CHAPTER 4

Reactions of the ternary complexes of o-hydroxy aldehydes with aromatic diamines : The binuclear complexes.

page

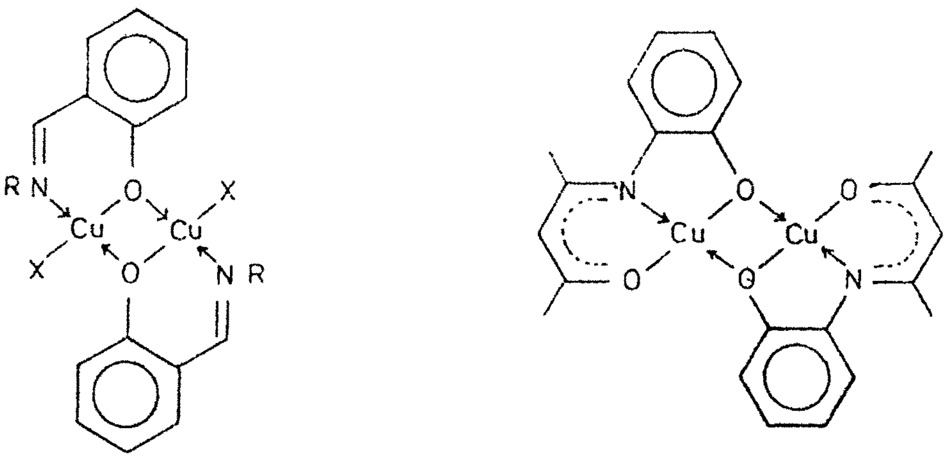
4.1 Introduction to the synthesis of binuclear complexes and the magnetic exchange.

The interest in binucleating ligands [1-10] centres around their ability to hold pairs of metal atoms or ions in close physical and electronic proximity. This allows strong magnetic interactions [11-14] between two metal centres and doubles the number of electrons that can participate in catalysis and electron transfer [15-21]. There is possible correlation between the redox properties and the strength of magnetic coupling between the metal atoms [21, 22]. Bimetallic complexes of binucleating ligands can also be used as speculative models for the metal environment in the active sites of many metalloproteins or metalloenzymes. Biomolecules involving bimetallic active sites include superoxide dismutase (Cu^{II}, Zn^{II}) [23-25], cytochrome C oxidase (Fe^{III}, Cu^{II}) [26, 27] , hemerythrin (Fe, Fe) [28-31] , hemocyanin (Cu, Cu) [32-34] , tyrosinase (Cu, Cu) [33-35] and several multicopper oxidases (Cu, Cu) [35-39]. Maximum attention has been paid to the modelling of the active sites in SOD [40-43] and in hemocyanin [44, 45] which contain two exchange coupled copper centres.

The term **binucleating ligands** was defined first by Robson as "polydentate chelating ligands capable of simultaneously binding two metal ions" [4]. Their complexes fall in two general classes [46],

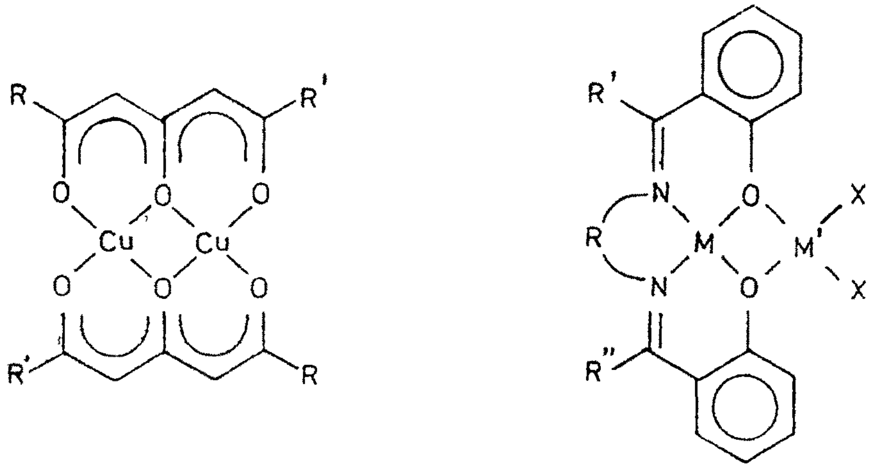
1. Compartmental ligands [47] with bridging donor sets · In these complexes the metals share at least one donor atom in species containing adjacent sites in which the central donor atom (s) provide a bridge. The ligands in this class are predominately 2, 6-disubstituted phenols, 1, 3, 5-triketones and β-ketophenols and Schiff bases derived from them. In these the central phenolic or keto-oxygen of the thiophenolic sulphur atom can act as the bridging donor atom. Complexes of the bi-, tri- and tetradentate ligands of this class can be shown as in Fig.4.1.1.

Fig. 4.1.1



a Ref [48]

b Ref [49]



c Ref [50]

d Ref [1,51-53]

Ligands derived from 2, 6-disubstituted phenols and thiophenols and 1, 3, 5-triketones can be either of the three types (Fig. 4.1.2) namely, macrocycle form (A) , "end-off" acyclic from (B) and "side off" acyclic form (C). Some of the ligands of these types which have been used for the synthesis of metal complexes or have been synthesized using metal templates are shown in Fig. 4.1.3.

