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SCHIFF BASE METAL COMPLEXES AS LIGANDS[1]

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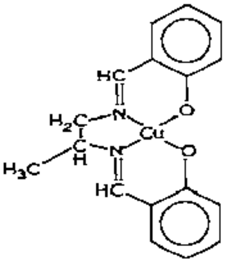
A. INTRODUCTION

Metal complexes of tetradentate Schiff bases (TSB), such as the salicylaldimines, may act as bidentate chelating agents, coordinating through their *cis*-oxygen atoms to form bi- and tri-nuclear metal complexes[2–5]. Thus, for example, the copper complex [i], derived from *N,N'*-1,2-propylene-bis(salicylaldimine) reacts with cupric chloride to form the binuclear complex [ii] or with cupric perchlorate to form the trinuclear complex [iii]. The compound [i] may be considered as a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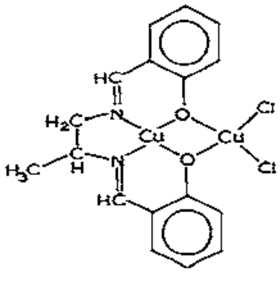
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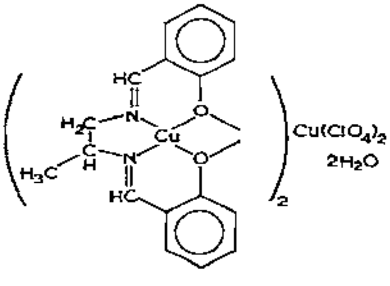
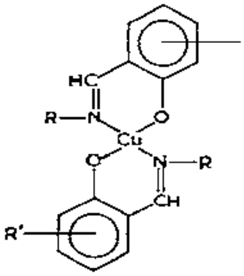

(iii)

simple bidentate ligand with two oxygen atoms acting as donor atoms. The complexes [ii] and [iii] are then mono and bis chelated derivatives of [i]. When the metal complexes such as [iv] of bidentate Schiff bases (BSB) are used as ligands



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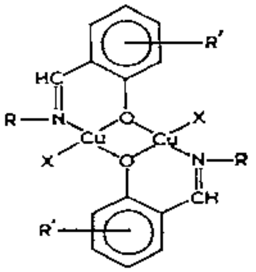


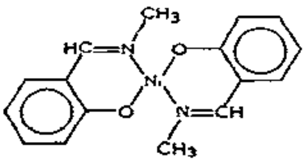
(v)

in the same way, a rearranged structure [v] is usually preferred (X = Cl, Br, NO_3)[5-8]. Copper(II) salicylaldimines of type [iv] also react with metal perchlorates, but the complexes analogous to [iii] are difficult to isolate. Copper(II) β-diketonates and aminoketonates form a limited number of complexes analogous to [ii] and [iii][9].

The mode of bridging is similar in all of the bi- and tri-nuclear complexes, and is worthy of detailed examination.

B. MODE OF BRIDGING

The formation of various oxygen-bridged bi- and tri-nuclear complexes invokes the well-known ability of two-coordinate oxygen atoms in many metal complexes to raise their coordination number to three. Solutions of many nickel(II) salicylaldimine complexes contain equilibrium mixtures of monomeric and oxygen-bridged dimeric species, the position of the equilibrium being dependent upon temperature[10,11], concentration[10-13] and pressure[14]. These nickel complexes can become paramagnetic by raising the coordination number of the metal atom from four in the monomeric complex to five or six in the oxygen-bridged dimers. By



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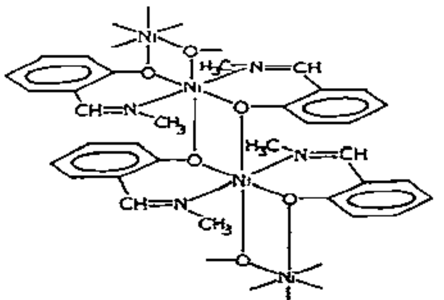
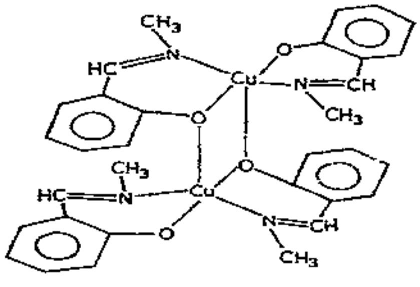


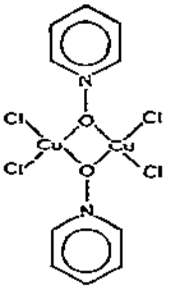
(vii)

suitable choice of conditions it is possible to isolate, in the solid state, both diamagnetic monomeric [vi] and paramagnetic, oxygen-bridged polymeric [vii] forms of bis(*N*-methylsalicylaldimino)nickel(II)[15], and of other analogous complexes[16]. Similarly, the complex bis(*N*-methylsalicylaldimino)copper(II) exists in both a monomeric and an oxygen-bridged dimeric [viii] form[17], while *N*,*N'*-ethylenebis(salicylaldimino)copper(II)[18] and bis(*N*-methylsalicylaldimino)zinc(II)[19] are dimeric in the solid state, the metal atoms linked by oxygen bridges.



(viii)

Bridging in these compounds occurs via phenolic oxygens, and the ability of tetradentate copper(II) salicylaldimine complexes such as [i], as well as of other metals, to coordinate via both oxygens to a metal in a halide or perchlorate, is no longer surprising. Formation of the binuclear compounds [v] from [iv] is likewise seen to be reasonable. However, three-coordinate oxygen atoms also form bridges between metal atoms in other bi- and poly-nuclear complexes. In pyridine *N*-oxide complexes with copper(II) halides, the oxygen atom is two-coordinate in some compounds, and three-coordinate in others such as [ix][20–23] whose structure resembles the phenolic complex dichlorodiphenoxytitanium(IV) [x][24]. Hydroxy and alkoxy complexes in which metal atoms are bridged by three-coordinate oxygens



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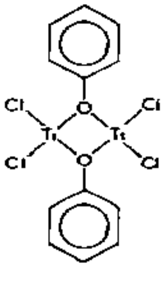
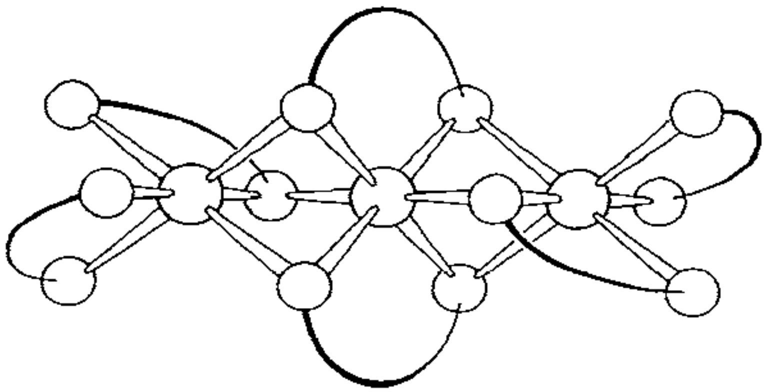


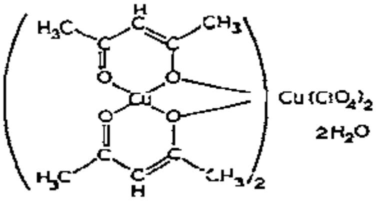
(x)

are quite common[25–34]. Anhydrous tris(acetylacetonato)nickel(II) [xi] is an oxygen-bridged trimer[35,36] involving octahedral nickel atoms; other nickel *β*-diketonates form equilibrium mixtures of monomeric and oxygen-bridged trimeric species[37,38]. Similar complexes are formed with other metals[38], *e.g.* the complex



(xi)

with copper(II) is dimeric in the solid state[39], with cobalt(II) it is tetrameric[40], and with iron(II)[41] it is apparently hexameric. Similar bonding occurs in the complex $[Cu(acac)_2]Cu(ClO_4)_2 \cdot 2H_2O$ of probable structure [xii], and other β-diketone analogues[9]. The aminoketone complexes of types [xiii] and [xiv], when M = Ni(II) are normally monomeric[11,42–45] in solution and in the solid unlike the corresponding salicylaldimines. However, some dimerisation can be induced under pressure in solutions of certain complexes [xiii][9], indicating some oxygen bridging between the metal atoms of adjacent molecules. Similarly, complexes of the type [xiv] can coordinate via the two *cis* oxygen atoms in the same way as in compounds [ii] and [iii], but not nearly as readily as the corresponding salicylaldimine complexes. Presumably, certain compounds of type [xiii] could react similarly with metal halides to form oxygen-bridged complexes.



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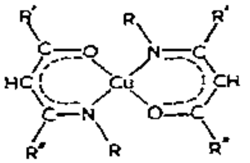

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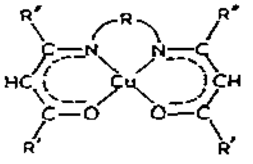

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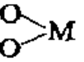
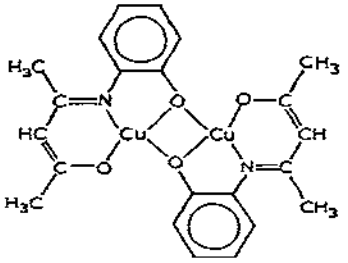
Clearly,  $M\langle{}^{O}_{O}\rangle M$ bridging occurs more readily via phenolic than via ketoamine oxygens. When a phenolic and a ketoamine oxygen occur in the same complex, as in the so-called "tricoordinated" copper(II) complex of acetylacetone-*o*-hydroxyanil [xv] and its analogues[46–52], bridging occurs preferentially via the phenolic rather than the ketoamine oxygen[49,50]. When two phenolic oxygens permit bridging, as in the copper complex of salicylaldehyde-*o*-hydroxyanil and its analogues[51], at least two structural isomers [xvi] and [xvii] are possible, and no choice can be made *a priori*.



