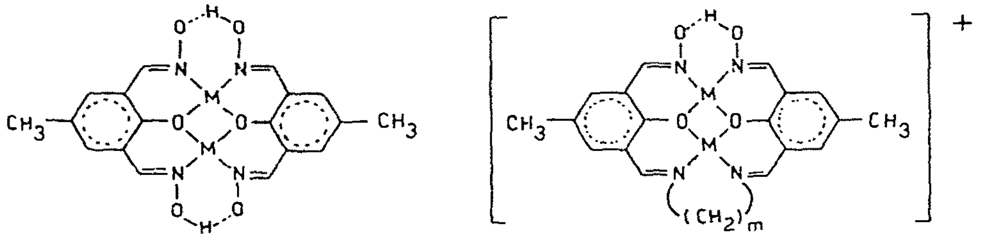
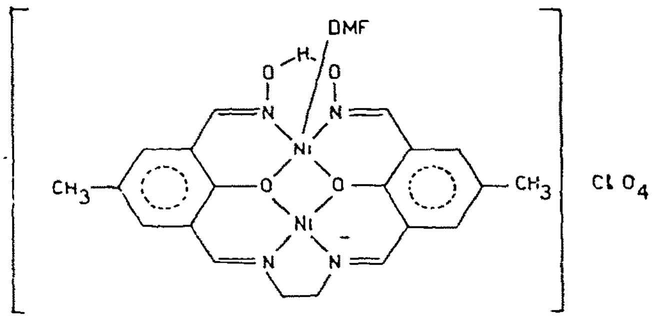


Fig. 13. The proposed structure of M_2fsal-3(H), 3(H) and [M_2fsal-*m*,3H]$^+$ ($M=Cu^{2+}$, Ni^{2+}; *m*=2,3).

copper(II) ion, the larger is the spin-exchange interaction between the copper(II) [126—128]. The reflectance spectra indicate that the geometry around the nickel(II) ion is practically octahedral.

The magnetic moment at room temperature is slightly lower (2.84 BM) than most octahedral nickel(II) complexes. The magnetic susceptibility of this complex obeys the Curie—Weiss law and the Weiss constant was determined to be —77 K, indicating an antiferromagnetic interaction between the pair of nickel ions. The magnetic moment of [Cu_2fsal-2,3(H)]ClO_4 at room temperature is very low (0.59 BM) and the best magnetic parameters obtained are: $-2J = 725\ cm^{-1}$; $g = 2.10$ and $N\alpha = 90 \cdot 10^{-6}$ cgsu. The properties of the complex [Ni_2fsal-2,3(H)(DMF)]ClO_4



are very complicated. The physico-chemical data have been interpreted with the assumption that the complex is composed of a binuclear system containing one high spin and one low spin nickel(II) ion.

The reflectance spectrum was interpreted as the superposition of the spectra of low spin planar and high spin tetragonal pyramidal nickel(II) ions. The solution spectrum in methanol, however, was very simplified and indicates that in this solvent neither DMF nor methanol are coordinated to the complex which keeps a planar structure. Attempts to prepare the binuclear cobalt(III) complexes of the ligand (L)

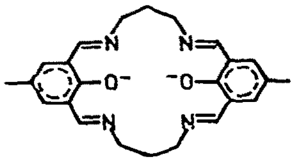


TABLE 18

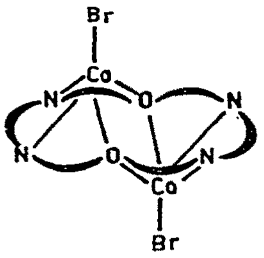
Properties of M_2fsal-3(H),3(H) and $[M_2\text{fsal-}m\text{,3(H)}]^+$ complexes

Complex	IR (cm^{-1})			Λ *	μ_{eff} (BM) ***
	O · · H · · O	C=N	C=O		
Cu_2fsal-3(H),3(H)	1750	1610			0.59
Ni_2fsal-3(H),3(H) · 3 H_2O	1740	1610			2.87
[Cu_2fsal-2,3(H)]ClO_4	1760	1635 1628		— **	0.59
[Cu_2fsal-3,3(H)]ClO_4 · H_2O	1770	1637 1629		109	0.61
[Ni_2fsal-2,3(H)]ClO_4 · DMF	1780	1680 1622	1635	95	2.25(3.31) ‡

* Molar conductivity (Ω^{-1} cm^2 mol^{-1}). ** Hardly soluble in methanol. *** At room temperature. ‡ This moment is obtained by assuming that one nickel(II) ion is diamagnetic.

by oxidation of the complex $Co_2LCl_2 \cdot 2CH_3OH$ led to the general disruption of the ligand L as indicated by the isolation of 1,3-diaminopropane hydrochloride [129].

As a starting material for attempted oxidations using bromine, the corresponding bromo derivative $Co_2LBr_2 \cdot CH_3OH$ was prepared. An X-ray crystallographic study of this complex was made [129c], which confirmed the initially predicted square-pyramidal geometry in a structure of the type



However, the methanol molecules, which are disordered, are very weakly bonded (Co—O = 2.503 Å) in a random fashion to half the cobalt centres from the side of the N_2O_2 plane opposite to the coordination bromine atom whilst the remaining cobalt atoms are truly 5-coordinate. The ligand is essentially planar except for the two central carbon atoms of the diaminopropane links.

The electronic spectra show *d*—*d* bands at 9300, 14 000 and 17 500 cm^{-1} (the last band appears as a shoulder on the tail of an intense band of charge transfer or *n*—π* origin). The magnetic properties are very similar to those of the chloride with an effective magnetic moment per Co atom of 4.7 BM at room temperature. These properties are in accordance with a square pyramidal ligand field of low basal symmetry as found by X-ray data. Recrystallization of this complex from water yielded the hydrated complex $Co_2LBr_2 \cdot H_2O$ which shows IR and electronic spectra very similar to those of the methanolate.

Oxidation of $Co_2LBr_2CH_3OH$ with molecular bromine yielded a number of products depending on reaction conditions. Species of composition $Co_2LBr_4CH_3OH$ and $Co_2LBr_3 \cdot H_2O$ were obtained. These complexes are moderately soluble with decomposition in methanol and in water but in CH_2Cl_2, in which they are slightly soluble, the decomposition is sufficiently slow at room temperature to allow physico-chemical measurements. The electronic spectra in this solvent and diffuse reflectance spectra were dominated by very intense bands, probably of charge transfer or n—π^* origin, which masked the d—d bands. The IR spectra show the same basic pattern of bands observed for all the $M_2LCl_2 \cdot$ solvent complexes [129,130] suggesting that the ligand L does not undergo any significant change. Pure 2-hydroxy-5-methylisophthalaldehyde was recovered in yield of 85% upon decomposition of the complexes with aqueous acid. The magnetic properties of $Co_2LBr_3H_2O$ and $Co_2LBr_4CH_3OH$ are summarized in Table 19.

Curie—Weiss behaviour was observed in the temperature range 300—100 K. The observed susceptibilities of the complex $Co_2LBr_3H_2O$ were best interpreted in terms of one diamagnetic cobalt(III) per binuclear unit and one paramagnetic cobalt(II) for which the experimental data require an effective magnetic moment of 4.8 BM at room temperature. The paramagnetism of the complex $Co_2LBr_4CH_3OH$ was interpreted in a similar way.

Single crystals of two isomeric forms A and B of $Co_2LBr_3 \cdot 2H_2O$ were obtained; the isomer A is orthorhombic and the isomer B is monoclinic. Both forms are unstable with respect to loss of water on exposure to the atmosphere and the isomer A rapidly loses one molecule of water at atmospheric pressure yielding $Co_2LBr_3H_2O$. The structures of the two isomers have been determined by X-ray methods. Both consist of discrete $(LCo(II)Co(III)Br_2(H_2O)_2)^+$ cations and bromide anions, the cations existing in the geometri-

TABLE 19

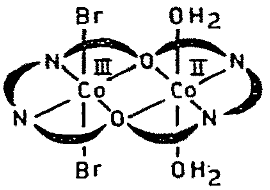
Magnetic properties of the cobalt complexes with the cyclic ligand H_2L

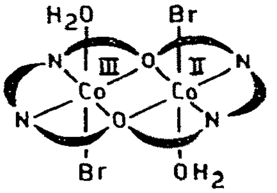
Complex	μ_{eff} BM (K)	Weiss Constant (K)
$Co_2LBr_2 \cdot CH_3OH$	4.68(304)	—55
$Co_2LCl_2 \cdot 2\ CH_3OH$	4.61(297)	—62
$Co_2LBr_2 \cdot H_2O$	4.53(296)	
$Co_2LBr_3 \cdot H_2O$	4.76(292)	—21
$Co_2LBr_4 \cdot CH_3OH$	4.64(303)	—20
$Co_2LBr_5 \cdot 2\ CH_3OH$	4.46(297)	

For the meaning of the signature H_2L see the text.

cally isomeric forms

A





B

In both cases the $N_2O_2N_2$ donor sets are very close to coplanar. In the isomer A the macrocycle is bent so that the two benzene rings are at an angle of 21.6° to each other, whilst in isomer B the two benzene rings are almost coplanar with each other and with the $N_2O_2N_2$ donor set. Attempts to prepare crystals of $Co_2LBr_4CH_3OH$ from methanolic reaction mixture of $Co_2LBr_2CH_3OH$ and bromine in equimolar ratio, yielded crystals indicated by X-ray studies to have the composition $Co_2LBr_5 \cdot 2CH_3OH$. The structural data show that the crystals consisted of tribromide anions and two non equivalent but very similar types of binuclear cations. $(LCo(II)Co(III)Br_2(CH_3OH)_2)^+$ (Fig. 14), both of which closely resembled the binuclear cations of the isomeric A form of $Co_2LBr_3 \cdot 2H_2O$, with a Co—Co distance in each of 3.16 (1) and 3.12 (2) Å. The macrocycle is bent so that the two benzene rings are at an angle of 22.7° and 17.9°, the ligand in each binuclear unit being bent considerably about the N···O···N axes as shown in Fig. 15. From these data it emerges that a binuclear Co(III)—Co(III) structure can be prepared and that it is very unstable reverting readily to Co(II)—Co(III). The initial black precipitate isolated in the approach to $Co_2LBr_4CH_3OH$ involving a large excess of bromine, readily loses Br_2 after isolation but if it is dried for a short time and then immediately analysed, the composition corresponds closely to $Co_2LBr_8 \cdot 4CH_3OH$. It is also significant that the freshly prepared material is effectively diamagnetic, and rapidly becomes paramagnetic as Br_2

