Studies on Binuclear Copper(II) Complexes involving Co-ordination of (Quadridentate Schiff base)copper(II) with (Tertiary diamine)copper(II)

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Dimeric copper(II) complexes of the type $[Cu(L)Cu(A)][ClO_4]_2$ have been prepared, where L = various quadridentate Schiff base ions derived by the condensation of salicylaldehyde or 2-hydroxyacetophenone with ethylenediamine or 1,3-propylenediamine and A = 2,2′-bipyridyl, 1,10-phenanthroline, or 2-(2′-pyridyl)benzimidazole. Magnetic moment values of the complexes are observed to be much lower than the spin-only value, due to antiferromagnetic interaction between the two Cu^{II} centres. $[Cu(L)]$ and $[Cu(A)]^{2+}$ seem to affect the ligand-field spectral band positions of each other when co-ordinated in the binuclear complexes $[Cu(L)Cu(A)]^{2+}$. Ultraviolet spectral studies of these complexes have also been carried out which show that there is no significant interaction between the π orbitals of the two ligands through metal ion *d* orbitals. Infrared spectra show a shift of ν(C–O) bands to higher energy in the binuclear complexes indicating bridging through phenolic O^-.

THE study of binuclear Cu^{II} complexes is attaining importance because of the fact that their electronic spectra and magnetic properties are interesting and they provide models for metalloenzymes.

Sinn and Harris [1] have reported the binuclear and trinuclear complexes of the type $[Cu(L)CuX_2]$ and $[Cu(L)]_2{\cdot}Cu[ClO_4]_2$, where X = Cl, Br, or NO_3 and L = various quadridentate Schiff base ions derived from salicylaldehyde. The quadridentate Schiff base complex with an additional lone pair of electrons over the two phenolic oxides is supposed to be acting as a ligand and becomes co-ordinated with CuX_2. Formation of binuclear copper complexes, bridging through O^-, has also been reported for some ' two-compartment ' macrocyclic ligands.[2,3]

In these binuclear Cu^{II} complexes, it has been observed that the magnetic moments are subnormal and decrease with decreasing temperature. This has been explained to be due to antiferromagnetic interaction between the two copper(II) centres.[4] In view of the large Cu^{II}–Cu^{II} distance, it seems unlikely that direct exchange due to overlap of copper *d* orbitals is significant. The possible exchange pathway is super-exchange involving the copper $d_{x^2-y^2}$ and oxygen p_x orbitals.[5]

It was observed by Sinn and co-workers [6] that if one of the metals in a binuclear 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 tetrahedral geometry. As distortion from planarity increases towards tetrahedral, there is a red shift in the *d–d* bands. The distortion from planarity also reduces the overlap of Cu^{II} orbitals with oxygen orbitals and hence there is a significant decrease in antiferromagnetic exchange interaction, resulting in an increase in the magnetic moment.[7]

It was, therefore, thought of interest to study the co-ordination of quadridentate Schiff base complexes with a metal ion already bound to another bidentate ligand. This paper reports the preparation of binuclear copper(II) complexes of the type $[Cu(L)Cu(A)][ClO_4]_2$, where L = the quadridentate Schiff bases *NN*′-ethylenebis(salicylaldiminate) (L^1), *NN*′-ethylenebis(2-hydroxyacetophenoniminate) (L^2), *NN*′-propylenebis(salicylaldiminate) (L^3), or *NN*′-propylenebis(2-hydroxyacetophenoniminate) (L^4); and A = the tertiary diamines 2,2′-bipyridyl (A^1), 1,10-phenanthroline (A^2), or 2-(2′-pyridyl)benzimidazole (A^3). An attempt has been made to see if there is any effect of the tertiary diamine (A), co-ordinated to the second copper ion, on the extent of Cu^{II}–Cu^{II} spin coupling and whether there is an interaction between the Schiff base and the ligand (A) through the metal ions.