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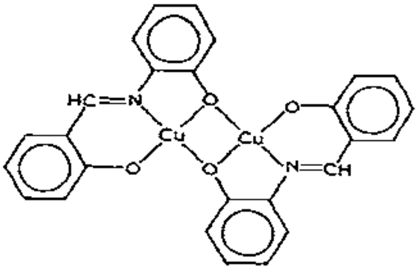

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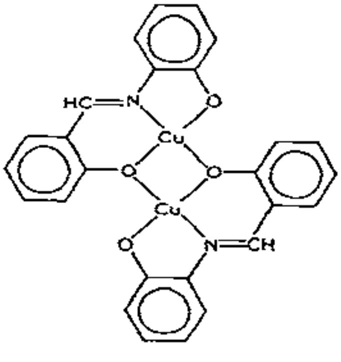
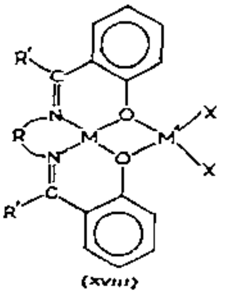


(xvii)

C. TYPES OF COMPLEXES

The general types of compounds (MTSB)M′X$_2$ [xviii] and (MTSB)$_2$-M′(ClO$_4$)$_2$ [xix] analogous to [ii] and [iii] span a large range of transition and non-



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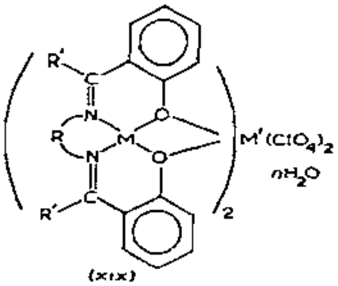
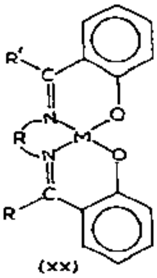


(xix)

transition metals M, M′ and a variety of TSB ligands[1–5]. The most interesting and most extensively studied of these two types of compounds contain copper(II) or nickel(II) inside the Schiff base as the metal M. When M is Ni(II), the complex ligand [xx] is diamagnetic, and remains so when it coordinates to a metal M′ to form a binuclear [xviii] or trinuclear [xix] complex[3,4]. Such compounds include M′ = Cu(II), Ni(II), Co(II), Fe(II), Mn(II), where the metal exhibits its normal high spin paramagnetism, indicating that the ligands [xx] exert a fairly weak ligand field[3,4,53].



(xx)

The corresponding complexes when M = Cu(II) and M′ is one of these five paramagnetic metals, generally have magnetic properties indicative of a discrete magnetic exchange interaction within systems containing either two or three interacting paramagnetic atoms. Magnetic, and especially antiferromagnetic, exchange interactions are frequently observed in oxygen bridged clusters of paramagnetic metals[1–9,20–24,27,26,30–34,46–58], and may often be taken as indicative of this type of bridging

In the compounds [xviii]–[xx], usually R′ = H, or sometimes CH_3. The bridging group R may be more varied *e g.* branched or unbranched alkyl chains, or an aryl group with the bridging links *ortho* to each other[3,4,55,56]. Further possibilities such as a 2,2′-diphenyl bridge[59,4] exist.

The formation of these complexes can usually be brought about simply by mixing a solution of the appropriate "complex ligand" [xx] (*e.g.* in chloroform or ethanol) with a solution of the desired metal halide or perchlorate (*e g.* in ethanol). In most cases, the resulting complex is precipitated immediately.

Formation of the complexes (MTSB)$M'X_2$ [xviii] and $(MTSB)_2M'(ClO_4)_2$ [xix] is governed to some extent by the relative solubilities of the complex ligand MTSB [xx] and the bi- and tri-nuclear complexes [xviii] and [xix], and by the relative stabilities of the complex ligands MTSB and M′TSB. If MTSB has a much lower stability constant than M′TSB, as when M = Zn(II), and M′ is a transition metal such as Cu(II) or Ni(II), then the reaction of MTSB, say ZnTSB with a halide or perchlorate of M′, say Cu, yields only (CuTSB)CuX_2 or (CuTSB)ZnX_2 with the halide, and $(CuTSB)_2Cu(ClO_4)_2 \cdot xH_2O$ or $(CuTSB)_2Zn(ClO_4)_2 \cdot xH_2O$ with the perchlorate[4,9]. Because of this metal exchange reaction, compounds of the type (ZnTSB)CuX_2 cannot be isolated. If M = M′ there is, of course, no problem.

When the relative stabilities of the complex ligand [xx] containing M or M′ are comparable, the desired complexes [xviii] and [xix] can be isolated if they are removed from solution fairly quickly. Thus structural isomers (CuTSB)$NiCl_2$ and (NiTSB)$CuCl_2$ having distinct spectral and magnetic properties [where TSB = *N*,*N*′-ethylenebis(salicylaldimine) (= ES) or *N*,*N*′-*o*-phenylenebis(salicylaldimine)] can be isolated; complementary complexes $(CuTSB)_2Ni(ClO_4)_2 \cdot xH_2O$ and $(NiTSB)_2Cu(ClO_4)_2 \cdot xH_2O$ also form[4,5,9,55]. In the complexes (NiTSB)$CuCl_2$ and $(NiTSB)_2Cu(ClO_4)_2 \cdot 3H_2O$ the nickel(II) atom is diamagnetic, and magnetic moments of 1.8–1.94 B.M., arising from the copper(II) atom, are observed. The temperature dependence of the magnetic properties of these complexes is in accord with the Curie–Weiss law $\chi \propto (T+\theta)^{-1}$, with small values of the constant θ, as expected of a normal paramagnet[2,4,5,9]. On the other hand, the compounds (CuTSB)$NiCl_2$ and $(CuTSB)_2Ni(ClO_4)_2 \cdot xH_2O$ have strongly temperature dependent magnetic moments, as a result of an antiferromagnetic interaction between the paramagnetic nickel and copper atoms[2,4,5,9,55,56].

When a complex MTSB has a much higher stability constant (*e g*. CuTSB) than the corresponding M′TSB (*e.g*. SrTSB), the metal exchange reaction does not occur when MTSB reacts with a salt of M′. Thus, compounds of the type $(CuTSB)_2Sr(ClO_4)_2 \cdot xH_2O$ (*e.g*. TSB = ES, $x = 1.5$) are formed readily when solutions of CuTSB and strontium perchlorate are mixed[4].

Since the formation of compounds [xviii] and [xix] depends on several factors, discussed above, and as the reaction is often carried out in mixed solvents, it does not seem profitable to determine the stability constants of [xviii] and [xix] in general. These compounds are usually fairly insoluble in organic solvents, and tend to decompose in solution. In some cases it was possible to measure the electrical conductivities in nitrobenzene solution, and it was found that complexes of type [xviii] were non-electrolytes while those of type [xix] behaved as bi-univalent electrolytes, confirming that the halides X in [xviii] are coordinated, while the perchlorates in [xix] are not[1–4].

Complexes of type [xviii] and [xix] have also been prepared with the substituents 5-Cl, 5-Br and 5,6-benzo in the phenyl ring of the salicylaldimine. When the nitro group was used as a ring substituent, the bi- or tri-nuclear complexes were not formed, probably because of the extreme insolubility of the complex ligand [xx] in this case[53].

Bi- and tri-nuclear zinc(II) complexes of types [xviii][4,60] and [xix][4] also form readily when the appropriate ZnTSB "ligand" reacts with a solution of zinc chloride or perchlorate.

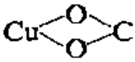
In section B we suggested that aminoketone oxygens could act as bridges between pairs of metals, but not as readily as phenolic oxygens. This is borne out by the reaction of metal complexes [xiv] of tetradentate ketoamines with metal halides or perchlorates. Colour changes, and spectrophotometric titrations indicate that complexing occurs readily in solution, but solid complexes are difficult to isolate and are often unstable. The same conclusions apply to β-diketonates. Complex [xii] involving acetylacetone can only be formed from concentrated solution, and is hydrolysed rapidly in air. This hydrolysis is easily followed since the complex is grass-green, and, on hydration, reverts to the starting materials, copper(II) acetylacetonate and copper perchlorate, both of which are blue. However, if kept dry, complex [xii] appears to keep indefinitely. By contrast, the complexes [xviii] and [xix], using metal salicylaldimines as ligands, are usually stable in air, but hydrolyse slowly when immersed in water. Complex [xii] resembles [iii] in its magnetic properties: both show significant magnetic exchange interactions Metal complexes with aromatic analogues of β-diketones, such as *o*-phenolic aldehydes (salicylaldehyde) and ketones also act as ligands to form multinuclear complexes. These reactions are under investigation at present[9].

The reaction of metal derivatives of bidentate salicylaldimines [iv] with metal salts is much more limited in the range of metals that may be used. Multinuclear complexes of copper(II), nickel(II) and cobalt(II) have been reported[2,5,6,61], but no pure, stable compounds containing dissimilar metals have been prepared. In the case of cobalt(II), stable solid complexes were isolated only from the reaction of bis(*N*-t-butylsalicylaldimino)cobalt(II) with cobalt(II) chloride or bromide. The nickel complexes are of considerable interest because of the dependence of the magnetic properties of nickel(II) upon environment: thus in trinuclear complexes derived from bis(*N*-n-alkylsalicylaldimino)nickel(II) complexes all the nickel atoms are paramagnetic, while the parent complexes are diamagnetic. These complexes are still under investigation but the copper(II) complexes have been studied extensively[2,5,6–9]. Most of the copper(II) compounds in this group are binuclear as in [v], and are prepared by reaction of the appropriate bis(*N*-R-salicylaldimino)-copper(II) complex with cupric chloride, bromide or nitrate solution. The effects of various nitrogen substituents R and of substituents in the phenyl ring of the salicylaldimine group have been investigated extensively[2,5,6–9,62]. The compounds usually form as lustrous black crystals and sometimes as greenish-brown powders. All exhibit pairwise antiferromagnetic interactions. In some cases, crystalline chloroform-solvated complexes $(\text{X-CuBSB})_2 \cdot 2\text{CHCl}_3$ (*e.g.* X = Cl, BSB = *N*-benzyl-5,6-benzosalicylaldimine) are formed; this chloroform can be removed by heat to leave the unsolvated complex $(\text{X-CuBSB})_2$, [v][63]. Crystalline chloroform solvates are also known of other kinds of complexes, such as [xix] and [xx], *e.g* CuPS. CHCl_3 where PS = *N*,*N'*-*o*-phenylenebis(salicylaldimine)[3].

Complexes of empirical formulae $(\text{MBSB})_2\text{AuCl}_3$ and $(\text{MTSB})\text{AuCl}_3$ (*e.g* where M = Ni) have also been prepared, but because of partial reduction of Au(III) during reaction, the synthesis is difficult, and the resulting complexes are rarely pure.