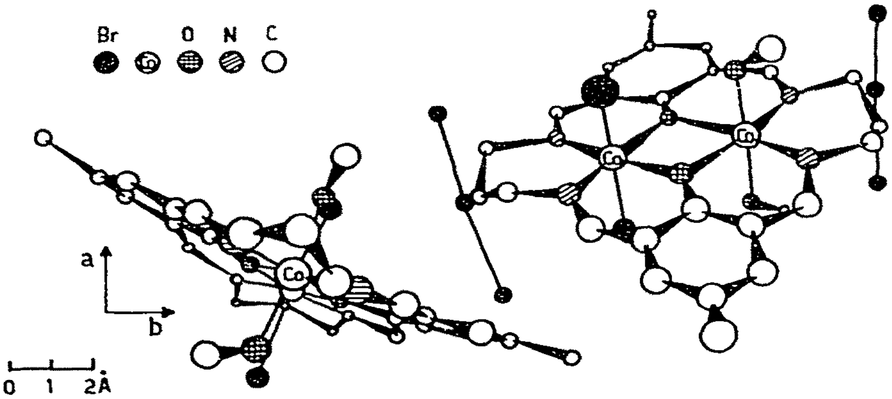


Fig. 14. The configuration of the asymmetric unit of $Co_2LBr_5 \cdot 2CH_3OH$.

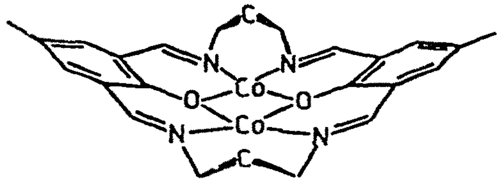
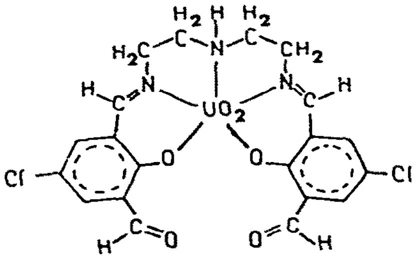


Fig. 15. Representation of the macrocyclic ligand geometry in $Co_2LBr_5 \cdot 2CH_3OH$.

is lost. After some months at atmospheric pressure and room temperature a susceptibility of the order of that of $Co_2LBr_4CH_3OH$ is reached. Therefore in the initial compound both the cobalt atoms are in the oxidation state (III), with both the central atom in a pseudooctahedral low spin state.

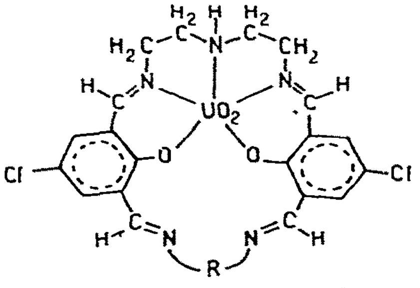
The synthesis and characterization of $[UO_2A]$



Complex $[UO_2A]$

by reaction of diethylenetriamine with 2,6-diformyl-4-chlorophenol in the presence of uranyl(VI) ion, has been recently reported [131,132]. This complex is quite similar to UO_2 (saldien).

In this complex the two uncoordinated formyl groups are sufficiently close to each other to allow an intramolecular cyclisation by treatment with diamines and the complexes

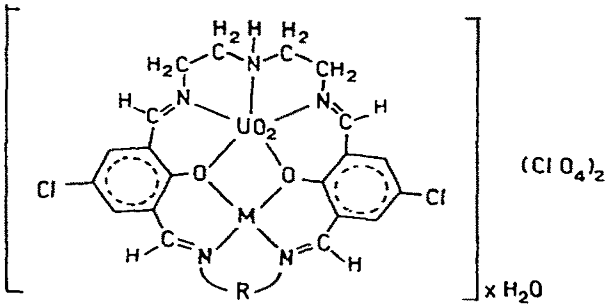


Complexes $[UO_2B]$

R	Complex
$-CH_2-CH_2-$	$[UO_2B_a]$
$-CH_2-CH_2-CH_2-$	$[UO_2B_b]$
$-CH_2-CH(CH_3)-$	$[UO_2B_c]$
$-CH_2-CH_2-NH-CH_2-CH_2-$	$[UO_2B_d]$

have been reported [132].

These complexes do not show IR bands due to the C=O groups while the absorptions of the coordinated and uncoordinated C=N azomethine groups are not resolved. No appreciable shift of the antisymmetric stretching ν_3 and bending ν_2 of the O—U—O group was observed after cyclisation. These cyclic complexes may act as ligands towards transition metal ions and the compounds



M = Co'', Ni'', Cu''

x = 0,2,3

Complexes $[UO_2BM](ClO_4)_2$

have been reported [132].

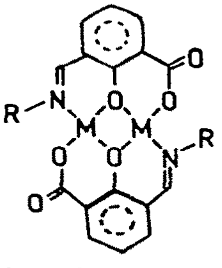
Marked differences upon coordination of the second metal ion are noted in the IR spectra, principally in the bands associated with νC=N, νC—O and ν_3-(O—U—O) modes. The νC=N is shifted to higher frequencies while the νC—O to lower. The simultaneous shift in the binuclear complexes to higher and lower frequencies for νC=N and νC—O modes, respectively, is due to the coordination of the second metal which localizes the C=N double bond and seems to reduce the amount of partial double character of the phenolic C—O link.

The only significant change in the modes of uranyl(VI) group is the shift to higher frequencies of the antisymmetric stretching ν_3(O—U—O) on going from mononuclear to binuclear complexes. This shift could be expected by a decreasing tendency to transfer charge from the phenolic oxygens to the uranium upon coordination of the second ion.

The electronic spectra of the binuclear complexes do not allow an unambiguous identification of the stereochemistry about the 3*d* transition metal ion. The magnetic moments agree well with a distortion of the N_2O_2 chromophore from planar towards tetrahedral arrangement.

D. COMPLEXES WITH 3-FORMYLSALICYLIC ACID AND ITS SCHIFF BASE DERIVATIVES

The syntheses and the characterization of the copper(II) and nickel(II) complexes of the Schiff bases derived from 3-formylsalicylic acid and the alkylamines (R—NH_2)

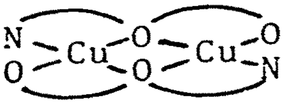


have been reported [133].

Properties of the copper(II) complexes ($Cu_2(fsalac—R)_2$) are given in Table 20.

The spectra and the effective magnetic moments at room temperature are much lower than spin-only and are consistent with a binuclear structure of the (CuO_3N)-chromophore. The complexes seem to maintain the binuclear structure in pyridine in which no coordination of the pyridine to the metal was supposed, since the shifts of the *d—d* bands are small. When the pyridine solution was concentrated, the pyridine-free complexes were recovered.

Judging from the —2*J* values of these complexes, it does not seem that the substituents attached to the imino-nitrogen exert any appreciable effect upon the spin-exchange interaction. These complexes seem to have a nearly coplanar structure in regard to the

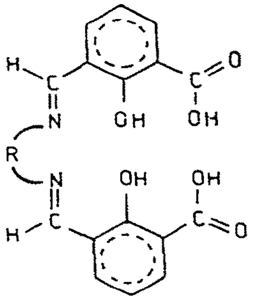


plane and exhibit a very strong antiferromagnetic spin-exchange interaction, as expected [134—136].

The nickel(II) complexes contain two, three or four water molecules and their properties are reported in Table 21. These physico-chemical properties indicate nearly octahedral geometry. In pyridine solution the complexes have solvent molecules in apical positions.

The magnetic moments at room temperature are comparable to the values for common octahedral nickel(II) complexes. The values near liquid nitrogen temperature are lower than the spin-only value, implying an antiferromagnetic spin-exchange interaction between nickel(II) ions. The Weiss constants obtained for $Ni_2(fsalac\text{-}R)_2nH_2O$ complexes are —35 K for R = methyl, —41 K for R = ethyl, —35 K for R = hydroxyethyl and —40 K for R = *n*-butyl. It was concluded that the demagnetization in these complexes is caused by intramolecular spin-exchange interaction through the oxygen bridges.