EXPERIMENTAL

All chemicals used were of A.R. grade. $Cu[ClO_4]_2{\cdot}6H_2O$ was prepared by dissolving $Cu[CO_3]$ (1 mol) in perchloric acid (2 mol). The resulting solid was recrystallized from ethanol and dried *in vacuo* to constant weight. The percentage of copper(II) was estimated and was found to correspond to the above formula. Quadridentate Schiff base complexes were prepared by the reaction of salicylaldehyde or 2-hydroxyacetophenone with ethylenediamine or 1,3-propylenediamine.[8] 2-(2′-Pyridyl)benzimidazole was prepared by the literature method.[9]

Preparation of $[Cu(L)Cu(A)][ClO_4]_2$.—A suspension of $[Cu(A)(ClO_4)_2]$ was prepared by adding A (3 mmol) in absolute ethanol (10 cm^3) to $Cu[ClO_4]_2{\cdot}6H_2O$ (3 mmol) in absolute ethanol (10 cm^3). This suspension was then added to [Cu(L)] (3.5 mmol) dissolved in chloroform (50 cm^3). The mixture was refluxed for about 2 h with constant stirring. The resulting solid was filtered off, washed thoroughly with chloroform to remove excess of [Cu(L)], and dried under vacuum.

The analyses and magnetic data are presented in Table 1. Electronic spectral data are presented in Table 2 and reflectance spectral data are given in Table 3. To check the purity of the compounds, thin-layer chromatography (t.l.c.) was used with ethanol as solvent. Electronic spectra in ethanol were obtained on a recording spectrophotometer SPECORD UV-VIS of CZ Jena with 1-cm quartz cells. Reflectance spectra were obtained on a VS U2-P of CZ Jena using magnesium carbonate as reference. Infrared spectra were recorded in Nujol on a Beckman spectrophotometer 21. Magnetic susceptibility measurements were carried out at room temperature using a Gouy balance. Diamagnetic corrections were done using Pascal's constants. Corrections were made using the equation

TABLE 1

Analytical and magnetic data for the binuclear complexes

Compound	Colour	Analyses[a] (%) Cu	N	C	H	$\mu_{eff.}$ per Cu^{II} ion/B.M.[b]
$[Cu(L^1)Cu(A^1)][ClO_4]_2$	Brown	16.8	6.8	41.1	3.35	1.19
		(17.0)	(7.5)	(41.1)	(2.95)	
$[Cu(L^2)Cu(A^1)][ClO_4]_2$	Brown	16.2	6.9	43.4	3.25	1.17
		(16.4)	(7.2)	(43.3)	(3.35)	
$[Cu(L^3)Cu(A^1)][ClO_4]_2$	Olive green	16.3	7.6	42.3	3.05	0.92
		(16.7)	(7.4)	(42.5)	(3.15)	
$[Cu(L^4)Cu(A^1)][ClO_4]_2$	Bluish black	15.6	7.3	44.5	3.90	0.83
		(16.1)	(7.1)	(44.1)	(3.55)	
$[Cu(L^1)Cu(A^2)][ClO_4]_2$	Brown	16.6	6.9	42.9	3.40	1.17
		(16.5)	(7.3)	(43.5)	(2.85)	
$[Cu(L^2)Cu(A^2)][ClO_4]_2$	Brown	15.7	7.3	45.4	3.45	1.12
		(15.9)	(7.0)	(45.0)	(3.10)	
$[Cu(L^3)Cu(A^2)][ClO_4]_2$	Olive green	15.9	6.5	44.2	3.20	0.95
		(16.2)	(7.1)	(44.3)	(3.05)	
$[Cu(L^4)Cu(A^2)][ClO_4]_2$	Grey	15.8	6.7	46.0	3.65	0.92
		(15.6)	(6.9)	(45.7)	(3.45)	
$[Cu(L^1)Cu(A^3)][ClO_4]_2$	Brown	16.0	9.1	41.9	3.25	1.20
		(16.2)	(8.9)	(42.6)	(2.90)	
$[Cu(L^2)Cu(A^3)][ClO_4]_2$	Brown	15.2	8.9	44.5	3.40	1.16
		(15.6)	(8.6)	(44.2)	(3.30)	
$[Cu(L^3)Cu(A^3)][ClO_4]_2$	Olive green	15.8	8.7	43.0	3.55	1.02
		(15.9)	(8.7)	(43.4)	(3.10)	
$[Cu(L^4)Cu(A^3)][ClO_4]_2$	Olive green	15.4	8.7	45.3	3.90	0.99
		(15.3)	(8.4)	(44.9)	(3.50)	

[a] Calculated values are given in parentheses. [b] 1 B.M. = 0.927×10^{-23} A m^2.