D. ANTIFERROMAGNETIC INTERACTIONS

(i) *Binuclear complexes*

Magnetic exchange interactions are frequently useful in elucidating the structures of polynuclear complexes of paramagnetic metals. The temperature dependence of the magnetic susceptibility[64–66] and the e.s.r. spectrum[66–70] of copper(II) acetate led to the prediction of its binuclear structure[71,72]. Both the complexes [ix] and [xv] exhibit pair-wise antiferromagnetic[20,49] interactions between the two copper atoms in each molecule and the binuclear structures were subsequently confirmed by X-ray work[22,23,49,50]. These compounds structurally resemble complex [ii] and other complexes of type [xviii], and the pair-wise antiferromagnetic interactions observed in the series (CuTSB)CuX_2 (X = Cl, Br) are thus strong evidence in favour of structure [xviii] for these complexes[3]. A more striking resemblance exists between structures [xv]–[xviii] and the binuclear compounds [v] with bidentate salicylaldimines, which have a *trans* arrangement of the coordinating groups with respect to the  $\mathrm{Cu}{<}\overset{\mathrm{O}}{\underset{\mathrm{O}}{}}{>}\mathrm{Cu}$ skeleton, as opposed to the *cis* arrangement of the complexes [xviii] with tetradentate ligands. Thus exchange interactions are expected to occur in the complexes [v] if this structure is correct. Such interactions are observed. In fact, all the binuclear copper(II) complexes of types [v] and [xviii] exhibit pair-wise antiferromagnetic interactions[1–3,5–9,53,62,63,73–75], so that the temperature dependence of their magnetic susceptibilities, χ_M, per mole of binuclear complex, may be represented by the well known Bleany–Bowers equation[67,74]. Fig. 1 compares the experimental magnetic properties for a typical complex of type [xviii] with those calculated from the Bleany–Bowers equation when $J = -166\ \mathrm{cm}^{-1}$ and $g = 2.11$ and $N\alpha$, the temperature independent paramagnetism of van Vleck[73], is assumed[74,75] to be 6×10^{-5} c.g.s.u./mole. Other complexes behave similarly, and values of J and g are listed in Tables 1 and 2.

(ii) *Trinuclear complexes*

Antiferromagnetic exchange interactions in discrete trinuclear complexes were first treated by Kambe[76], who postulated that the magnetic properties of a group of trinuclear acetato complexes of iron(III) and chromium(III)[77] could be explained in terms of spin–spin interactions, the strength of the interaction being the same between each pair of atoms in the group of three. This hypothesis was confirmed by subsequent X-ray work[78] which showed that in the complex $[(H_2O \cdot Cr)_3O \cdot (CH_3 \cdot COO)_6]Cl \cdot 6H_2O$ the metals are grouped around the central oxygen atom and bridged by the acetato groups such that the environment about each chromium atom is identical.

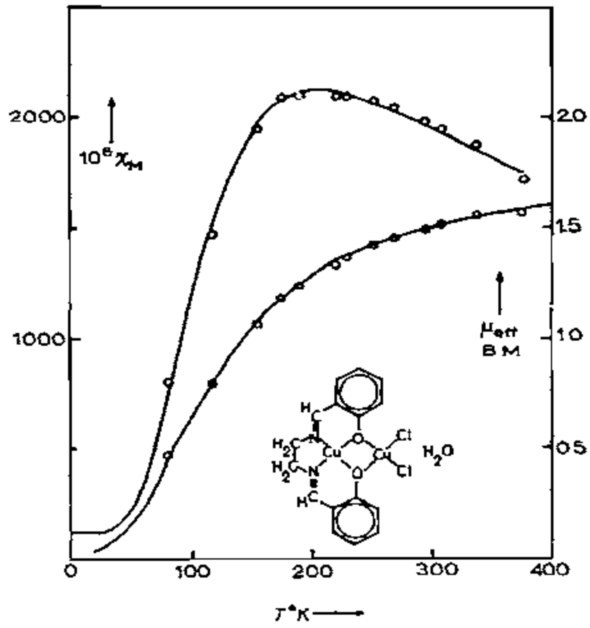


Fig 1. Temperature dependence of the magnetic susceptibility per mole of binuclear complex χ_M, and of the magnetic moment per copper atom μ_{eff}, for the first compound listed in Table 1. The curves give the theoretical values of χ_M and μ_{eff} calculated from the Bleany–Bowers equation using $J = -166$ cm^{-1} and $g = 2.11$.

Other evidence indicates[4] that the most likely structure for the complexes $(\mathrm{MTSB})_2\mathrm{M'(ClO_4)_2}$ [xix], which will be discussed further in Section E, is one in which the metals $\mathrm{M}\overset{\mathrm{M'}}{\diagup\;\diagdown}\mathrm{M}$ lie at the vertices of an isosceles triangle. (The possibility of a linear structure will not alter the treatment of the magnetic properties.) Moreover, temperature dependent studies on a number of $(\mathrm{CuTSB})_2\mathrm{M'}$-

TABLE 1

VALUES OF THE EXCHANGE INTEGRAL J AND THE AVERAGE g-FACTOR IN THE BINUCLEAR COMPLEXES [xviii] WHERE $\mathrm{M = M' = Cu}$, $\mathrm{(CuTSB)CuCl_2 \cdot nH_2O}$ AND R, R′ AND X ARE AS LISTED. WHERE THE COMPLEXES ARE SOLVATED, THE NUMBER OF MOLECULES OF WATER IS GIVEN BY n

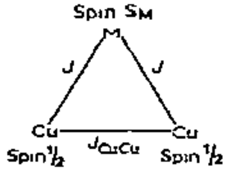
R	*R′*	*n*	*X*	*J(cm⁻¹)*	*g*	*Ref.*
$-(\mathrm{CH_2})_2-$	–H	1	Cl	−166	2.11	2, 3
$-(\mathrm{CH_2})_3-$	–H	0	Cl	− 49	2.14	3
$-\mathrm{CH_2{\cdot}CH(CH_3)}-$	–H	0	Cl	−106	2.15	3
–*o*-phenylene–	–H	1	Cl	− 97	2.07	3
–4-methyl-*o*-phenylene–	–H	1	Cl	− 91	2.08	3
$-(\mathrm{CH_2})_2-$	$-\mathrm{CH_3}$	0	Cl	−236	2.35	3
$-(\mathrm{CH_2})_3-$	$-\mathrm{CH_3}$	1	Cl	−140	2.05	3
–*o*-phenylene–	–H	$\frac{1}{2}$	Br	−194	2.28	3
–*o*-phenylene–	–H	1	Br	− 95	2.09	3
$-(\mathrm{CH_2})_6-$	–H	0	Cl	−139	2.29	6

TABLE 2

VALUES OF THE EXCHANGE INTEGRAL J AND THE AVERAGE g-FACTOR IN THE BINUCLEAR COMPLEXES [v]

R	R'	X	$J(cm^{-1})$	g	Ref.
$-CH_3$	$-H$	Cl	−149	2.17	6
$-CH_2CH_3$	$-H$	Cl	−240	2.18	6
$-(CH_2)_2CH_3$	$-H$	Cl	−255	2.08	6
$-(CH_2)_3CH_3$	$-H$	Cl	−205	2.14	6
$-(CH_2)_5CH_3$	$-H$	Cl	−188	2.12	6
$-(CH_2)_7CH_3$	$-H$	Cl	−180	2.14	6
$-CH_2{\cdot}CH\,(CH_3)_2$	$-H$	Cl	−245	2.12	6
$-CH{\cdot}(CH_3)_2$	$-H$	Cl	−145	2.17	6
$-CH{\cdot}(CH_3)CH_2CH_3$	$-H$	Cl	−155	2.11	6
–cyclohexyl	$-H$	Cl	−220	2.18	6
$-C_6H_5$	$-H$	Cl	−180	2.16	6
$-CH_2CH_3$	–5-Cl	Cl	−140	2.14	8
$-(CH_2)_2CH_3$	–5-Cl	Cl	−188	2.35	8
$-CH(CH_3)_2$	–5-Cl	Cl	−138	2.38	8
$-CH_3$	–5-Br	Cl	−220	2.20	8
$-CH_2CH_3$	–5-Br	Cl	−200	2.30	8
$-CH(CH_3)_2$	–5-Br	Cl	−195	2.22	8
$-CH_3$	–5,6-benzo	Br	−175	2.20	8
$-CH_3$	–5-Cl	Br	−146	2.36	8
$-CH_3$	–5-Br	Br	−180	2.35	8
$-CH_3$	–5-Cl	NO_3	−139	2.23	62

$(ClO_4)_2$ complexes[4], in which M′ is diamagnetic, yielding such groupings as $\mathrm{Cu}\overset{\diagup\mathrm{Mg}\diagdown}{\quad}\mathrm{Cu}$, have shown that the magnetic properties of these compounds conform well to the Curie–Weiss law $\chi \propto (T+\theta)^{-1}$ with small values of θ. Hence, if there is any interaction between the terminal atoms, then it is never greater, numerically, than $-5\ cm^{-1}$. When the terminal atoms M of [xix] $\mathrm{M}\overset{\diagup\mathrm{M'}\diagdown}{\quad}\mathrm{M}$ are diamagnetic, the magnetic properties are similar (Section C), and the θ values are again small, indicating that there are no significant intermolecular interactions[4,55,56]. In view of the probable isosceles triangular (or linear) arrangement of the metal atoms, and the failure of the terminal copper atoms to interact significantly when the central metal is diamagnetic, it would be unreasonable to assume equal interactions between each pair of metal atoms when all three metals are paramagnetic.



(xxi)

For the arrangement [xxi] of the metals[55,56], where the spin quantum numbers and the exchange integrals are as shown, the magnetic susceptibility per mole of trimeric complex is given by equation (1)

$$\chi_M = \frac{Ng^2\beta^2}{kT} \times \frac{\sum_{i=1}^{4} a_i e^{-E_i/kT}}{\sum_{i=1}^{4} b_i e^{-E_i/kT}} + N\alpha \tag{1}$$

where

$$a_1 = \sum_{q=0}^{m-4} (S_M - 1 - q)^2 \qquad b_1 = m-3 \qquad E_1 = mJ - \tfrac{1}{2}J_{\mathrm{CuCu}}$$

$$b_2 = b_3 = m-1 \qquad E_2 = 2J - \tfrac{1}{2}J_{\mathrm{CuCu}}$$

$$a_2 = a_3 = \sum_{q=0}^{m-2} (S_M - q)^2 \qquad b_4 = m+1 \qquad E_3 = \tfrac{3}{2}J_{\mathrm{CuCu}}$$

$$E_4 = (2-m)J + \tfrac{1}{2}J_{\mathrm{CuCu}}$$

$$a_4 = \sum_{q=0}^{m} (S_M + 1 - q)^2$$

$$m = 2S_M + 2$$

Thus, in the system $\mathrm{Cu}\overset{\mathrm{Cu'}}{\diagup\quad\diagdown}\mathrm{Cu}$ $(d^9-d^9-d^9)$, the susceptibility per gram-ion of copper(II) is given by

$$\chi = \frac{Ng^2\beta^2}{12kT} \times \frac{e^{-2J/kT} + e^{-2J_{\mathrm{CuCu}}/kT} + 10e^{J/kT}}{e^{-2J/kT} + e^{-2J_{\mathrm{CuCu}}/kT} + 2e^{J/kT}} + N\alpha \tag{2}$$

where $N\alpha$ is about 6×10^{-5} c.g.s.u. as before, and $J_{\mathrm{CuCu'}} = J_{\mathrm{Cu'Cu}} = J$. The agreement of experimental results with equation (4) is best when J_{CuCu} is small or zero. Fig. 2 compares the observed magnetic results with the curves calculated from equation (2), using the listed values of J and g, and assuming $J_{\mathrm{CuCu}} = 0$, for the complexes [iii], [xxii]–[xxiv] The complexes [xxii]–[xxiv] correspond to [xix] with M = M′ = Cu and [xxii] R = $-(\mathrm{CH_2})_3-$, R′ = H, [xxiii] R = $-(\mathrm{CH_2})_2-$, R′ = $\mathrm{CH_3}$, [xxiv] R = $-(\mathrm{CH_2})_2-$, R′ = H.