The synthesis and the characterization of new binucleating ligands derived from 3-formylsalicylic acid and diamine and their mononuclear and binuclear complexes of the type



R	
$-CH_2-CH_2-$	H_4 fsalacen
$-CH_2-CH_2-CH_2-$	H_4 fsalacprop
$-CH_2-CH_2-\underset{H}{N}-CH_2-CH_2-$	H_4 fsalacdien

TABLE 20

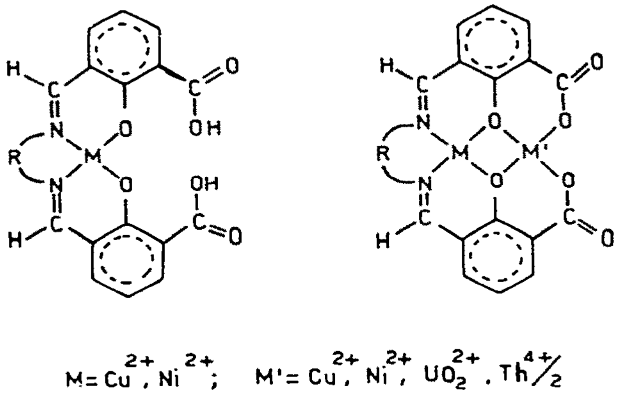
Physico-chemical properties and magnetic parameters of $Cu_2(fsalac\text{-}R)_2$ complexes

Complex	IR (cm^{-1})		d–d (nm)		μ_{eff} BM (K)	$-2J$ (cm^{-1})	g	$N\alpha \cdot 10^6$ (cgsu/mole)
	C=N	COO^-	Solid	Py(ε)				
$Cu_2(fsalac\text{-}Me)_2$	1645	1550	654	662(124)	0.68(297.7)	720	2.20	55
$Cu_2(fsalac\text{-}Et)_2$	1640	1545	671	676(118)	0.66(291.6)	715	2.20	27
$Cu_2(fsalacen\text{-}OH)_2$	1635	1540	649	662(128)	0.54(297.7)	820	2.20	37
$Cu_2(fsalac\text{-}Pr)_2$	1635	1540	680	694(114)	0.66(294.2)	725	2.20	55
$Cu_2(fsalac\text{-}n\text{-}Bt)_2$	1635	1545	676	685(101)	0.71(296.6)	705	2.20	35
$Cu_2(fsalac\text{-}i\text{-}Bt)_2$	1630	1550	676	685(119)	0.63(294.1)	735	2.17	65
$Cu_2(fsalac\text{-}s\text{-}Bt)_2$	1635	1545	680	694(101)	0.63(295.4)	750	2.20	50

TABLE 21

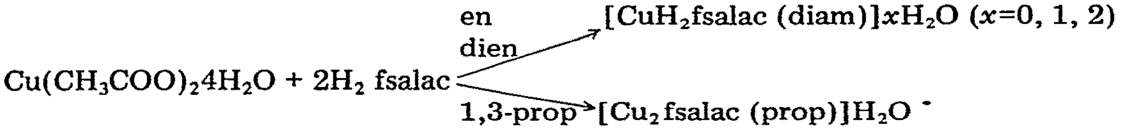
Properties of $Ni_2(fsalac\text{-}R)_2 \cdot n\ H_2O$

Complex	IR (cm^{-1})			d–d (nm)				μ_{eff} BM (K)	
	O–H	C=N	COO^-	Powder		Py(ε)			
$Ni_2(fsalac\text{-}Me)_2 \cdot 2\ H_2O$	3300	1640	1560	1136	649	1042(42)	629(38)	3.14(297.8)	2.76(87.0)
$Ni_2(fsalac\text{-}Et)_2 \cdot 3\ H_2O$	3300	1640	1560	1149	637	1052(35)	637(33)	3.10(293.0)	2.64(77.5)
$Ni_2(fsalacen\text{-}OH)_2 \cdot 2\ H_2O$	3300	1630	1570	1149	641	1042(37)	625(35)	3.06(291.7)	2.74(83.5)
$Ni_2(fsalac\text{-}n\text{-}Bt)_2 \cdot 4\ H_2O$.	3300	1635	1570	1123	645	1042(42)	621(40)	3.17(296.6)	2.72(87.1)



have been reported [137].

The copper(II) complexes were prepared from the reaction of stoichiometric amounts, of 3-formylsalicylic acid, diamine and copper(II) acetate in methanol according to the scheme



$$Cu(CH_3COO)_2 4H_2O + 2H_2\ fsalac \begin{cases} \xrightarrow{\text{en, dien}} [CuH_2fsalac\ (diam)]xH_2O\ (x=0, 1, 2) \\ \xrightarrow{\text{1,3-prop}} [Cu_2fsalac\ (prop)]H_2O \end{cases}$$

Attempts to prepare the mononuclear uranyl(VI) complex from the 3-formylsalicylic acid and ethylenediamine under a variety of conditions

TABLE 22

Some significant IR frequencies of the mononuclear and binuclear complexes derived from H_2fsalac and H_4(fsalac)$_2$diam

Compound	ν(C=N)	ν(C=O)	Other bands
H_2fsalac	—	1675	3543 ν(OH)
H_4(fsalac)$_2$en	1652	1700	3430 ν(OH)
CuH_2(fsalac)$_2$en	1642	1705	
CuH_2(fsalac)$_2$dien	1645	1695	3220 ν(N—H)
Cu_2(fsalac)$_2$prop	1640	1595	
CuNi(fsalac)$_2$en	1640	1610	3420 ν(OH)
$CuUO_2$(fsalac)$_2$en	1650	1595	919 ν_3(O—U—O), 260 ν_2(O—U—O)
CuTh(fsalac)$_2$en · 2 H_2O	1640	1598	3460 ν(OH), 3400 ν(OH), 1680 ν(—CH=O)
$Li_2[UO_2$(fsalac)$_2$ · $H_2O]$	—	1600	920 ν_3(O—U—O), 260 ν_2(O—U—O)
$Li_2[UO_2$(fsalac)$_2$en · $H_2O]$	1650	1600	3400 ν(OH), 900 ν_3(O—U—O), 268 ν_2(O—U—O)

yielded products of unknown composition; well defined complexes were obtained only through the following reactions

$$1)\ UO_2(NO_3)_2 \cdot 6H_2O + 2H_2\,\mathrm{fsalac} + 4LiOH \xrightarrow{\mathrm{EtOH}} Li_2[UO_2\,(\mathrm{fsalac})_2\,(H_2O)_2] + 2LiNO_3 + 8H_2O$$

$$2)\ Li_2[UO_2\,(\mathrm{fsalac})_2\,(H_2O)_2] + \mathrm{en} \xrightarrow{\mathrm{EtOH}} Li_2[UO_2\,(\mathrm{fsalac(en)})\,H_2O] + H_2O$$

It is reasonable to suppose that the coordination around the uranyl(VI) ion occurs through the carboxylic oxygen and the two phenolic oxygen atoms.

The mononuclear $CuH_2(\mathrm{fsalac})_2\mathrm{en}$ readily forms binuclear complexes when treated with nickel(II), thorium(VI) and uranyl(VI) acetates. The significant IR frequencies of these complexes are given in Table 22.

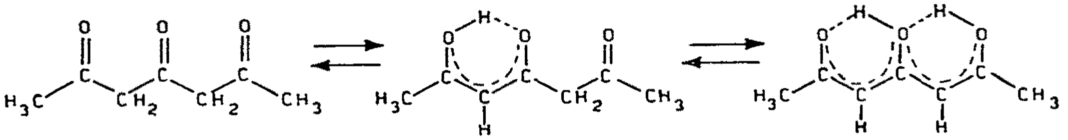
E. COMPLEXES WITH TRIKETONES

The presence of β-carbonyl groups with at least one proton on the carbon between them, allows a keto $\rightleftharpoons$ enol tautomerism to occur [138] and, under appropriate conditions the enolic proton can be removed.

The β,δ-tricarbonyl compounds are the higher analogues of the dicarbonyl compounds and can take triketo-, monoenol- and bisenol- forms in their tautomeric equilibrium. Accordingly, they can behave as bidentate or terdentate ligands to form metal chelate complexes.

The investigation of these keto-monoenol and -dienol equilibria has been studied by IR and ^1H NMR spectroscopy [139,140].

The ^1H NMR spectra of heptane-2,4,6-trione (H_2daa) in various solvents, which show the following tautomeric forms



and its keto-enol ratio at various temperatures are reported in Tables 23 and 24. The bisenol content of the heptane-2,4,6-trione increases with decrease in the polarity of the solvent used and a high percentage of the triketo form was found in solvents of high dielectric constant. This tendency being in good agreement with that observed in related 2,4-pentanedione, indicates the highly polar character of keto form rather than an enol form with intramolecular hydrogen bonding [141,142]. A temperature increase favours a greater abundance of the triketo form, as observed in the simpler β-diketone system [143].

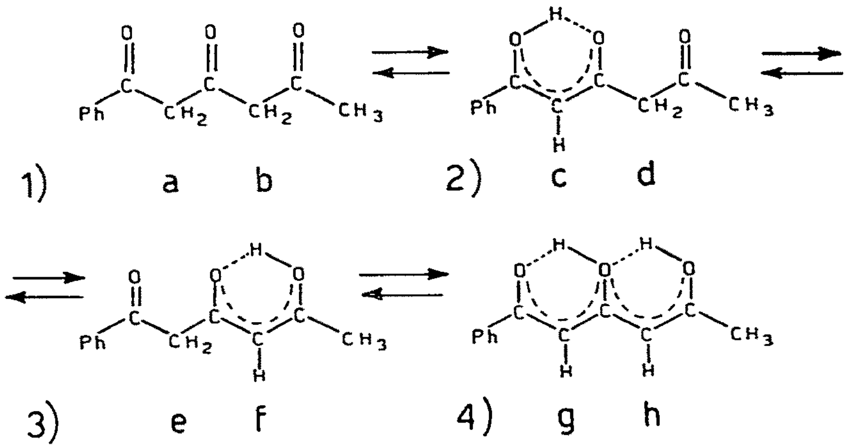
The IR spectrum of heptane-2,4,6-trione shows a band diffused over 3400 to 2200 cm^{-1}, combined together with a broad absorption at 1650 cm^{-1}, indicating the presence of a *cis*-β-ketoenol system with strong intramolecular hydrogen bonding. The unsymmetrical triketone 1-phenylhexane-1,3,5-trione (H_2phdaa) has more tautomeric forms than the more symmetric

TABLE 23

^1H NMR spectra of H_2daa at 38° C (c = 1.0 M)