$\mu_{eff.} = 2.84\sqrt{(\chi_m - N_\alpha)T}$, where N_α = temperature independent paramagnetism = 60×10^{-6}.[3]

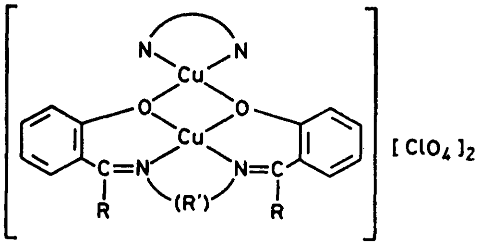
RESULTS AND DISCUSSION

T.l.c. of all the compounds showed a single dot, confirming their purity. The elemental analyses of the complexes corresponded to the expected formulae.

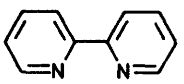
The structures can be represented as shown below. The metal Schiff base complex becomes co-ordinated with $[Cu(A)]^{2+}$ through the lone pair of electrons over O^-, forming σ bonds, as in the case of $[Cu(L)CuX_2]$ complexes.[1]

Infrared Spectra of the Complexes.—The complexes are not very soluble in organic solvents and hence molar conductances could not be determined. The presence of perchlorate in the outer sphere was confirmed by the i.r. spectra. There is one band obtained at *ca.* 1 100 cm^{-1} corresponding to $\nu_{asym}(ClO_4^-)$. The absence of $\nu_{sym}(ClO_4^-)$ at *ca.* 900 cm^{-1} indicates T_d geometry and hence the presence of ionic ClO_4^-.[10] The i.r. spectral bands of binuclear complexes of the type $[Cu(L)CuX_2]$ have been discussed by Sinn and co-workers.[4,6] Bands due to the Schiff base L in the present $[Cu(L)Cu(A)]^{2+}$ complexes also show a small shift of 5—10 cm^{-1} from those in [Cu(L)]. This shows that the effect of co-ordination with CuX_2 or with $[Cu(A)]^{2+}$ on the i.r. spectral bands of [Cu(L)] is approximately equal. It is interesting to observe the band positions of ν(C–O) for [Cu(L)] and its binuclear complexes. [Cu(L)] shows ν(C–O) at *ca.* 1 530—1 540 cm^{-1}, whereas $[Cu(L)Cu(A)][ClO_4]_2$ shows ν(C–O) at higher energy indicating bridging through phenolic O^-.[6]

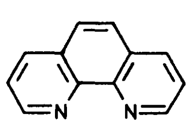
Ligand-field Spectra of the Complexes.—Reflectance spectra for selected binuclear complexes were obtained and the results are as follows. In the mononuclear [Cu(L)] complex, there is a broad band present at 18 180 cm^{-1} as expected for a square-planar Cu^{II} complex.[11] In binuclear $[Cu(L)CuX_2]$ complexes, Harris and Sinn[4] observed *d–d* bands for two non-equivalent copper(II) centres. In the present complexes $[Cu(L)Cu(A)]^{2+}$, two bands are also observed. The $>Cu(A)^{2+}$ centre shows a *d–d* band at higher energy (*ca.* 12 500 cm^{-1}) than that



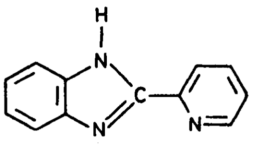
R = H or CH_3
R' = —$(CH_2)_2$— or —$(CH_2)_3$—
$N\frown N$ = A^1, A^2, or A^3



2,2'-bipyridyl (A^1)



1,10-phenanthroline (A^2)



2-(2'-pyridyl)benzimidazole (A^3)

observed earlier for the $\rangle CuCl_2$ (*ca.* 8 100 cm^{-1}) part in [Cu(L)CuCl$_2$] complexes. This is because the diamine A creates a stronger field than two chlorides. The band due to the Cu(L) part of the binuclear complex also shows a shift from the value in free [Cu(L)]. This is because of the change in the planarity of [Cu(L)] on co-ordination with [Cu(A)]$^{2+}$, as suggested in the case of [Cu(L)CuCl$_2$] complexes.[6] Further, co-ordination with CuCl$_2$ or [Cu(A)]$^{2+}$ also lowers the strength of the Cu^{II}–O bond in the Cu(L) part and hence there should be lowering in the ligand-field band energy. The change in the position of the Cu(L) band supports the formation of binuclear complexes.