In the system $\mathrm{Cu}\overset{\mathrm{Ni}}{\diagup\quad\diagdown}\mathrm{Cu}$ $(d^9-d^8-d^9)$, $S_M = 1$, and on substituting in equation (1), the susceptibility per mole of trinuclear complex is given by

$$\chi = \frac{2Ng^2\beta^2}{kT} \times \frac{e^{-2J/kT} + e^{-2J_{\mathrm{CuCu}}/kT} + 5e^{2J/kT}}{e^{-4J/kT} + 3e^{-2J/kT} + 3e^{-2J_{\mathrm{CuCu}}/kT} + 5e^{2J/kT}} + N\alpha \tag{3}$$

Again the agreement with experimental results is best when J_{CuCu} is small or zero. Fig. 3 gives the experimental and theoretical results for a typical $d^9-d^8-d^9$ complex when $J = -64\ \mathrm{cm}^{-1}$, $g = 2.30$, $J_{\mathrm{CuCu}} = 0$

For the systems $\mathrm{Cu}\overset{\mathrm{Co}}{\diagup\quad\diagdown}\mathrm{Cu}$ $(d^9-d^7-d^9)$, $\mathrm{Cu}\overset{\mathrm{Fe}}{\diagup\quad\diagdown}\mathrm{Cu}$ $(d^9-d^6-d^9)$ and

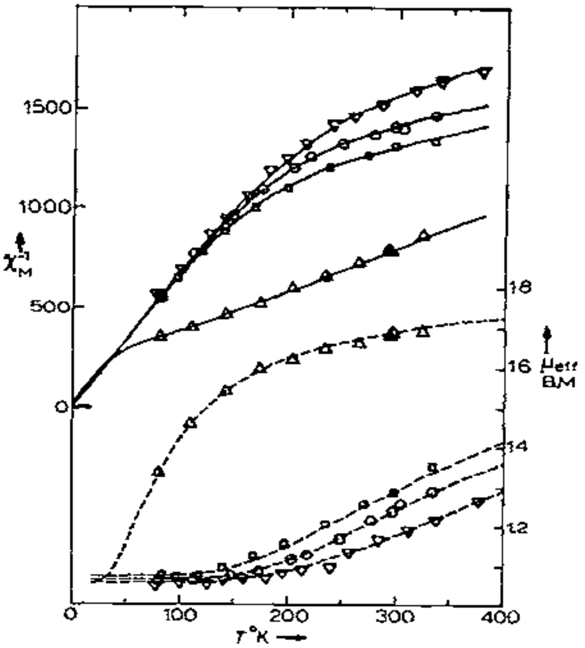
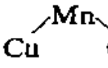


Fig. 2 Temperature dependence of the inverse magnetic susceptibilities χ_M^{-1} and of the magnetic moment μ_{eff} (per copper atom) for complexes of type [xix] containing the system CuCuCu. □, [iii], ▽ [xxii]; △ [xxiii], ○ [xxiv] (see text) The curves give the values calculated from the theory, using $J = -180$ cm^{-1}, $g = 2.15$ for [iii]; $J = -230$ cm^{-1}, $g = 2.12$ for [xxii]; $J = -200$ cm^{-1}, $g = 2.13$ for [xxiii], $J = -40$ cm^{-1}, $g = 2.10$ for [xxiv], and $J_{CuCu} = 0$ in equation (2).


$\overset{\text{Mn}}{\text{Cu}\quad\text{Cu}}$ ($d^9-d^5-d^9$), S_M is $\frac{3}{2}$, 2 and $\frac{5}{2}$ so that equation (1) yields equations (4), (5) and (6) respectively per mole of trinuclear complex:

$$\chi = \frac{Ng^2\beta^2}{4kT} \times \frac{e^{-5J/kT}+10e^{-2J/kT}+10e^{-2J_{CuCu}/kT}+35e^{3J/kT}}{e^{-5J/kT}+2e^{-2J/kT}+2e^{-2J_{CuCu}/kT}+3e^{3J/kT}} + N\alpha \tag{4}$$

$$\chi = \frac{2Ng^2\beta^2}{kT} \times \frac{e^{-6J/kT}+5e^{-2J/kT}+5e^{-2J_{CuCu}/kT}+14e^{4J/kT}}{3e^{-6J/kT}+5e^{-2J/kT}+5e^{-2J_{CuCu}/kT}+7e^{4J/kT}} + N\alpha \tag{5}$$

$$\chi = \frac{Ng^2\beta^2}{4kT} \times \frac{10e^{-7J/kT}+35e^{-2J/kT}+35e^{-2J_{CuCu}/kT}+84e^{5J/kT}}{2e^{-7J/kT}+3e^{-2J/kT}+3e^{-2J_{CuCu}/kT}+4e^{5J/kT}} + N\alpha \tag{6}$$

Fig. 4 compares the experimental magnetic results for a typical member of each of the groupings CuCoCu, CuFeCu and CuMnCu with the theoretical values calculated from equations (4), (5) and (6) respectively, using the listed values of J and g when $J_{CuCu} = 0$.

The effect upon the theoretical magnetic susceptibilities and moments, of variations in the relative values of J and J_{CuCu} has been investigated[55]. This can

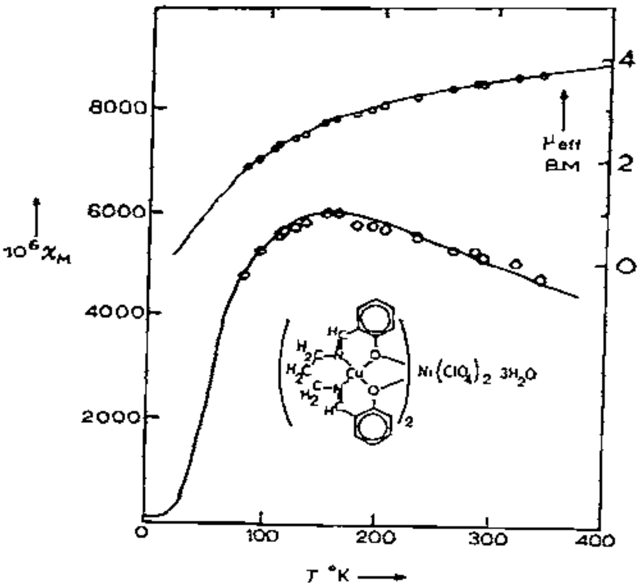


Fig 3 Temperature dependence of the magnetic susceptibility per mole of trinuclear complex χ_M, and the magnetic moment μ_{eff} per trinuclear molecule, for a compound of type [xix] containing the system CuNiCu The curves give the value calculated from the theory using $J_{CuCu} = 0$, $J = -64$ cm^{-1} and $g = 2\ 30$ in equation (3)

be seen schematically in Fig. 5 and Fig. 6 which show the energy levels available to the systems CuCuCu ($d^9-d^9-d^9$) and CuNiCu ($d^9-d^8-d^9$) respectively, under three different circumstances: $J_{CuCu} = J$, $J_{CuCu} = 0$ and the general case $0 < J_{CuCu} < J$. Fig 7 shows the calculated μ_{eff} *vs.* T curves for the CuMCu systems for various values of J_{CuCu} for a constant J. The influence of the value of J_{CuCu} on the magnetic properties becomes less as S_M becomes larger. Thus in the systems CuCu'Cu and CuNiCu, the shapes of the theoretical χ or μ_{eff} *vs* T curves are significantly different for different values of J_{CuCu}/J, and accurate experimental results can give a reasonable measure of this ratio. On the other hand, when $S_M = \frac{5}{2}$ as in the grouping CuMnCu ($d^9-d^5-d^9$), the relative values of J and J_{CuCu} are less important in determining the shapes of the theoretical χ or μ_{eff} *vs* T curves than the experimental errors are in shaping the observed curves.

An important property of J_{CuCu}/J is that its effect on χ and μ_{eff} is not linear; its influence decreases as J_{CuCu} decreases. Thus, when $J_{CuCu} \sim 0.2J$, the χ and μ_{eff} *vs* T curves are not very different in shape to the curves obtained when $J_{CuCu} = 0$. This is important in two ways: firstly the observation, in groupings CuM'Cu where M' is diamagnetic, that there is little interaction between the terminal metals[2,4,5] (Section C) is confirmed; secondly, any interactions that do occur between the terminal metals may be ignored[55,56]. J_{CuCu} may now be equated to zero, and the mathematical treatment constrained to the two para-

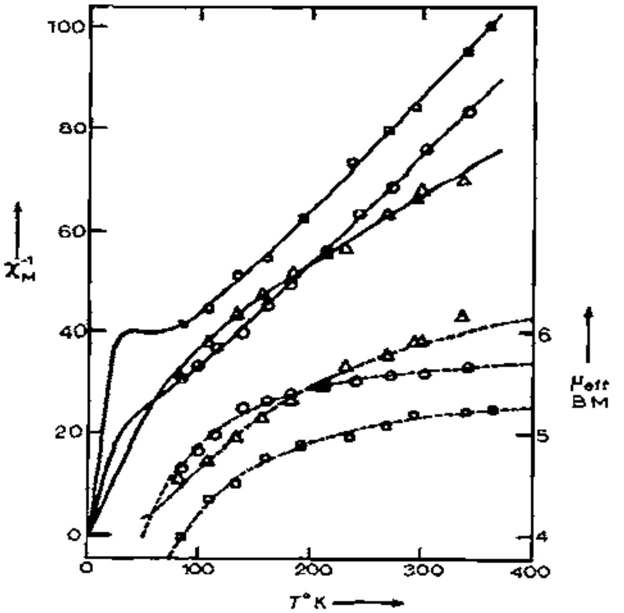


Fig 4 Temperature dependence of the inverse magnetic susceptibilities χ_M^{-1} and of the magnetic moments μ_{eff} (per trinuclear molecule) for complexes of type [xix] containing the groupings CuCoCu, CuFeCu, CuMnCu. The curves are calculated from equations (4)–(6) using $J_{CuCu} = 0$ and the following values of J and g:

□ CuCoCu, R = $-(CH_2)_3-$, R′ = $-CH_3$, $J = -24$ cm^{-1}, $g = 2.44$
E = 192 cm^{-1}

○ CuFeCu, R = $-(CH_2)_3-$, R′ = $-H$, $J = -15$ cm^{-1}, $g = 2.18$
E = 150 cm^{-1}

△ CuMnCu, R = $-(CH_2)_3-$, R′ = $-CH_3$, $J = -30$ cm^{-1}, $g = 2.12$
E = 360 cm^{-1}

E is the energy difference between the highest and lowest levels available to the system.

meters J and g. The parameter g is already constrained to values of acceptable magnitudes for the groupings of metals, as averaged over the three metals, and the only free variable is the strength of the antiferromagnetic interaction as measured by the exchange integral J. Even under these conditions, the experimental data can be fitted with a small range of values of J and g. It would be possible to obtain unique values for one of the parameters only by constraining the other at a fixed value, and EPR measurements are being made in order to fix the values of g[79].