Assignment	Chemical shift in the solvent			
	Methanol	$CDCl_3$	CCl_4	Benzene
Bisenol CH_3	1.97	1.97	1.94	1.63
C=C—H		5.12	5.02	4.88
Monoenol				
CH_3 enol side	2.05	2.07	2.04	1.63
CH_3 keto side	2.19	2.23	2.19	1.82
CH_2		3.38	3.27	2.97
C=C—H		5.53	5.45	5.15
Triketo CH_3		2.23	2.19	1.73
CH_2		3.67	3.57	3.20
Enol OH		14.10	14.20	14.53

heptane-2,4,6-trione



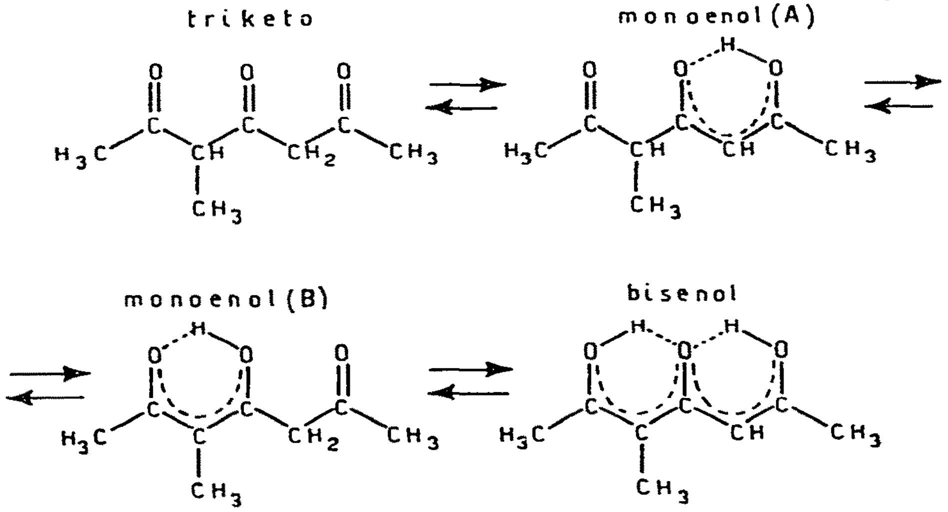
and these are shown in their different ^1H NMR spectra. Comparison of peak areas shows a 10% $CHCl_3$ solution at 40° C to be a mixture of monoenol (43%) bisenol (52%) and triketone (5%) tautomers. In a similar way the ^1H NMR spectrum of 1,5-diphenylpentane-1,3,5-trione (H_2dba) shows that at 40° C a 10% $CDCl_3$ solution is a mixture of monoenol (38%), bisenol (60%), and triketo (2%) tautomers. It may be concluded that the equilibrium moves to favour the dienol as the bulk of R^1 and R^2 groups is increased. The ligands 3-methylheptane-2,4,6-trione (H_2mmd) and 3,5-dimethylheptane-2,4,6-trione (H_2dmd) offer two dissociable enol protons as shown by its

TABLE 24

Keto-enol ratio of H_2daa at various temperatures (c = 1.0 M)

Temperature (°C)	Monoenol (%)	Bisenol (%)	Triketo (%)
In $CDCl_3$			
48	74	17	9
36	73	21	6
5	68	27	5
—41	68	25	5
In CCl_4			
56	54	43	3
36	45	54	2
5	36	62	2

tautomeric forms. For the ligand H_2mmd the equilibrium

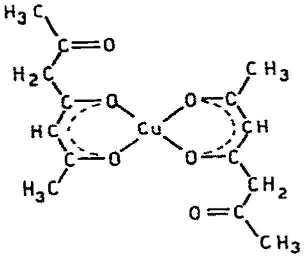


takes place. H_2mmd in CCl_4 solution exhibits a very diffuse IR band over the range 3600—2200 cm^{-1}, a sharp absorption at 1720 cm^{-1} (ν C=O) and a broad more intense band from 1650 to 1550 cm^{-1}. In $CDCl_3$ solution the ν CO at 1720 cm^{-1} increases in its intensity. These results and the ^1H NMR data indicate that this ligand in the solution phase has as its major component a *cis*-monoenol as well as a *cis,cis*-bisenol form in agreement with heptane-2,4,6-trione.

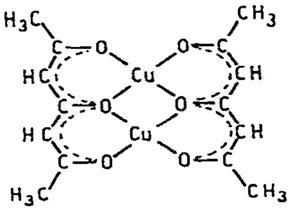
The temperature causes substantial effects on the tautomeric composition of 3-methyl-2,4,6-trione in CCl_4, whereas it causes little effect in $CDCl_3$, the keto-enol contents being invariable in the range 55—0°C.

Signals assignable to a bisenol form of 3,5-dimethylheptane-2,4,6-trione have not been found in ^1H NRM spectra either in $CDCl_3$ nor in CCl_4. As already reported [141,142], the methyl group interposed between two carbonyl groups in a β-diketone does not prevent the formation of a *cis*-enol with cyclic intramolecular hydrogen bonding. The coplanar *cis,cis*-bisenol form is accompanied by strong steric hindrance due to the overlapping of the methyl groups. In this ligand only the tautomeric forms with a side or a central monoenol are possible.

The 1,3,5-triketones are potentially dinegative, tridentate ligands and the well-developed π-system of the dianion gives to the ligands a preference for a planar configuration, thus precluding tridentate coordination to one metal ion. Copper(II) reacts with heptane-2,4,6-trione to give both the mononuclear 1 : 2, (metal/ligand), and dinuclear 2 : 2 complexes.



a



b

The formation of various oxygen bridged polynuclear complexes invokes the well known ability of the two coordinate oxygen atoms in many β-diketonato complexes to raise their coordination number to three [144—148]. The blue mononuclear copper complex $Cu(Hdaa)_2 \cdot 2H_2O$ precipitates when an aqueous cupric acetate solution is added to a methanolic solution of the triketone at about 0° C [149]. When the preparation is carried out at about 30° C, the green binuclear complex $Cu_2(daa)_2$ is obtained.

The binuclear complex shows a multiplet absorption between 1500 and 1600 cm^{-1} ascribable to the ν C=C and ν C=O of the ethylenic and coordinated carbonyl groups; the mononuclear complex, in addition to those, shows a band at 1715 cm^{-1} due to ν C=O of free carbonyl group. The mononuclear compound dissolves in methanol, acetone, and chloroform as long as the solution is kept at a low temperature; the binuclear dissolves only in pyridine, affording the pyridine adduct $Cu_2(daa)_2(py)_2$.

The blue complex transforms into the green at about 80° C under reduced pressure,or when dissolved in boiling methanol liberating an excess of the ligand. On the other hand the green complex changes into the blue one in pyridine in the presence of a large excess of the ligand when the solvent is removed at 0° C under reduced pressure. These transformations indicate that the green binuclear compound is stable at elevated temperature, while the blue one prefers a lowered temperature and that the conversion from one to the other is reversible.

As shown in Table 25 the 3-methyl derivative of heptane-2,4,6-trione gives

TABLE 25

Copper chelates of heptane-2,4,6-trione and its methylated derivatives

Chelate	Reaction conditions	Soluble in	Colour
$Cu_2(daa)_2$	Methanol or water at 30° C	Pyridine, THF	Green
$Cu(Hdaa)_2 \cdot 2\ H_2O$	Methanol or water at 0° C	Methanol, chloroform, acetone, THF	Blue
$Cu_2(mmd)_2$	Reflux in methanol (from $Cu(Hmmd)_2$)	Pyridine	Green
$Cu(Hmmd)_2$	Water at room temperature	Chloroform	Blue-violet
$Cu_2(dmd)_2$	Not obtainable	—	—
$Cu(Hdmd)_2$	Water at room temperature	Chloroform	Blue-violet

both types of copper(II) chelates while the 3,5-dimethyl derivative affords only the mononuclear one [150]. The maximum temperature below which $Cu(Hmmd)_2$ is stable in methanol is 30° C. The IR spectra of 1 : 2 chelates are very similar to that of $Cu(Hdaa)_2 \cdot 2H_2O$. The physico-chemical properties, similar to $Cu(acac)_2$, suggest a square planar configuration; the axial coordination of two moles of water to the copper ion is not strong enough to influence the electronic spectra.

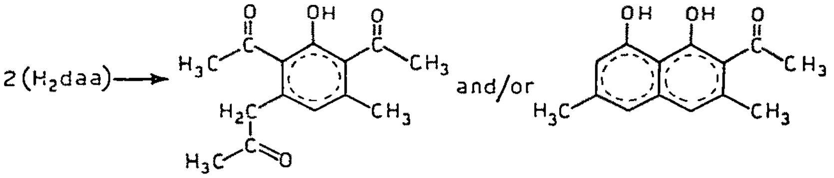
In the case of $Cu(Hmmd)_2$ there is a question as to the site of coordination of the ligand, because the ligand is no longer symmetric. The most plausible hypothesis seems to be the one in which the methyl group is located on the middle carbon of the uncoordinated site.

The blue mononuclear complex $Cu(Hdaa)_2 \cdot 2H_2O$ shows unusual behaviour for a distorted octahedral copper(II) compound with a room temperature moment of 1.86 BM which barely changed over the temperature range measured (1.85 BM at 85 K). Because of the instability of the remaining 1 : 2 complexes, accurate magnetic measurements could not be completed.

The facility to form the 2 : 2 chelate of H_2daa as compared with the 3-methyl derivative can be related to the relative enolisability of uncoordinated carbonyl group in 1 : 2 chelate. Partial enolisation of uncoordinated carbonyl group was suggested on $Cu(Hdaa)_2$; no observation of enolization being observed on $Cu(Hmmd)_2$. Thus the 2 : 2 chelate of H_2daa can be obtained at relatively lower temperature whereas the 2 : 2 chelate of the methylated ligand needs a higher temperature in order to overcome the steric repulsion of the methyl group. In the case of H_2dmd, it was not possible to synthesize the 2 : 2 chelate owing to the absence of the *cis*-bisenol form [140]. The syntheses and properties of nickel(II), cobalt(II), palladium(II) and beryllium(II) heptane-2,4,6-trione chelates have been also reported

[151]. The 2 : 2 chelates of nickel(II) and cobalt(II) can be isolated as tetrahydrates by a procedure similar to that for the copper(II) analogue; on the other hand, the analogous palladium(II) chelate was not prepared, probably owing to the larger ionic size of the metal. The 1 : 2 palladium chelate can be obtained in a dihydrated form as well as in an anhydrous form, while the chelates of copper(II), nickel(II) and cobalt(II) are obtained only in a hydrated form.