TABLE 2

Electronic spectral band energies (cm^{-1}) and absorption coefficients (log ε) of [Cu(A)]$^{2+}$, [Cu(L)], and their binuclear complexes in ethanol

Compound	λ (log ε)
[Cu(A^1)]$^{2+}$	49 000, 41 000 (4.10), 33 200 (4.17), 32 000 (4.17)
[Cu(A^2)]$^{2+}$	48 000, 44 200 (4.54), 36 400 (4.28), 34 000 (sh) (3.76)
[Cu(A^3)]$^{2+}$	48 500, 41 300 (4.21), 40 400 (3.90), 31 000 (4.32)
[Cu(L^1)]	43 250 (4 .79), 41 250 (4.74), 36 500 (4.52), 28 900 (4.09), 17 750
[Cu(L^2)]	47 250, 42 250 (4.76), 36 230 (4.45), 28 000 (4.09), 18 120
[Cu(L^3)]	43 500 (4.87), 41 500 (4.83), 36 300 (4.56), 27 500 (4.21), 16 880
[Cu(L^4)]	48 000, 43 000 (4.99), 36 750 (4.54), 28 500 (4.28)
[Cu(L^1)Cu(A^1)][ClO$_4$]$_2$	48 000, 43 800 (4.54), 41 000 (4.51), 36 000 (4.27), 33 200 (4.06), 32 000 (3.98), 28 000 (4.50), 17 800
[Cu(L^1)Cu(A^2)][ClO$_4$]$_2$	48 000, 43 800 (5.02), 41 000 (4.84), 36 600 (4.85), 33 800 (sh) (4.30), 28 000 (4.17)
[Cu(L^1)Cu(A^3)][ClO$_4$]$_2$	48 000, 43 800 (4.86), 41 000 (4.83), 36 400 (4.58), 29 200 (4.30), 17 800
[Cu(L^2)Cu(A^1)][ClO$_4$]$_2$	48 500, 42 800 (4.68), 36 400 (4.36), 33 200 (4.04), 32 000 (3.90), 28 200 (3.94), 18 500
[Cu(L^2)Cu(A^2)][ClO$_4$]$_2$	48 000, 42 800 (4.90), 36 600 (4.70), 33 800 (sh) (4.18), 28 200 (4.08)
[Cu(L^2)Cu(A^3)][ClO$_4$]$_2$	47 780, 42 800 (5.03), 36 500 (4.68), 28 800 (4.45)
[Cu(L^3)Cu(A^1)][ClO$_4$]$_2$	48 000, 44 000 (4.75), 41 200 (4.74), 36 000 (4.49), 33 200 (4.34), 32 000 (4.28), 28 800 (4.08), 16 000
[Cu(L^3)Cu(A^2)][ClO$_4$]$_2$	48 000, 44 000 (4.70), 41 000 (sh) (4.53), 36 400 (4.56), 33 800 (sh) (4.15), 27 800 (4.06)
[Cu(L^3)Cu(A^3)][ClO$_4$]$_2$	48 100, 44 000 (4.79), 41 900 (4.78), 36 000 (4.48), 29 200 (4.26)
[Cu(L^4)Cu(A^1)][ClO$_4$]$_2$	48 000 (sh), 43 000 (4.91), 37 000 (sh) (4.53), 33 200 (4.51), 32 000 (4.46), 28 500 (4.15)
[Cu(L^4)Cu(A^2)][ClO$_4$]$_2$	48 000 (sh), 44 000 (4.68), 36 400 (4.51), 33 800 (sh) (4.15), 28 750 (4.11)
[Cu(L^4)Cu(A^3)][ClO$_4$]$_2$	48 000 (sh), 43 000 (4.62), 36 500 (4.25), 30 000 (4.20)

The room-temperature magnetic moments of the binuclear complexes are lower than the expected spin-only value for one unpaired electron on each Cu^{II} ion. This indicates antiferromagnetic Cu^{II}–Cu^{II} interaction. As in the case of [Cu(L)CuCl$_2$], direct interaction between two metal ions is ruled out. Super-exchange can take place through the *s* and *p* orbitals of bridging diamagnetic O$^-$ of the Schiff base. This interaction gives rise to a diamagnetic spin singlet ground state and an excited paramagnetic triplet state. At room temperature, the singlet ground state is more populated and hence there is lowering of the magnetic moment.