The EPR spectra indicate completely anisotropic g values, in good agreement with the low-symmetry structures proposed for these complexes[2,4] (Section E). A difficulty with the EPR work is that the metal exchange reactions, discussed in Section C, make impossible the preparation of "doped" samples in which the antiferromagnetic trinuclear complex molecules are dispersed in a

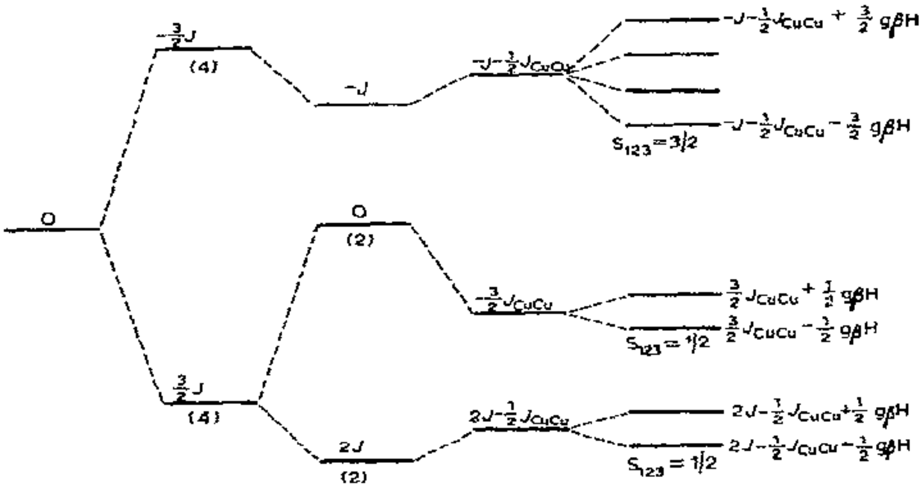


Fig. 5 Energy levels (schematic) available to an interacting system CuCu′Cu where $J_{CuCu'} = J_{Cu'Cu} = J$. For level (i) there is no interaction The levels (ii)–(iv) result from the spin-spin interaction with (ii) $J_{CuCu} = J$, (iii) $J_{CuCu} = 0$, and (iv) $0 < J_{CuCu} < J$, and no magnetic field Levels (v) represent the case $0 < J_{CuCu} < J$ when a magnetic field H is applied.

medium of an analogous diamagnetic complex. In the binuclear complexes, the same difficulty arises, and no EPR spectra are observed at all.

As a result of the fairly low symmetry of the environment about the three metal atoms, the orbital contribution to the magnetism should be correspondingly small, a conclusion supported by the fact that the g values estimated from the

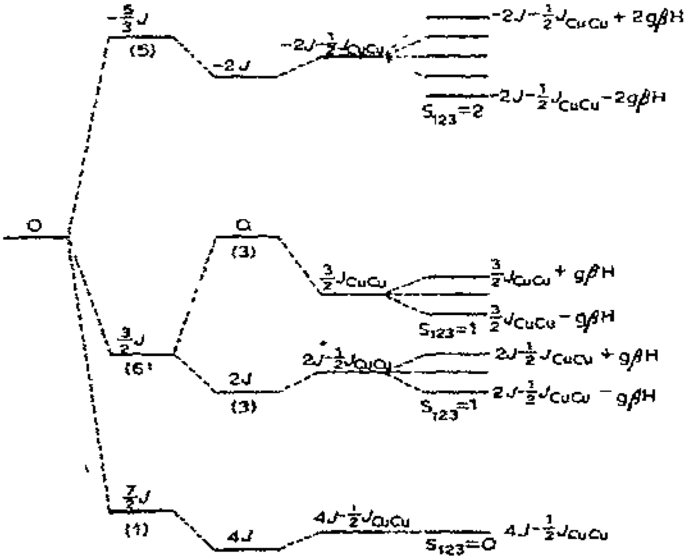


Fig. 6. Energy levels (schematic) available to an interacting system CuNiCu, where $J_{CuNi} = J_{NiCu} = J$. The levels (i)–(v) are analogous to those in Fig. 5

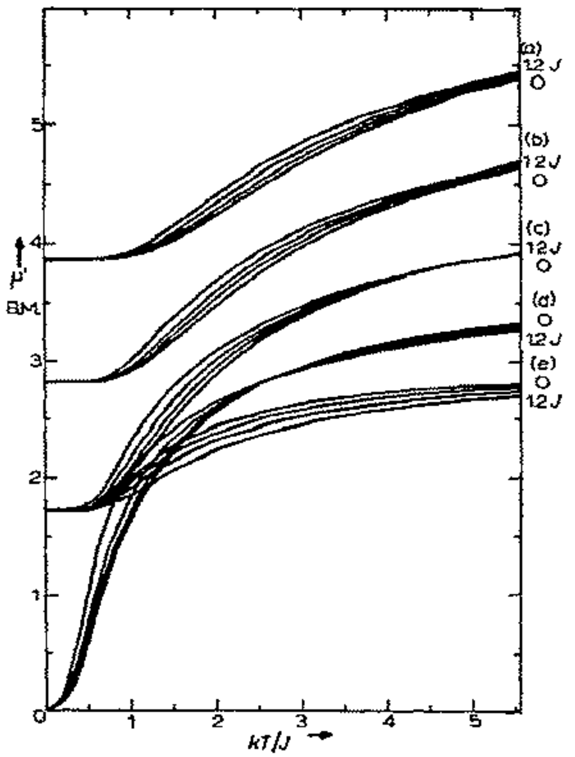


Fig 7. Reduced magnetic moment μ' ($= \mu_{eff}/g$) plotted as a function of kT/J for the systems (a) CuMnCu, (b) CuFeCu, (c) CuCoCu, (d) CuNiCu and (e) CuCu′Cu, where each of the metals are in the oxidation state (II).

magnetic results do not differ[55] too greatly from 2.0. The assumption that g, as used in equations (1)–(6), is constant over the temperature range, will therefore not lead to any significant errors. This approximation would almost certainly be invalid in analogous complexes containing rare earth metals, if these turn out to be antiferromagnetic.

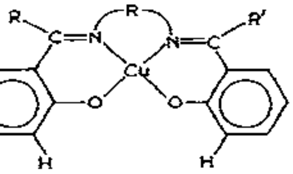
Theoretical treatment of both binuclear and trinuclear complexes has been confined to the first-order Zeeman splitting, as is the common practice[1–3,5,6,16,20–22,30–34,49,51–57,67,74,76,78,80–85]. Contribution of the second-order Zeeman effect is not highly temperature dependent in these systems ("temperature independent paramagnetism"), especially in the absence of appreciable orbital contribution to the magnetism, and it may quite reasonably be added as a constant $N\alpha$. Opinions vary[75] about the magnitude applicable to metals other than octahedral copper(II) (6×10^{-5} c.g.s.u./mole). The susceptibilities for all combinations CuMCu, where M is a metal other than copper, are so large that it makes little difference what value of $N\alpha$ is used for M, provided a reasonable value is used. The values used in equations (3)–(6) were selected arbitrarily because they seemed reasonable from an extensive survey of the literature[75]: 2×10^{-4} c.g.s.u/mole for CuNiCu; 5×10^{-4} for CuCoCu; 2×10^{-4} for CuFeCu; and 1.2×10^{-4} for CuMnCu.

Clearly the trinuclear model adopted here adequately explains the magnetic properties of the series of complexes. Antiferromagnetic interactions involving bi- and poly-nuclear copper compounds are quite common[75], but the present series of trinuclears containing similar and dissimilar metals is the first of its kind. Only one other observation of exchange coupling between dissimilar transition metals has been reported[86]. This arose from an EPR investigation of a nickel-doped monohydrate of complex [ix].

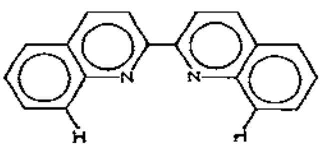
E. STRUCTURES

The binuclear complexes of type [xviii] with tetradentate Schiff bases are constrained by their nature to the structure postulated for them, and no reasonable alternatives present themselves. The existence of distinct structural isomers of the type (CuTSB)NiX$_2$ and (NiTSB)CuX$_2$ (Section C) rules out a possible infinite polymeric structure for [xviii] in which the metals M and M′ are in similar sites. In a crystal lattice, molecules of [xviii] would most likely pack on top of one another, with the copper atoms of each molecule as close as sterically possible to a halogen or oxygen of an adjacent molecule.

A metal complex of a tetradentate salicylaldimine [xx], [xxv] may be regarded as a bidentate complex ligand, whose steric requirements, when it is reasonably close to planar, have been likened[3] to those of 2,2′-biquinolyl (biq) [xxvi].



(xxv)

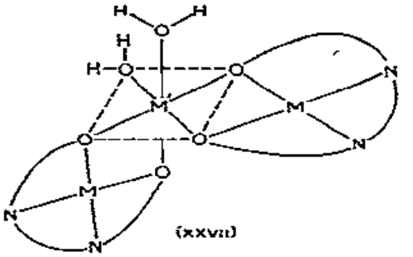


(xxvi)

This steric requirement forces a pseudo-tetrahedral environment on the dihalo- and dinitrato-complexes [Cu(biq)X$_2$] and on [Cu(biq)$_2$] (ClO$_4$)$_2$[87] and leads to an unprecedented five-coordinate structure in the gold(III) complex Au(biq)Cl$_3$[88]. Thus it appears from steric considerations that if the complex ligand [xx], [xxv] is planar, then the metal to which it coordinates, in forming complexes of the type [xviii], is unlikely to have a planar configuration Similarly, in the trinuclear complexes [xix], two planar complex ligands would not fit around the central metal atom in a *trans*-planar configuration. Similar steric hindrance, though to a lesser degree, will tend to oppose the formation of tetranuclear complexes having three complex ligands coordinated octahedrally.

The trinuclear complexes of type [xix] usually form as di- or tri-hydrates.