In contrast to the relative ease of obtaining 2 : 2 chelates with nickel(II) and cobalt(II), the corresponding 1 : 2 chelates could not be obtained by the procedure employed in the synthesis of the 1 : 2 copper(II) chelate. When nickel(II) or cobalt(II) ion was allowed to react with an excess of heptane-2,4,6-trione with the purpose of obtaining a 1 : 2 chelate, the reaction products were always the 2 : 2 chelate and products derived from the bimolecular condensation of heptane-2,4,6-trione according to the following reaction scheme

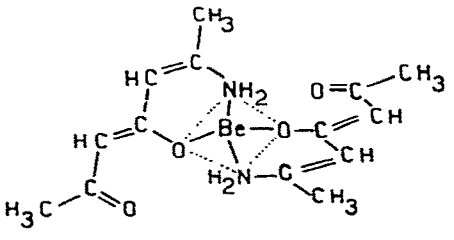


The 1 : 2 chelate has to be prepared by the ligand exchange reaction between a bis(acetylacetonato)-metal chelate and heptane-2,4,6-trione in anhydrous diethylether or by the reaction between 2 : 2 metal chelates and molten heptane-2,4,6-trione at temperature slightly above its melting point.

The IR spectra of these 1 : 2 chelates suggest rather strong coordination of water molecules to the central metal ion along the *z* axis and they are very similar to that of 1 : 2 copper(II) chelate in the 1500—1700 cm^{-1} region.

The powder reflectance spectra of these nickel(II) and cobalt(II) chelates are very similar to those of $Ni(acac)_2(H_2O)_2$ [152] and $Co(acac)_2(H_2O)_2$ [153], and indicated the octahedral coordination structure around the central metal ion.

In the case of beryllium chelate, the use of NH_3 to adjust the pH of reaction medium resulted in the amination of the terminal carbonyl group in heptane-2,4,6-trione so that only 1 : 2 chelate of the amino derivative was obtained. Two sharp IR bands at 3390 and 3300 cm^{-1} show that the amino group is coordinated to beryllium ion [154] and other bands at 1635 and 1525 cm^{-1} have been assigned to uncoordinated and coordinated carbonyl groups. A structure of the type



was proposed. It was also assumed that chelation occurs between heptane-2,4,6-trione and beryllium(II) to give Be(Hdaa)$_2$ as an intermediate product, which in turn reacts with ammonia to afford the 2-aminoheptane-4,6-dionato chelate. It must be noted that when H$_2$daa reacts with ammonia in the absence of metal ion, amination occurs on the terminal carbonyl group affording 2,6-dimethyl-4-pyridone as a cyclization product [155].

Coordinated water in 2 : 2 nickel(II) and cobalt(II) heptane-2,4,6-trionato chelates can easily be replaced by pyridine affording the pyridine adducts having the formula M$_2$(daa)$_2$(py)$_4$. Infrared and solid reflectance spectra indicate an octahedral coordinate structure around nickel(II) or cobalt(II) ion. These conclusions have been confirmed by X-ray structural studies on the complexes bis-(1,5-diphenyl-1,3,5-pentanetrionato)tetrapyridine dicobalt(II) [156] or dinickel(II) [157]. Their molecular configuration is given in Fig. 16.

The molecular structure of the dicobalt(II) complex consists of two cobalt atoms chelated to two ligands of the triketonate 1,5-diphenyl-1,3,5-pentanetrionate and linked to four pyridine such that each cobalt is octahedrally coordinated to four coplanar carbonyl oxygen atoms and two pyridine nitrogen atoms situated above and below the metal-oxygen plane.

In addition to the coordinated pyridines, there are eight uncoordinated pyridine molecules in the unit cell occupying the empty space between adjacent phenyl rings of the triketones and it may be this that permits crystallization of this species. The chelate rings and the cobalt atoms are

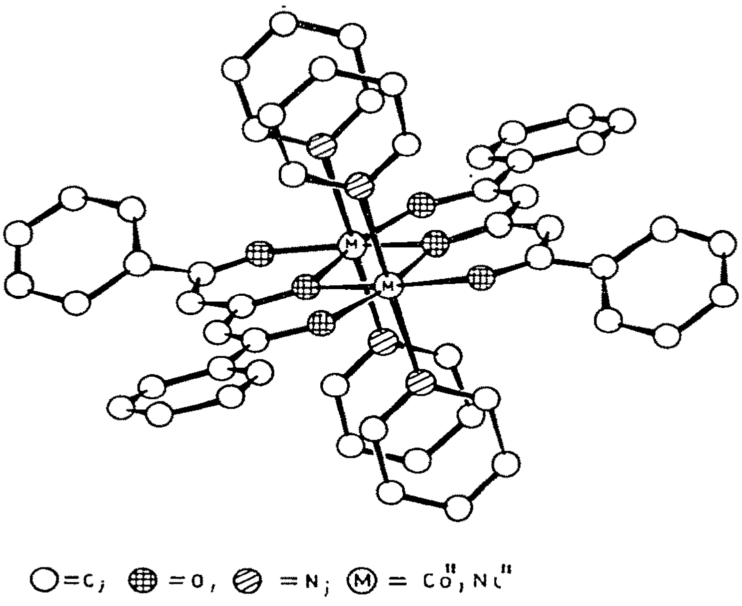
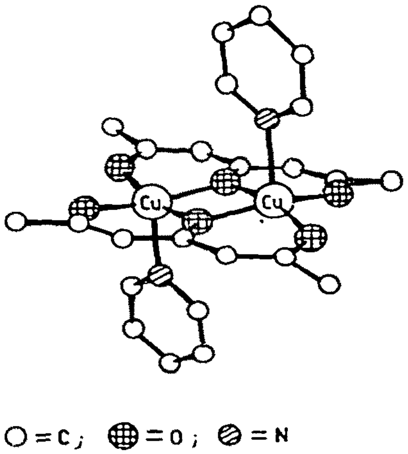


Fig. 16. Molecular structure of the complexes bis-(1,5-diphenyl-1,3,5-pentanetrionato)-tetrapyridinedicobalt(II) or dinickel(II).

essentially coplanar in marked contrast to the results reported for the cobalt(II) 1,3-diketonate complexes where in each case the cobalt atom is appreciably removed from the plane of the chelate rings [148,158—160]. In Co(acac)$_2$(py)$_2$, indeed, the cobalt atom was found to be displaced 0.131 Å from the plane of the four oxygens toward one of the pyridine nitrogens.

The structure of the bis-(1,5-diphenyl-1,3,5-pentanetrionato)tetrapyridine dinickel(II)-tetrapyridine Ni$_2$(dba)$_2$(py)$_4$ · 4py is similar to that determined for the corresponding cobalt(II) complex and has the same space group P2$_1$/n. The Ni—N distances (2.155 (8) Å average) and the Ni—O (bridge) distances (2.044 (6) Å average) are approximately 0.05 Å shorter than the corresponding distances in the cobalt(II) complex; this has resulted in a Ni—Ni distance of 3.166 (3) Å which is 0.106 Å shorter than the Co—Co distance. The crystal and molecular structure of Cu$_2$(daa)$_2$(py)$_2$ have been determined by single-crystal X-ray diffraction photography [161]. The unit cell contains a single centrosymmetric binuclear molecule with the two copper atoms bridged by two approximately planar heptanetrionato ligands. A view of the molecule from a point on the positive *b* axis is shown in Fig. 17. The structure is similar to that of the analogous complexes M$_2$(daa)$_2$(py)$_4$ · 4py (M=Ni(II) and Co(II)) [156,157], except that each copper atom has only a single pyridine ligand, with a relatively long Cu—N bond (2.32 Å).

The coordination geometry is square pyramidal, the four oxygen atoms attached to each Cu atom being coplanar. The angles within the Cu$_2$O$_2$ ring are quite close to the corresponding angles in the cobalt and nickel compounds (M—O—M 102.7°, 101.5°, and 103°; O—M—O 77.3°, 78.5°, and 77° for M = Co, Ni and Cu) but the decrease in metal—oxygen bond lengths in



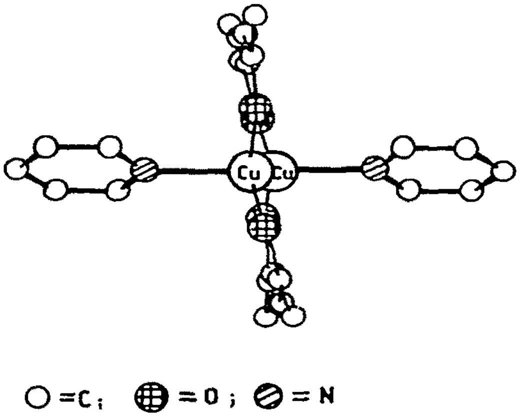


Fig. 17. A view of the molecular structure of Cu$_2$(daa)$_2$(py)$_2$ from a point on the positive *b* axis.

Fig. 18. The twisting effect on the ligands in the complex Cu$_2$(daa)$_2$(py)$_2$.

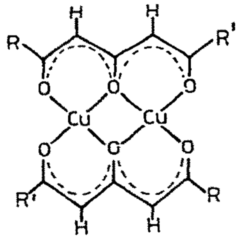
the series Co, Ni, Cu is reflected in a progressive reduction in the distances M···M (3.27, 3.17, and 3.05 Å, respectively).

The parameters which characterize the ligands show no significant differences between the nickel and cobalt compounds. The bond lengths and angle in the 1,3,5-triketonato fragments are virtually invariant in the two compounds and are consistent with a delocalized π-electron system.

In $Cu_2(daa)_2(py)_2$ there are greater deviations from planarity presumably as a result of the displacement of the two Cu atoms from the plane of their coordinated oxygen atoms. This twisting effect on the ligands is shown in Fig. 18.

The dimeric complexes $Cu_2(triketonato)_2$ had a magnetic behaviour independent of field, indicative of a very strong magnetic interaction. The magnetic moments of these binuclear complexes increase with temperature and the values of J for the three complexes $Cu_2(daa)_2$, $Cu_2(phdaa)_2$ and $Cu_2(dba)_2$ were found to be $-395\ cm^{-1}$, $-410\ cm^{-1}$ and $-438\ cm^{-1}$, respectively. In all these complexes the values of $-2J$ is 800—900 cm^{-1}; therefore these complexes would appear to be very strong antiferromagnetic copper(II) systems [162].

Some different conclusions have been reported for these and other similar complexes [163].