Sinn and other workers observed that in the case of [Cu(L)] with a long –(CH$_2$)$_n$– chain, there is distortion from planarity. This reduces the super-exchange in [Cu(L)CuCl$_2$] and hence the lowering in the magnetic moment is less.[6,12–14] However, in the present complexes [Cu(L)Cu(A)][ClO$_4$]$_2$, there is greater lowering in $\mu_{eff.}$ value where [Cu(L)] has a –(CH$_2$)$_3$– chain than in the case where it is –(CH$_2$)$_2$–. Any attempt to explain this should await variable-temperature magnetic measurement and *X*-ray structural studies.

TABLE 3

Reflectance spectra (cm^{-1})

Compound	
[Cu(L^2)]	28 570, 18 180
[Cu(L^2)CuCl$_2$]	26 665, 17 390, 10 640
[Cu(L^2)Cu(A^1)][ClO$_4$]$_2$	27 780, 17 860, 12 500 (sh)
[Cu(L^2)Cu(A^2)][ClO$_4$]$_2$	27 780, 16 660—12 500 (broad band)
[Cu(L^2)Cu(A^3)][ClO$_4$]$_2$	27 780, 19 610, 12 500

It is interesting to see if there is any exchange interaction between the π-electron clouds over the ligands on the two Cu^{II} centres through the p_z orbital of the O$^-$ bridge. This can be realised by comparing the u.v. spectra (Table 2) of L, [Cu(L)], [Cu(A)]$^{2+}$, and [Cu(L)-Cu(A)]$^{2+}$. The representative case of [Cu(L^1)Cu(A^1)][ClO$_4$]$_2$ is discussed here.

The Schiff base L^1 shows bands at 44 330, 41 170, 36 170, and 24 800 cm^{-1}. The first three are known to be $\pi \longrightarrow \pi^*$ transitions in the aromatic ring and the C=N chromophore. This assignment is on the basis of the high intensity of the bands and the solvent dependence of the band positions.[15] The band at 24 800 cm^{-1} is an $n \longrightarrow \pi^*$ transition.

[Cu(L^1)] shows bands at 43 250, 41 250, 36 500, and 28 900 cm^{-1}. The high-intensity bands at 41 250, 36 500, and 28 900 cm^{-1} have been assigned to charge-transfer transitions. There may be intra-ligand bands also in this region.[6] The shift in the position of $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ bands of L^1 in [Cu(L)^1)] shows that there is a π interaction between the Cu^{II} and L^1 π orbitals.

2,2′-Bipyridyl (A^1) shows bands at 49 500, 42 200, and 35 200 cm^{-1}. The latter two high-intensity bands correspond to a $\pi \longrightarrow \pi^*$ transition. In [Cu(A^1)]$^{2+}$, the bands are observed at 49 000, 41 000, 33 200, and 32 000 cm^{-1}; similar spectra have been reported earlier for 2,2′-bipyridylcopper(II) complexes.[16] The appearance of a new band (with high intensity) and the shift in the $\pi \longrightarrow \pi^*$ transition shows that there is an interaction between the π orbitals of Cu^{II} and those of the 2,2′-bipyridyl molecule. The spectrum of the binuclear complex [Cu(L^1)Cu(A^1)][ClO$_4$]$_2$ has bands at 48 000, 43 800, 41 000, 36 000, 33 200, 32 000, and 28 000 cm^{-1}, showing all the electronic transitions possible in [Cu(L^1)] and [Cu(A^1)]$^{2+}$ without any significant change. It can thus be concluded that, although there is a super-exchange interaction in the binuclear complex, there is no π interaction between the ligands over the two Cu^{II} ions. Any interaction between the π orbitals of L^1 and A^1, through the metal ions, would have changed the positions of the near-u.v. bands in the binuclear complex.

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