If the central metal M′ in such a trinuclear complex is six-coordinate with two molecules of water attached, then the steric effects will most likely require the two complex ligands to occupy *cis*-octahedral positions [xxvii]. This will place the two waters in *cis*-coordination sites, and if the structure were a perfect octahedron, the three metal atoms would be at the corners of an equilateral triangle. Residual steric crowding between the two complex ligands will manifest itself in a distortion of the *cis*-octahedral structure such that the equilateral triangle of metal atoms is flattened into an isosceles triangle, the apex of which is formed by the "central" metal. While simple *trans*-planar and *trans*-octahedral configurations are ruled out, other conceivable *trans* arrangements are represented by "chair" [xxviii] and "boat" [xxix] structures, which correspond to a linear and an isosceles triangular arrangement respectively. However, deviation of the three metal planes from co-planarity would need to be considerable in either of the structures [xxviii] and [xxix], and it is not certain that such sharp bending could occur at the linking three-coordinate oxygen atoms. On the other hand, at least one analogous complex[89,90] involving sulphur bridges is known from a crystal structure determination[91] to occupy a "chair" configuration: [xxx] $[\mathrm{Ni(MEA)_2}]\mathrm{Ni}^{++}$. However, steric hindrance is not nearly so great in [xxx] as it is in the trinuclear Shiff base compounds.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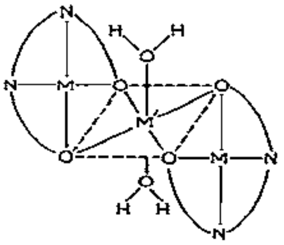
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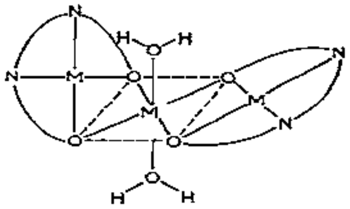
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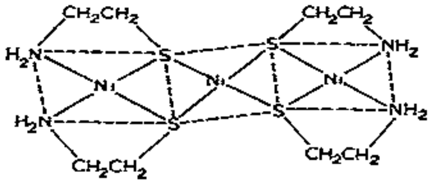
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Recently Milburn, Truter and Vickery[92] have determined the crystal structure of $(CuES)_2NaClO_4 \cdot C_8H_8$ (ES = *N,N'*-ethylenebis(salicyladimine) and C_8H_8 = *p*-xylene), an analogue of the compound $(CuES)_2NaClO_4 \cdot CHCl_3$ reported previously[4]. The structure was found to correspond to [xxvii] above, which had been postulated as the most probable structure for the trinuclear complexes [xix][4]. Although it is best not to regard the sodium ion as coordinated in the normal sense, the sodium ion occupies the position M' of the distorted[4,55] octahedron [xxvii], where M = Cu, surrounded by six oxygen atoms, four from the two complex ligands CuES (Na...O = 2.3 Å) and two from the perchlorate ion which acts as a "bidentate" (Na...O = 2.6 Å). The neighbouring trinuclear molecules are well separated, in agreement with the observation that there are no significant magnetic interactions between neighbouring trinuclear molecules in cases where M or M' are paramagnetic[4,55].

It is possible *a priori* for the binuclear copper(II) complexes with bidentate salicylaldimines to possess the "*trans*" structure [v] or a "*cis*" structure analogous to [ii]. However, entropy effects would make structure [v] more likely. Moreover, since copper(II) strongly prefers a planar structure to a tetrahedral one, structure [v] which minimises steric interference with the R-groups on the nitrogens in a planar configuration is favoured over a *trans* structure which maximises steric crowding. This reasoning is equally applicable to the parent Schiff base complexes [iv], whose structure has been shown to be *trans* in all cases investigated[17,93–99]. *Trans* structures are also preferred by four-coordinate complexes of other metals with bidentate salicylaldimine both when they are planar and when they are pseudo-tetrahedral[11,93].

The electronic spectra of multinuclear complexes containing CuTSB as complex ligand neatly support the assignments of the general structures [xviii] and [xix] for these compounds[4]. The spectra of some of these compounds are listed in Table 3. An important feature of the spectrum of the pseudo-tetrahedral $CuCl_4^{2-}$ ion is the ligand field transition at 8,500 cm^{-1}, a region free from absorptions of the complex ligands CuTSB[100,4] (Table 3). It is reasonable to expect that a copper atom bonded to two halogens, and placed in an environment roughly approximating to the pseudo-tetrahedral one in $CuCl_4^{2-}$ would show a ligand field absorption in the neighbourhood of the $CuCl_4^{2-}$ band at 8,500 cm^{-1}. Indeed, the complexes $(CuTSB)CuCl_2$ and $(CuTSB)CuBr_2$ all show a band in the region 8,000–12,000 cm^{-1}, which is absent in the corresponding CuTSB and its bi- and tri-nuclear complexes with non-transition metals which are not expected to have any absorptions in the ligand field region. In the trinuclear complex [xix], where M = M' = Cu, R = $-(CH_2)_2-$, and R' = H, there is a band at 11,200 cm^{-1} due to the central copper atom which is compatible with the proposed six-coordinate arrangement about this atom, two of the water molecules being coordinated.

In structure [v], the bulkiness of the nitrogen substituents R should have very little effect on the stereochemistries of the copper atoms and hence on properties

TABLE 3

(i) LIGAND FIELD SPECTRA OF (A) COMPLEX LIGANDS CuTSB ([XIX] WITH M = Cu) AND OF THEIR BINUCLEAR COMPLEXES (CuTSB)M′$X_2 \cdot nH_2O$, WHERE (B) M′ = Zn AND (C) M′ = Cu R, R′, X AND *n* ARE AS LISTED

R	*R′*	*n*	*X*	*Spectra* $^{-}$*(cm*^{1}*)*				*References*
				(A) Cu	*(B) CuZn*	*(C) CuCu*		
$-(CH_2)_2-$	–H	1	Cl	17700		18800	10800	4, 44, 60, 61, 105, 106
$-(CH_2)_2-$	–H	0	Cl	17700	19300	18700	10700	4, 44, 60, 61, 105, 106
–*o*-phenylene	–H	1	Cl	17900	18500 (sh)[a] 18000 (sh) 17500 (sh)	18300 (sh)	12000	4, 44, 106
–*o*-phenylene	–H	1	Br	17900		18400 (sh)	11700	4, 44, 106
$-CH_2\,CH\,(CH_3)-$	–H	0	Cl	17800	18800	18200	10900	4, 44
$-(CH_2)_3-$	–H	0	Cl	16600	17000	17100	9800	4, 44, 60, 61
$-(CH_2)_3-$	$-CH_3$	—	—	16500	—	—		4,44
2,2′-biphenyl	–H	—	—	15200, 11500 (sh)	—	—		110
$-(CH_2)_4-$	–H	0	Cl	15400, 12000	—	17100, 14500	9300	4, 44, 60, 61

(ii) LIGAND FIELD SPECTRA OF TRINUCLEAR COMPLEXES [XIX] $(CuES)_2M'(ClO_4)_2 \cdot nH_2O$ WHERE ES = N,N′-ETHYLENEBIS(SALICYLALDIMINE) (i e R = $-(CH_2)_2-$ AND R′ = –H)

Complex	*Spectra (cm*$^{-1}$*)*		*References*
CuES	17700		See above (i)
$(CuES)_2Cu(ClO_4)_2 \cdot 3H_2O$	19500	11200	4,61
$(CuES)_2Ba(ClO_4)_2$	18500		4
$(CuES)_2Sr(ClO_4)_2 \cdot 1.5H_2O$	18200		4
$(CuES)_2Mg(ClO_4)_2 \cdot 3H_2O$	19400		4,61
$(CuES)_2AgClO_4 \cdot 2H_2O$	18400		4

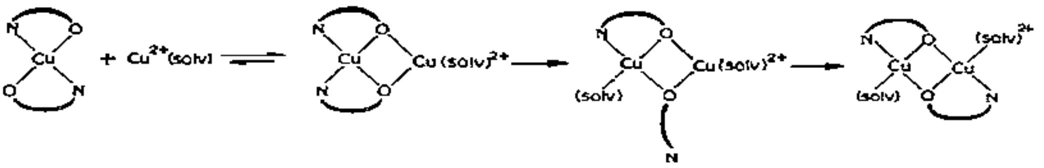
[a] $n = \frac{1}{2}$

dependent on stereochemistry. In the corresponding *cis* structure the great steric interference between the two R groups should lead to a dramatic difference in properties in going from complexes with R = methyl or n-alkyl to those with R = isopropyl. In fact, very little dependence on the nature of the R group is observed in either the magnetic or spectroscopic properties of these complexes[6–8]. The values of the exchange integral *J* for these complexes fall into a fairly small range (Table 2). It seems that for the complexes [v] without ring substituents (R′ = H), the *J* values are a little lower when R = sec-alkyl than when R = n-alkyl, except in the cases of the methyl and the cyclo-hexyl substituents, though in the latter case the experimental results and hence the *J* value are somewhat less accurate than those for the other complexes[6]. The electronic spectra of these complexes show only a slight dependence on the size of R in the ligand field region. These results have been interpreted in terms of a slight distortion from planar towards tetrahedral as R becomes more bulky[6] (Section F). No such distortion is evident from either the magnetic or spectral data in these binuclear complexes with substituents (R′) in the phenyl rings of the salicylaldimine group. Only the *trans* structure [v] for the complexes with no ring substituents (R′ = H), and for those with ring substituents (R′) can satisfactorily account for these results.

The electronic spectra of the binuclear complexes with bidentate salicylaldimines, unlike those of complexes [xviii] and [xix], suggest a single copper environment, as would be expected for structure [v]. In structure [v] the copper atoms should not be too distorted from a planar environment, and the *g* values (Table 2) are in agreement with this[6–9].

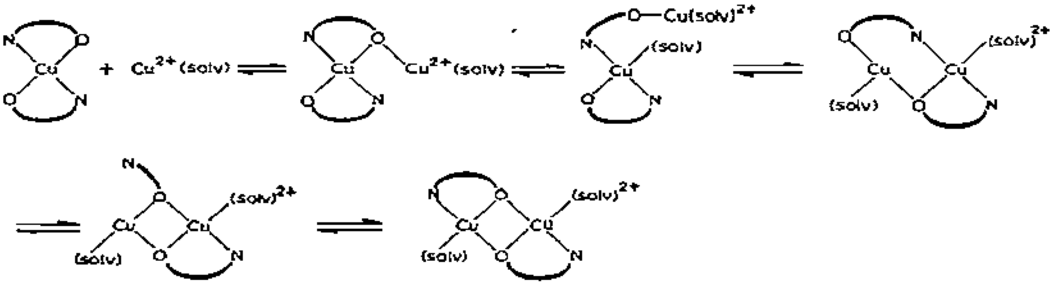
The synthesis of the complexes [v] from complexes [iv] and a copper(II) halide or nitrate is generally carried out in the presence of solvents, such as ethanol or methanol, which can coordinate to copper(II) ions and in which the CuX_2 (cupric halide or nitrate) is ionised. When solutions of a complex of type [iv] and of CuX_2 are mixed, the colour change associated with the formation of [v] occurs very rapidly or immediately, while the formation of a solid complex [v] takes from hours to weeks[6–9,62], even though the concentration of the solution is many times greater than the solubility of complex [v] would allow. This indicates that the rate determining step in the formation of solid complex [v] is the coordination of the halide or nitrate group prior to crystallisation. Two possible mechanisms suggest themselves for the initial reaction between the two solvated copper(II) species:

(a) Preliminary formation of a *cis* complex.