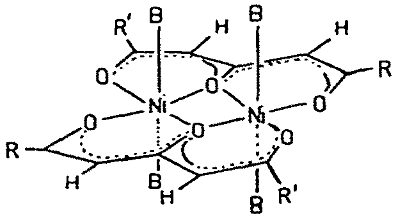


R	R'
C_6H_5	p-BrC_6H_5
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$
C_6H_5	CH_3
p-ClC_6H_4	p-C_6H_4
C_6H_5	p-ClC_6H_5
C_6H_5	p-$CH_3OC_6H_4$
C_6H_5	m-BrC_6H_4
CH_3	CH_3
C_6H_5	C_6H_5

Several of these complexes showed marked ferromagnetic exchange at room temperature and also at 150° C.

Ferromagnetism is indicated by the abnormally high moments of the complexes at low field strengths and all the complexes showed a characteristic decrease in χ_A and μ_{eff} with increasing field strength. At lower temperatures the moments of all the chelates were significantly lowered and from the temperature data it was concluded that ferromagnetism predominates at high temperatures and antiferromagnetism begins to predominate as the temperature is lowered. The large difference in magnetic properties among the compounds studied cannot be accounted for by the electronic effects of various functional groups.

The magnetic properties of the bis(1,3,5-triketonato)dinickel(II) chelates



R	R'
CH_3	CH_3
CH_3	C_6H_5
C_6H_5	C_6H_5
C_6H_5	p-BrC_6H_4
C_6H_5	p-IC_6H_5
p-BrC_6H_5	p-BrC_6H_5

$B = H_2O$ or pyridine

have been reported [157]. It was found that there is no appreciable field strength dependence in the range 3000—9000 gauss. The complexes have moments typical of magnetically dilute complexes at room temperature. However there is evidence for spin coupling at lower temperatures [157].

The calculation of J for $Ni_2(dba)_2(H_2O)_4$ presents some unusual difficulties since the molar susceptibility vs. T plot is not a straight line throughout the high temperature region. There appear to be two distinct straight-line regions, one from about 300 to 420 K and another from about 40 to 300 K. The most obvious explanation is that the effective g factor is different in the high temperature region and in the low temperature region. In the high temperature region the compound behaves as a simple paramagnet with an average μ_{eff} of 3.32 BM. The susceptibilities in this region are well reproduced by $g = 2.46$ and $J = -10.4$ cm^{-1} and $N\alpha = 250 \cdot 10^{-6}$ cgsu. These values do not account for the susceptibilities at the lower temperatures and in this region g and/or J must be temperature dependent in order to achieve fits.

The presence of strong magnetic interaction between the two cobalt(II) atoms in the $Co_2(dba)_2(py)_4$ molecule is evidenced by the low magnetic moment measured at room temperature (4.28 BM at 300 K). A sharp decrease in the magnetic moment at lower temperatures is a further indication of a strong antiferromagnetic coupling.

The Co—Co distance in $Co_2(dba)_2(py)_4$ of 3.272 (3) Å, considerably longer than the Co—Co distance of 2.70 Å calculated from the atomic radius, suggests that these low magnetic moments are caused by a superexchange mechanism involving the bridging oxygens. By comparison with monomeric cobalt(II) complexes in distorted octahedral environments, $Co_2(dba)_2(py)_4$ shows a sharper decrease in the magnetic moment with decreasing temperature and this is a clear indication that a high distortion in the octahedron does not give such a strong temperature dependence [156].

The magnetic behaviour of $Cu_2(daa)_2(py)_2$ has been investigated [161] and by the method of least squares a value was found for $g = 2.09$ and for $J = -345$ cm^{-1}. It was not possible to determine g directly because the sample did not give a detectable ESR signal. The effective magnetic moment per Cu atom falls from 0.75 at 335 K to 0.0 BM at 87 K, consistent with intramolecular exchange giving a singlet—triplet separation $-2J = 690$ cm^{-1}.

A series of complexes of diethylcyclopentanone-2,5-diglyoxylate with divalent transition metals have been reported [164]. The ligand, [165], reacts in its dienolic form and gives binuclear complexes of the type

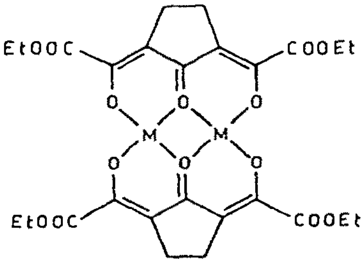


TABLE 26

Magnetic properties for a series of complexes of diethylcyclopentanone-2,5-diglyoxylate (H_2ecg)

Complex	Temperature (K)	μ_{eff} (BM)
$Mn_2(ecg)_2(H_2O)_4$	292	5.5
$Mn_2(ecg)_2(py)_4$	292	5.9
$Fe_2(ecg)_2(H_2O)_4$	292	4.7
$Fe_2(ecg)_2(py)_2$	292	4.9
$Co_2(ecg)_2(H_2O)_4$	292	4.6
$Co_2(ecg)_2(py)_4$	291	4.4
$Ni_2(ecg)_2(H_2O)_4$	291	3.2
$Ni_2(ecg)_2(py)_4$	291	3.3
$Cu_2(ecg)_2H_2O$	291	1.6

Their IR spectra show in the range 1700—1720 cm^{-1}, absorption bands due to the non-chelating ethoxycarbonyl groups, in addition to the strong bands near 1360 and 1600 cm^{-1}, typical of chelated β-diketones. The visible and near-IR spectra support an octahedral stereochemistry for the nickel(II) and cobalt(II) complexes. Although complexes of this type could be expected to involve magnetic interaction between the metal atoms, room-temperature magnetic measurements give values for each ion in the normal range for the high spin configuration in an octahedral environment. The values found for the cobalt(II) and copper(II) complexes only are lower than usual (Table 26).

An EPR study of the copper(II) chelate of 2,5-diethoxalylcyclopentanone supports the conclusion that the dimeric species are formed in which exchange coupling takes place [166]. On the basis of the room temperature susceptibility and using the formula derived by Bleaney and Bowers [94], it was deduced that the exchange coupling J is ca. -200 cm^{-1}.

In dimethylformamide the introduction of zinc(II) results in the replacement of copper(II) in the copper(II) pairs, forming a hetero-ion chelate. In trimethylphosphate the same process gives a novel species involving both

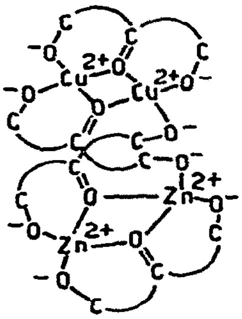


Fig. 19. A schematic drawing of the polynuclear mixed ion chelate involving copper(II) and zinc(II) ions.

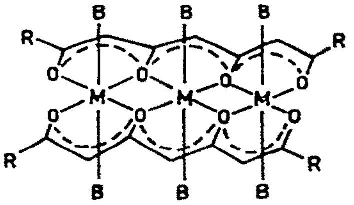
copper(II) and zinc(II) ions in which exchange coupling persists between the copper(II)-copper(II) pairs. In Fig. 19 the essential framework of the structure of this polynuclear mixed ion chelate, involving the assumption of tetrahedral symmetry about each zinc ion, is reported.

F. COMPLEXES WITH TETRAKETONES

Recently, copper(II), nickel(II) and cobalt(II) chelates of the tetraketone 1,7-diphenyl-1,3,5,7-heptanetetraone (H_3dbaa) have been prepared [167]. The ligand may be prepared by benzoylation of acetylacetone and 1-phenyl-1,3,5-hexanetrione [168] through a Claisen condensation using NaH as the base and monoglyme as solvent. The molecule contains three enolisable protons and may function as a mono, di, or trianionic ligand.

The copper(II), nickel(II) and cobalt(II) chelates may be obtained with two or three metal ions, this depending upon preparative details such as the solvent, temperature and the base used. The infrared spectra of these compounds are very similar, none of them exhibiting absorption due to free unchelated carbonyl groups. Preliminary magnetic susceptibility measurements between 77 and 300 K are shown in Table 27.

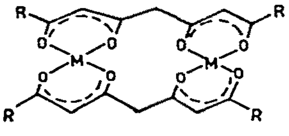
The moment of $Cu_3(dbaa)_3(H_2O)_3$ is low, indicating inter- as well as intramolecular exchange, the high moments for $Ni_3(dbaa)_2(H_2O)_6$ have been ascribed to quite strong ferromagnetic exchange and the temperature dependence of the $Co_3(dbaa)_2(H_2O)_6$ magnetic moments have been assumed to be indicative of reasonably strong antiferromagnetism. Structural data for these complexes have not been obtained, but it may be reasonable to suppose the structural configuration

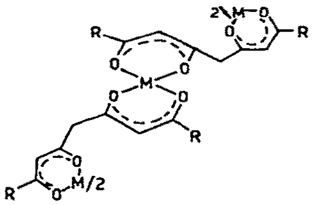


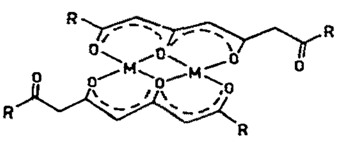
B = neutral monodentate ligand

for these 3 : 3 tetraketonates.

The complexes with two metal ions may have the three probable structures







1

2

3

TABLE 27

Magnetic moments (BM) reported on a per metal basis for the cobalt(II), nickel(II) and copper(II) complexes with tetraketones

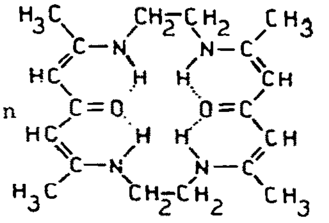
Complex	Temperature (K)			
	300	276	195	77
$Co_3(dbaa)_2(H_2O)_6$	4.71		4.66	4.09
$Ni_3(dbaa)_2(H_2O)_6$	3.95	3.74	3.52	3.35
$Ni_2(Hdbaa)_2(H_2O)_4 \cdot H_2O$	3.14		3.08	2.88
$Cu_3(dbaa)_2(H_2O)_3$	0.90	0.82	0.63	0.49
$Cu_2(Hdbaa)_2(H_2O)$	1.89	1.80	1.78	1.63

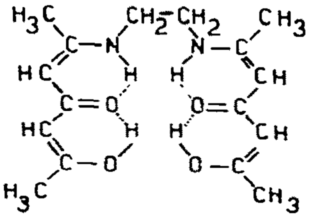
Configurations 1 and 2 have been reported as the most reasonable because no absorption bands due to free carbonyl appear in the IR spectra. The somewhat depressed magnetic moments of the binuclear complexes may be ascribed to exchange through the bridging ligand system of 1 and 2 and, if the metals were in the environment shown in 3, much different magnetic behaviour would be expected.

G. COMPLEXES WITH SCHIFF BASES DERIVED FROM TRIKETONES

The triketones can form Schiff bases, when treated with amines, in an analogous manner to the Schiff bases of β-diketones [169]. In the case of heptane-2,4,6-trione (H_2daa) and diamine (ethylenediamine for instance), two kinds of Schiff bases can be formed

$H_4daaden$





H_4daaen

The first sexadentate ligand ($H_4daaden$) was easily obtained, on mixing ethylenediamine and H_2daa in methanol [170]. Attempts to synthesize the open sexadentate ligand (H_4daaen) from H_2daa under various reaction conditions failed [170] although it was found [171] that ethylenediamine reacts with the triketones benzoylacetylacetone, anisoylacetylacetone, *p*-toluylacetylacetone and *p*-bromobenzoylacetylacetone in ethanol to give yellow crystals of the corresponding open Schiff bases. The Schiff bases obtained are shown in Fig. 20, where it is shown that the condensation takes place only on the carbonyl group with the methyl in the α position [171,172].

The reaction of a $CHCl_3$ solution of the cyclic ligand ($H_4daaden$) with an

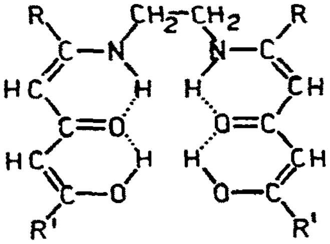
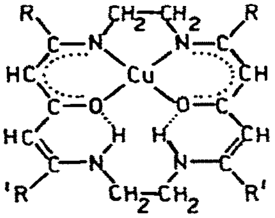
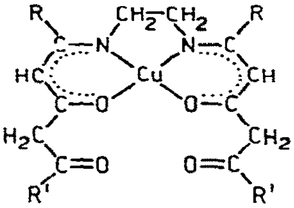


Fig. 20. The prepared open sexadentate ligands (R=CH_3; R′ = substituted phenyl group).

ethanolic solution of copper(II) acetate gives, on dilution with ethanol, a greenish-brown precipitate which was formulated as



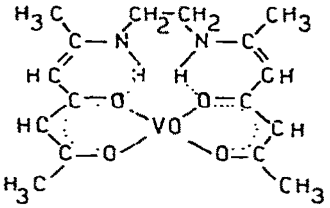
If a $CHCl_3$ solution of the cyclic ligand was added to an aqueous solution, a green precipitate of $Cu_2(daa)_2$ was recovered from the aqueous layer leaving a deep violet chloroform layer. This $CHCl_3$ layer, eluted on alumina with $CHCl_3$, gives purple crystals of the copper(II) complex of the acyclic Schiff base [170]



The two complexes differ strongly in their physico-chemical properties. The IR spectra of the first cyclic complex show a N—H stretching at 3160 cm^{-1} absent in the second acyclic complex, while the two peaks at 1720 and 1705 cm^{-1} present in the open complex and attributed to uncoordinated carbonyl groups are absent in the first one. Both complexes show a coordinated carbonyl band at 1590 cm^{-1}. The reaction of 1,2-diaminopropane and 1,3-diaminopropane gave with heptane-2,4,6-trione the corresponding macrocyclic Schiff bases. The reaction of the first cyclic ligand with Cu(II) and Ni(II) gave the cyclic complex but it was not possible to isolate complexes with the second Schiff bases [174].

The reaction of the cyclic ligand H_4daaden with oxovanadium(IV) salts in

H_2O media did not give any product of definite composition, but the reaction between H_2daa, ethylenediamine and $VO(OH)_2$ under a nitrogen atmosphere gives [170]

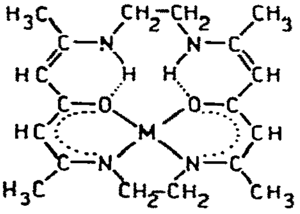


Its IR spectrum is characterized by absorption bands due to an N—H group, a coordinated carbonyl group and a V=O band at 3220, 1628 and 980 cm^{-1}, respectively. The bands assignable to uncoordinated carbonyl groups are not observed.

By reacting H_4daaden with uranyl(VI), nickel(II) or cobalt(II), different complexes have been obtained, their nature depending on the metal ion used [175,176].

The cyclic Schiff base ligand suffers partial hydrolysis by reaction with uranyl(VI) salts. The crystal and molecular structure of this complex has been determined by X-ray diffraction study [177] and is reported in Fig. 21. The crystal consists of discrete $UO_2(H_2daaen)MeOH$ units which are involved in hydrogen bonding.

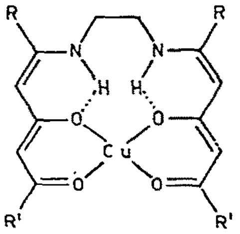
Surprisingly the chemical composition of the ligand is not the same in the two molecules of the asymmetric unit (A and B in Fig. 21). The X-ray data show that whereas in A the ligand has the expected formula and the nitrogen atoms are bonded through a $—CH_2—CH_2—$ aliphatic chain, in the B there is a $—CH=CH—$ chain. The two resulting complexes are consequently similar but chemically different and this explains the presence of eight molecules in a cell which has only four equivalent positions. Apart from this, the main structures are the same in A and B and most bond lengths and angles are fully comparable. The uranium atoms are seven coordinated with the linear uranyl group perpendicular to the base plane in which four oxygen atoms from the anionic ligands and one alcoholic oxygen atom are coordinated to uranium. The resulting polyhedron is a slightly distorted pentagonal bipyramid. Nickel(II) and cobalt(II) salts give



M=Ni^{II}, Co^{II}

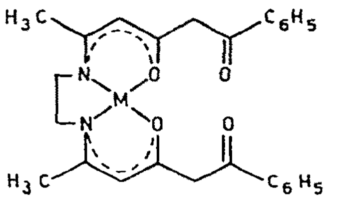
with the ligand. The magnetic susceptibility data and electronic spectra indicate an almost planar configuration around the central metal ion.

The reaction of the sexadentate open Schiff bases of Fig. 20, in $CHCl_3$ solution, with ethanolic copper(II) acetate, in equimolecular ratio, yields the green precipitate

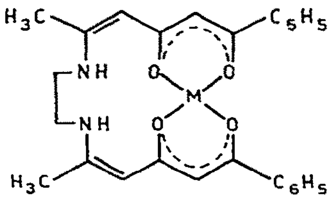


The IR and diffuse reflectance spectra support the formulation of these complexes [171]. For R = CH_3 and R′ = C_6H_5 the IR spectrum shows bands at 1631, 1598, 1545 and 1527 cm^{-1} and their diffuse reflectance spectrum shows a peak at 574 nm comparable with the value of 560 nm for $Cu(acac)_2$ [178].

Similarly for R = CH_3 and R′ = C_6H_5 a number of mononuclear chelates have been prepared [179] by allowing 1 : 1 molar ratios of metal acetates or fresh hydroxides and the ligand to react in H_2O—acetone mixture. In each case two isomers may result



ISOMER I



ISOMER II

The mononuclear Ni(II) chelate, Ni(H_2baaen), is an example of isomer I. The IR spectrum shows an intense unchelated carbonyl band at 1700 cm^{-1} and its visible spectrum is practically identical to that of $Ni(acac)_2en$. The product is diamagnetic giving a square planar configuration around the central ion. It can be noted that an O_2O_2 environment would give a situation similar to that found in the bis(benzoylacetonate)nickel(II) which achieves a coordination number of six by binding two adduct ligands such as water or by oligomerization [180]; in either of these environments Ni(II) is paramagnetic.

As discussed above, two mononuclear chelates with the structure (II) have been prepared in which M = Cu(II) and VO(IV). X-ray determinations confirm that both chelates contain metals bonded to four oxygens [181]. The