Even though the copper atoms are in a *trans* arrangement about the copper in complexes [iv][17,92–99], distortion from planar towards tetrahedral symmetry of the copper atom will bring these oxygens closer than they would be in a truly planar complex. This will in turn facilitate coordination to both oxygens simultaneously.

(b) Preliminary coordination to a single oxygen atom. This mechanism seems the more likely in the presence of coordinating solvents.



Similarly, in the formation of the complexes (MTSB)M'X_2 [xviii] and $(MTSB)_2M'(ClO_4)_2$, precipitation of the product is usually preceded by a colour change, suggesting a mechanism

$$\mathrm{MTSB} + \mathrm{M'^{2+}} \rightleftharpoons \mathrm{(MTSB)M'^{2+}} \xrightarrow{2X^-} \mathrm{(MTSB)_2M'X_2}$$

$$\mathrm{(MTSB)M'^{2+}} + \mathrm{MTSB} \rightleftharpoons \mathrm{(MTSB)_2M'^{2+}} \xrightarrow{2ClO_4^-} \mathrm{(MTSB)_2M'(ClO_4)_2}.$$

F. STEREOCHEMISTRY

The room temperature magnetic moments of the complex ligands CuTSB ([xx] with M = Cu) show a slight overall trend towards higher values with increase in the number of carbon atoms in the chain R linking the two *cis* nitrogen atoms in the tetradentate Schiff base. The moments are 1.82 B.M. for the linkage –O ..N–C–C–N ..O– (averaged over five compounds), 1.90 B.M. for the linkage –O...N–C–C–C–N...O– (averaged over two compounds), and 1.94 B.M. for the linkage –O...N–C–C–C–C–N...O– (where R = $-(CH_2)_4-$, R' = H)[4,61]. This trend is compatible with an increasing distortion away from a planar configuration with increasing –N–R–N– chain length, and is to be expected from the steric requirements of the tetradentate Schiff bases[4,61]. Similarly, the higher magnetic moments (1.90–1.92 B M.) for the N-sec-alkyl and N-t-butyl substituted copper(II) complexes [iv] (with no ring substituents, R' = H) than those (1.85–1.86 B.M.) of the n-alkyl analogues have been associated[101] with the greater distortion from planarity of the branched-alkyl[98,99] than in the n-alkyl[92,95,97] substituted complexes[101]. A further example of this correlation of magnetic moments and stereochemistry is provided by the planar $CuCl_4^{2-}$ ion in $[Pt(NH_3)_4]CuCl_4$ (μ_{eff} = 1.77 B.M.) and the flattened tetrahedral $CuCl_4^{2-}$ ion in Cs_2CuCl_4 (μ_{eff} = 2.0 B M.)[102]. Such a trend has also been observed in a series of copper(II) complexes with[87] biq [xxvi]. In a completely undistorted tetrahedron, copper(II) should have a room temperature moment of about 2 2 B M.[75,103].

The CuTSB complex with R = $-(CH_2)_6-$ and R' = H is an exception to the trend of magnetic moments with increasing –N–R–N– chain length, but its structure is probably polymeric[4,104] and may be regarded as a derivative of bis-(*N*-n-propylsalicylaldimino)copper(II) polymerised by joining the ends of the propyl groups. The very low solubility, the low magnetic moment, as well as the spectrum support this view[4].

The electronic spectra of the CuTSB complexes [xx] have been studied fairly extensively, especially in the ligand field region[44,61,105–108], and are typified fairly well by CuES (R = $-(CH_2)_2-$ and R' = H), which has three very intense charge transfer bands near 41,000, 35,000 and 27,000 cm^{-1}, and a weaker ligand field band at 17,500 cm^{-1}. A band corresponding to the latter is readily observable in most CuTSB complexes (Table 3), and is often asymmetric, or has a small shoulder in a few cases, suggesting a further lower energy ligand field transition of lower intensity[4,60]. However, the position of this band could not be obtained with any accuracy, and the higher energy band is the more important. The latter band shifts to lower energies as the –N–R–N– chain is lengthened, indicating that environment about the copper(II) atom is distorted from planar towards tetrahedral with increasing length of the –N–R–N– chain[4,60,61] (Table 3). This is similar to the trend observed by Sacconi and Ciampolini[109] in the copper(II) complexes with the bidentate copper(II) *N*-alkylsalicylaldimines ([iv] when R′ = H), whose spectra in the ligand field region are given in Table 4. Further proof is provided by the spectrum[110] of the complex *N*,*N*′-2,2′-biphenylbis(salicylaldimino)copper(II) ([xx] with M = Cu, R = 2,2′-biphenyl, R′ = H), which fits well into the CuTSB series in Table 3 at the pseudo-tetrahedral end of the scale; that this compound indeed possesses a pseudo-tetrahedral structure has been established by X-ray analysis[59]. The electronic spectrum of the complex [xx] with R = –(CH$_2$)$_6$–, R′ = H, M = Cu, does not fit into the series of CuTSB in Table 3, but resembles the spectra of the bis(*N*-n-alkylsalicylaldimino)copper(II) complexes in Table 4[6,60,61,109]; this is further evidence in favour of a polymeric structure for this compound.

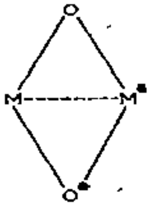
TABLE 4

LIGAND FIELD SPECTRA OF COMPLEXES [IV] AND THEIR BINUCLEAR DERIVATIVES [V], WHERE R, R′ AND X ARE AS LISTED

R	*R′*	*X*	*Spectra (cm^{-1})*				*References*
			[*iv*]		[*v*]		
–CH$_3$	–H	Cl	16900	15100	14800	12200	6, 60
–CH$_2$·CH$_3$	–H	Cl	16400	15100	16100	12600	6
–(CH$_2$)$_2$CH$_3$	–H	Cl	16400	14800	16000	12500	6, 60
–(CH$_2$)$_5$CH$_3$	–H	Cl	16400	14800	15900	12300	6, 61
–(CH$_2$)$_2$·CH(CH$_3$)$_2$	–H	Cl	16500	14800	15500	12200	60
–CH$_2$·CH·(CH$_3$)$_2$	–H	Cl	16000	12600	15600	12300	6, 60
–CH (CH$_3$)$_2$	–H	Cl	14000	9000	14200	11300	6
–cyclohexyl	–H	Cl	13400	8500	14100	11000	6, 61
–CH·(CH$_3$)CH$_2$·CH$_3$	–H	Cl	13300	8600	14000	10900	6, 60
–C(CH$_3$)$_3$	–H	Cl	13100	8500	13100	10700	6
–CH$_3$	–H	Br	(a)		13200	—	7
–(CH$_2$)$_3$CH$_3$	–H	Br	16500	—	12800	9800 (sh)	7
–cyclohexyl	–H	Br	(a)		12800	8500 (sh)	7
–CH$_3$	–5,6-benzo	Cl	—	14600	—	11200	8, 62
–CH$_2$ CH$_3$	–5,6-benzo	Cl	15800	14100			8, 62
–CH (CH$_3$)$_2$	–5,6-benzo	Cl	16000	12700	14000	11600	8, 62
–cyclohexyl	–5,6-benzo	Cl	15700	13800	14700	10300	8, 62
–CH(CH$_3$)$_2$	–5-Br	Cl	18100	15000	15000	12100	8, 62
–cyclohexyl	–5-Br	Cl	17500	15300	16000	12600	8, 62
–CH$_3$	–5-Cl	Br	17200	14600	15500	12600	8, 62
–CH$_3$	–5-Br	Br	16200	—	15300	12300	8, 62
–CH$_3$	–H	NO$_3$	(a)		14700	—	62
–CH$_3$	–5-Cl	NO$_3$	(a)		15900	—	62

(a) See above

The steric requirements[3,4,87] (Section E) of a planar complex ligand MTSB [xx], [xxv] make it unlikely that a metal M′, to which the MTSB coordinates, will be planar. These steric requirements must work equally well from the opposite direction: if the metal M′ in such a complex as [xviii] were planar, then the complex ligand MTSB would probably need to be distorted from planarity. In a trinuclear complex, such as [xix], the complex ligands would need to be even more distorted if they were forced to be in *trans*-planar or *trans*-octahedral positions about the central metal atom M′. Conversely, when the complex ligand is intrinsically non-planar (*e.g.* when R in [xx] is a long chain, or when the complex ligand MTSB is five-coordinate *e.g.* with a molecule of water in the fifth position[111]), the metal M′ need not be very distorted from planarity. Moreover, two adjacent metal atoms are unlikely to be bridged together as perfect tetrahedra, because of the close approach of the metal atoms that would be required. The metal–metal distance MM* in an oxygen-bridged structure MOM*O* [xxxi] is given by equation (7)

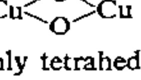


(xxxi)

$$MM^* = 2.MO. \cos\left(\frac{OMO^*}{2}\right) \qquad (7)$$

If M and M* are planar metal atoms, $OMO^* = 90°$, and $MM^* = MO\sqrt{2}$. If M and M* are tetrahedral, $OMO^* = 109°28'$ and $MM^* = 1.155$ MO. Thus, assuming a (large) value of 1.9 Å for MO[112], $MM^* = 2.7$ Å for square planar metal atoms, and $MM^* = 2.2$ Å for tetrahedra.

The geometries that may reasonably be expected from steric considerations may be summarised by the generalisation that: if one of the metals in a binuclear or trinuclear complex is in a planar environment, the adjacent metal will be distorted away from planarity, and if one of them is in a tetrahedral environment, the adjacent metal will be distorted away from a tetrahedral stereochemistry. However, in the case of copper(II), although steric effects lead to distortion from planar towards tetrahedral stereochemistry about the metal atom, the degree of distortion is generally much less than would be expected purely from steric considerations. Instead, the ligands themselves undergo considerable distortion[59,95,99].