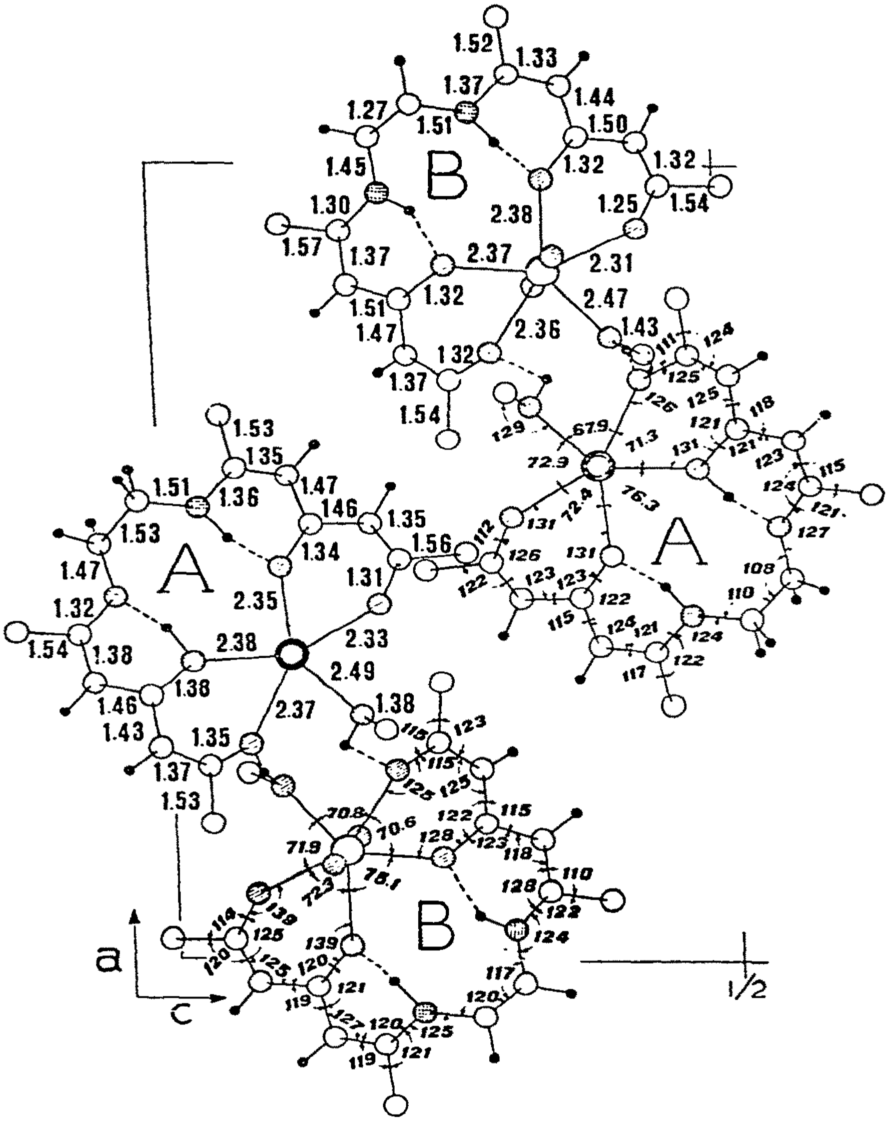
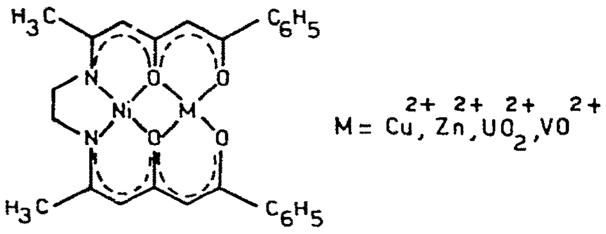


Fig. 21. The molecular structure of $UO_2(H_2daaen)CH_3OH$.

two types of isomers differ strongly in their solubility. The nickel(II) chelate is soluble in $CHCl_3$ and C_6H_6 but considerably less soluble in acetone and alcohol and insoluble in water; copper(II) and vanadyl(IV) complexes are insoluble in water, fairly soluble in acetone and alcohols, soluble in strongly coordinating solvents and quite insoluble in non polar organic solvents. All these mononuclear complexes may act as ligands to form polymeric chelates. Syntheses of heteronuclear chelates using $Ni(H_2baaen)$ as a ligand for a second metal to be coordinated at the O_2O_2 site have been reported [179]. Preliminary spectral and magnetic data are consistent with the formulation



None of the IR spectra exhibits bands attributable to unchelated carbonyl groups. The magnetic susceptibility of NiCu(baaen) and NiVO(baaen) indicates the presence of one unpaired electron per molecule. NiZn(baaen) is diamagnetic and $NiUO_2$(baaen) is slightly paramagnetic.

A three-dimensional single-crystal structure determination was carried out on crystals obtained by recrystallization of NiZn(baaen) from pyridine. A view of the single molecule is shown in Fig. 22. The N_2O_2 site is occupied by four coordinate square planar Ni and the O_2O_2 site is occupied by zinc; the coordinated pyridine completes the five-coordination of the zinc atom. Although the X-ray study cannot distinguish between the scattering of zinc and nickel, the diamagnetism of the complex requires the nickel to be the four-coordinate species. The reaction of $UO_2(H_2daaen)$ and $Cu(H_2daaen)$ with nickel(II) and copper(II) salts has been studied to compare the influence of the ions in the formation of the binuclear compounds and

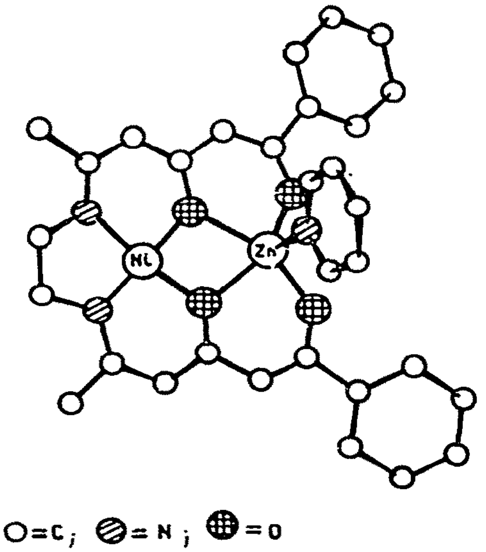
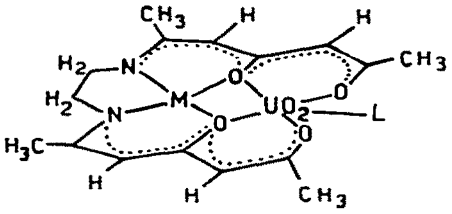


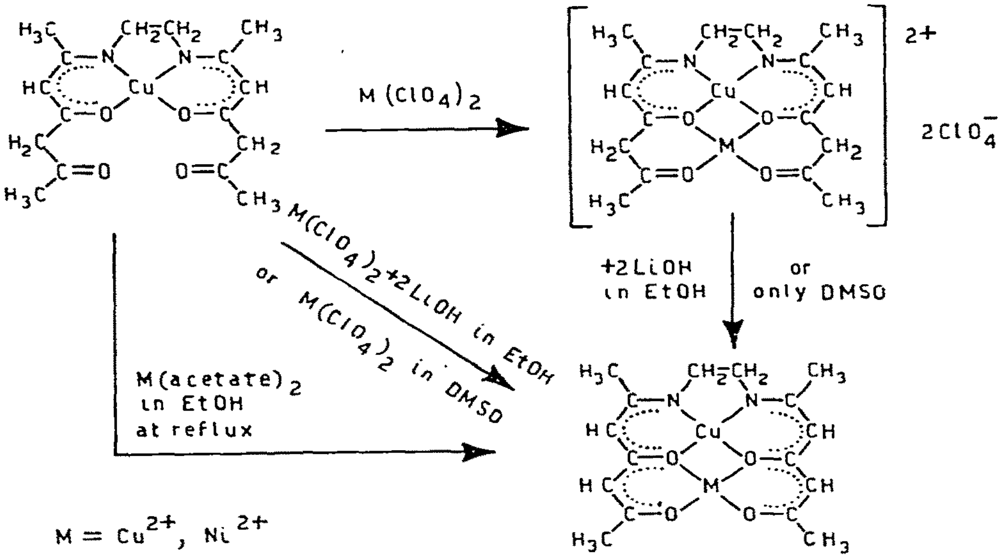
Fig. 22. A view of the molecular structure of NiZn(baaen)(py).

coordinating behaviour of the two different free sets [182]. From the reaction of $UO_2(H_2daaen)MeOH$ with copper(II) and nickel(II) in ethanol solution, brown powders have been isolated and their proposed configuration is



M = Cu″ , Ni″

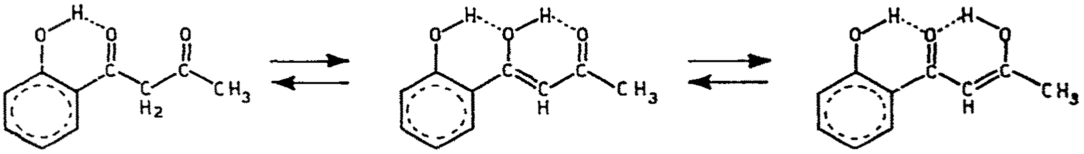
$Cu(H_2daaen)$ reacts with nickel(II) and copper(II) salts to form binuclear complexes according to the scheme



The IR spectra of the binuclear complexes CuM(daaen) and $[CuM(H_2daaen)](ClO_4)_2$ show marked differences, yet for the same type of complexes the IR are comparable, irrespective of the second transition metal. A band at 1650 cm^{-1} in the IR spectrum of $[CuM(H_2daaen)](ClO_4)_2$ and absent in the IR spectrum of CuM(daaen) is attributed to a carbonyl group coordinated to a second metal. The magnetic values at room temperature are low, and have been assumed to be indicative of the presence of magnetic interaction.

H. COMPLEXES WITH 2-ACETOACETYLPHENOL [183]

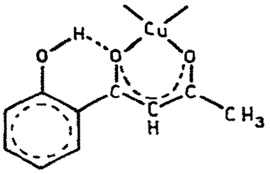
For the ligand 2-acetoacetylphenol (H_2aph), three tautomeric forms may be written



I II III

The ν C=O at 1730 cm^{-1}, observed in $CHCl_3$ solution, due to a free carbonyl group, can not be found in the IR spectra of the solid state, where only the II or III forms seems to exist. In the solid state the bands observed at 1680, 1615 and 1580 cm^{-1} can be assigned to the stretching of hydrogen-bonded carbonyl and conjugated olefinic groups.

The mononuclear copper(II) chelate, which may be obtained below 15°C does not show bands due to free carbonyl groups, but shows new bands at 1570 and 1515 cm^{-1} which may be related to the coordinated carbonyl groups. The two structures



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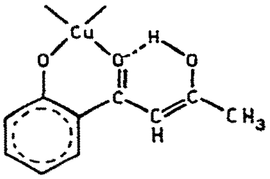
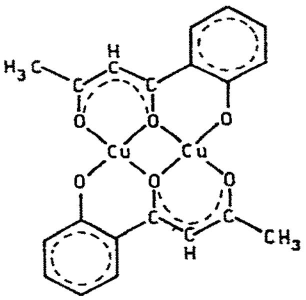


II

are compatible with such a composition.

The binuclear chelate $Cu_2(aph)_2 \cdot H_2O$ can be obtained by heating the mononuclear complex or by using equimolar amounts of the ligand and of copper(II) acetate. The binuclear composition



is supported by molecular weight determination. No significant differences in their IR spectra are observed between 1 : 2 and 2 : 2 chelates

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