In the bi- and tri-nuclear complexes (CuTSB)$M'X_2$ and $(CuTSB)_2M'(ClO_4)_2$ ([xviii] and [xix] with M = Cu), the ligand field absorption peaks (Table 3) are invariably at higher energies than in the parent CuTSB complexes, indicating as expected that the complex ligand CuTSB becomes more planar when it coordinates to a metal halide or perchlorate. The spectra of the (CuTSB)MX_2 compounds also indicate the expected trend towards pseudo-tetrahedral structure of the copper, but to a lesser degree than in the uncoordinated CuTSB complex ligands. At the same time, a very slight shift to lower energies of the band due to $CuCl_2$ in the complexes (CuTSB)$CuCl_2$ is observed, indicating that the halogen-bonded copper atom (M′ in [xviii]) becomes slightly more tetrahedral as the –N–R–N– chain length increases. Hence the two copper atoms are not held too close together, and this confirms again that the copper in the CuTSB ligand is fairly close to planar (the metal–metal distance in a system  $\mathrm{Cu}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Cu}$ where one of the copper atoms is roughly planar and the other roughly tetrahedral, and where Cu–O = 1.9 Å, would be about 2.5 Å, a reasonable distance in a copper–copper binuclear[71,72] derivative). The effect of steric interaction upon the configuration of the copper atom in the CuTSB ligand is not nearly as great as would be expected if the CuTSB molecule were rigid. Thus, a large part of the steric crowding must be relieved by distortion of the organic part of the CuTSB ligand.

The ligand field spectra of the binuclear copper(II) complexes [v] (Table 4) resemble those of the parent complexes [iv]. When there is no substituent in the phenyl ring of the salicylaldimine group (R′ = H) of complexes [v], there is a slight shift to lower energies of the main ligand field bands as the nitrogen substituent R becomes more bulky. This shift is similar to, but much less pronounced than the shift observed in the parent complexes [iv][109], and is compatible with a slight trend from planar towards tetrahedral stereochemistry in the copper atoms of [v] as the R group becomes more bulky[6,60,61]. On the other hand, no such trend is observed when the substituents 5-chloro, 5-bromo or 5,6-benzo are inserted in the phenyl rings of the salicylaldimine groups of the complexes [v] Thus complexes [v] are essentially planar, and the steric crowding is again largely relieved by distortions in the organic part of the molecules[8].

A complication to be considered is the possibility that a water molecule present in some of the binuclear complexes [xviii] may be coordinated to one of the metal atoms. In fact, there is little difference between the spectra of (CuES)-$CuCl_2$ and (CuES)$CuCl_2 \cdot H_2O$. If water were coordinated to the chlorine-bonded copper, it should result in a very crowded five-coordinated structure, and an appreciable change in the band near 10,000 cm^{-1}. However, when tetradentate and bidentate Schiff base and other complexes of copper(II) form adducts with water[113–115] or pyridine[116], the additional Cu–O or Cu–N bonds are often elongated, and the effect on the spectrum is not very great[117–119]. Hence, if the water is coordinated at all, it is coordinated to the CuTSB part of the binuclear molecule[4].

The Mössbauer spectra of complexes [xix] where the central metal M′ =

Fe(II) are compatible with a distorted octahedral configuration about this atom, as in structure [xxvii][79].

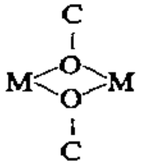
It has been suggested[105] that the stereochemistry about the *oxygen atom* bridging pairs of paramagnetic metals is important in determining whether magnetic exchange interactions occur between the metal pairs. Thus, appreciable interactions are observed when pairs of metals (M) are joined by a linear oxygen, as in the system Ru–O–Ru in $K_4[Ru_2OCl_{10}] \cdot H_2O$[120] or Fe–O–Fe in $(FeTSB)_2O$ complexes[121–125], while in the non-linear system Cu–O–Cu in CuES[18,126] no exchange interactions are observed[3,105]. However, there is reason to believe that the bond lengths in M–O–M systems are more important[4].

Most Cu–O–Cu linkages and many other M–O–M linkages that lead to appreciable magnetic exchange interactions are in fact non-linear (*e.g.* structures [ii], [iii], [v], [ix], [xii], [xv]–[xix]), and where the crystal structures were determined, the M–O–M links were always found to correspond to fairly strong bonds[2–9,20–34,46–56,76–78,86]. On the other hand, the complex CuES crystallises with pairs of monomeric molecules joined by weak (2.4 Å) Cu–O links, and such weak intermolecular links have never been found to lead to any appreciable antiferromagnetism.

G. INFRARED SPECTRA

The infrared spectra of complexes of types [xviii] and [xix] are independent of the nature of the metals M and M′ and therefore provide further evidence for a similar structure for these complexes for various metals[3–9,53,61], even when these are non-transition metals. However, the formation of complexes [v], [xviii] or [xix] from the appropriate parent compounds [iv] or [xx] leads to significant and consistent changes in the infrared spectrum of the parent complex. These changes are sufficiently specific to be considered as diagnostic of the bi- or trinuclear complex formation.

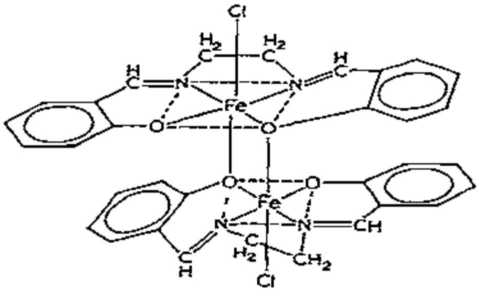
The effects of coordination are expected to be greatest for bands associated with the bridging oxygens, and progressively less for linkages further from the coordination sites. This fact, and the large number of distinct but similar complexes available, have assisted in the interpretation of the infrared spectra of these complexes, and of earlier infrared work on the parent complexes [iv] and [xx][127–132]. By far the most dramatic change observed upon coordination to the complex ligand is the shift (15–20 cm^{-1}) to higher energies of the band which occurs near 1530 cm^{-1} in the MTSB complexes [xx] and near 1540 cm^{-1} in the MSBS complexes such as [iv][4–9,133]. If this band is assigned to the C–O vibration, the shift to higher energy is compatible with the increasing constraint, introduced by the oxygen bridging. C–O links in metal acetylacetonates have vibrational absorptions at similar energies[134], and similar shifts are observed upon formation of complexes such as [xii]. Moreover, bis(*N*-methylsalicylaldimino)zinc(II), a dimer with two bridging and two non-bridging molecules per dimer[19], has two bands in this region[135] (1534–1553 cm^{-1})[4] of which one may be associated with the bridging and one with the non-bridging oxygens. An earlier assignment of this band to the C=N vibration[127] is not compatible with the shift associated with oxygen bridging, with the occurrence of a band near 1530 cm^{-1} in metal salicylaldehydes[4,9], nor with the results of ^{15}N data on some MTSB complexes[136]. The assignments of bands[127] near 1080 cm^{-1} and[128,129] near 1340 cm^{-1} to the phenolic C–O vibration are now in doubt because all bands near these are insensitive to the change from two-coordinate oxygen in [iv] and [xx] to three-coordinate oxygen in bi- and tri-nuclear complexes [v], [xviii] and [xix]. On the other hand, the band near 1340 cm^{-1} in MTSB complexes [xx] is strongly affected when R = –(CH$_2$)$_2$– is replaced by R = *o*-phenylene, and it may therefore be due to the –CH$_2$– deformation[4]. Although the assignment of the band near 1530 cm^{-1} to the phenolic C–O frequency is not completely confirmed without ^{18}O data, the shift in this frequency is certainly diagnostic of the formation of bi- and tri-nuclear complexes, whether it arises from the C–O stretch or not.

The increasing constraint imposed upon the vibrations in going from parent [iv] to the binuclear complexes [v] results in smaller but significant (5–10 cm^{-1}) shifts to higher energies, in bands near 1620, 1480, 1140 and 760 cm^{-1}. New bands appear near 1275, 1210 and 1150 cm^{-1}, the bands near 1190 and 970 cm^{-1} vanish and the band near 910 cm^{-1} is lowered in energy[6–9,62,63]. Complex formation with MTSB complexes results in small shifts to higher energies (0–5 cm^{-1}) in bands near 1630 and 1140 cm^{-1}, a larger shift (~10 cm^{-1}) in the band near 1025 cm^{-1}, while new bands appear near 1280, 1150 and 790 cm^{-1}, and bands near 950 and 730 cm^{-1} vanish[4]. Some of the new bands most likely arise from some kind of vibrational modes of the  $M\overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{<^{O}_{O}>}}M$ skeleton, but more specific assignments do not seem profitable at this stage.

H. OTHER TYPES OF "COMPLEX LIGANDS"

A consideration of the various types of stable multinuclear complexes that could be formed by the use of various metal derivatives of Schiff bases or β-diketonates indicates that the number of such multinuclear complexes potentially obtainable is of the order of 10^8–10^9. Only a small selection of these compounds have so far been prepared and examined, and though some generalisations have been drawn here, the possibility exists of some as yet unsuspected properties in complexes of this type. The readiness with which some of these polynuclear complexes form from common inorganic reagents makes it surprising that they have not previously been discovered, even by accident. Although this review has deliberately been restricted to the multinuclear complexes introduced in Section A, the definition of "complex ligands" has obvious extensions in the direction of certain other types of multinuclear complexes. Most notably the well-known work of Busch and Jicha, and others, on the complex $[\mathrm{Ni(MEA)_2}]\mathrm{Ni}^{2+}$ [xxx] and related compounds falls in this category[89–91,137,138]. Complex [xxx] contains three planar diagmagnetic nickel(II) atoms[89,91], linked by three-coordinate sulphur bridges. Similar complexes $[\mathrm{Ni(MEA)_2}]\mathrm{M}^{n+}$ have been prepared[137], where $\mathrm{M}^{n+} = \mathrm{Cu}^{+}$, Cu^{2+}, Pd^{2+}, Pt^{2+} and Cd^{2+}; other bi- and tri-nuclear complexes containing similar sulphur bridges have been prepared, which, structurally at least, bear some resemblance to certain of the complexes discussed in the previous sections[138–141]. However, no sulphur-bridged analogues of [xviii], and no antiferromagnetically interacting complexes analogous to the oxygen-bridged polynuclears appear to have been reported to date.

A somewhat different kind of complex ligand is formed by the series $(\mathrm{X{-}FeTSB})_2$ (where X = Cl, Br) which commonly exists as oxygen-bridged magnetically interacting dimers, but can also be isolated as five coordinated monomers[142–144]. Thus single crystal X-ray studies have shown that $(\mathrm{Cl{-}FeES})_2$ can have the dimeric structure[143] [xxxii], or the analogous monomeric structure[144]. These complexes have two phenolic oxygens, in a *cis* arrangement about the iron atom, and the analogy with complex ligands of type [xx] is obvious. As expected, the $(\mathrm{X{-}FeTSB})_2$ complexes form complexes with a number of metal halides and perchlorates[9], though none of the polynuclear dissimilar metal complexes of this type have been reported to date.



(xxxii)

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