2. Complexes of the ligands with isolated donor sets. In these complexes donor atoms are not shared. A wide spectrum of ligand and bridge types is available with this kind of ligands . (Fig. 4.1.4).

Magnetic Interactions :

Intramolecular magnetic exchange in binuclear complexes can take place in three different ways.

1. Direct metal - metal interaction : This involves the direct overlap of the orbitals of the two paramagnetic centres containing the unpaired electrons. Figgis and Martin [78] in 1956 first put forth the idea that the antiferromagnetic interaction in $[Cu(O_2CCH_3)_2(H_2O)]_2$ is due to the existance of a δ bond between the copper ions as shown in Fig. 4.1.5. The interaction between the d orbitals of two metal ions gives rise to the formation of one bonding and one antibonding orbital. The pairing of two unpaired electrons in the lower energy orbital gives rise to a diamagnetic (singlet) ground state for the molecule. The subnormal magnetic moments can be explained by considering thermal population of the spin triplet state.

The controversy about the exchange pathway in cupric acetate monohydrate spawned considerable work [79]. Later work by Hansen and Ballhausen [80] and by Goodgame et al [81] supported the idea that copper-copper bonding is not important in explaining the antiferromagnetism, but that spin coupling

Fig. 4.1.2

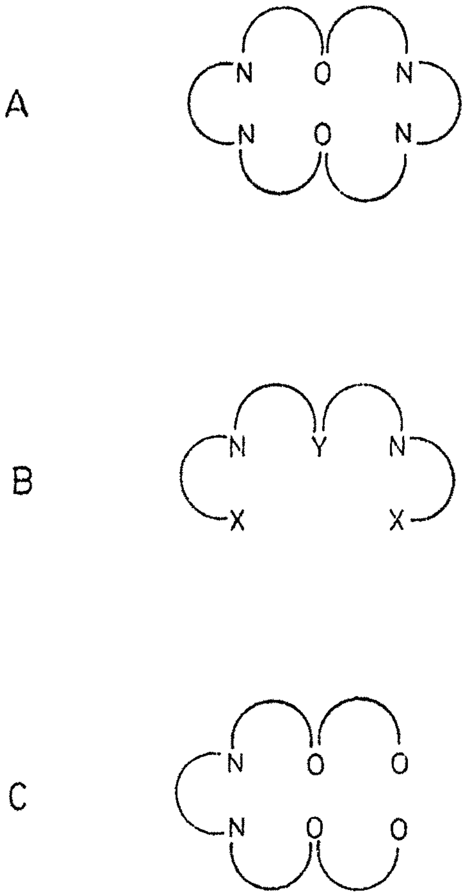
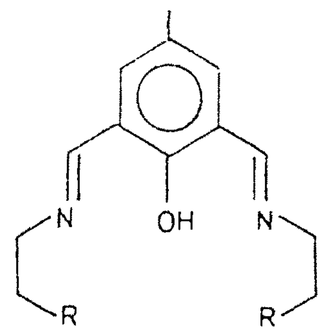
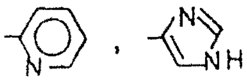
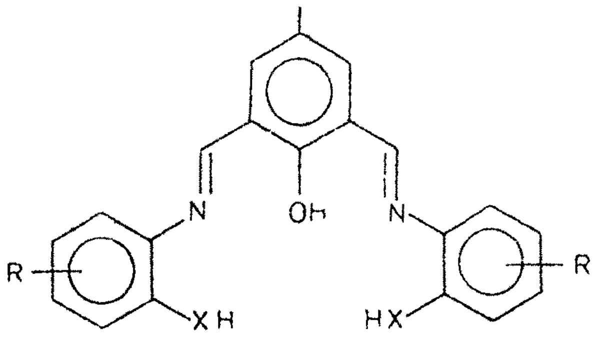


Fig. 4.1.3

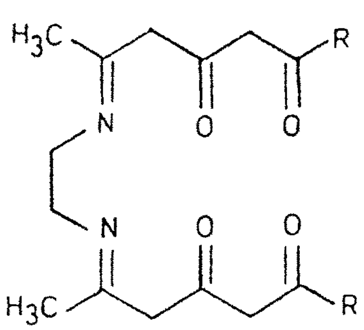


R = -NR$_2$ [Ref. 8,54,55]

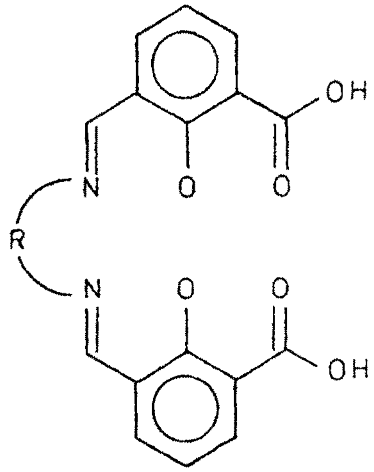
R =  [Ref 56,57]



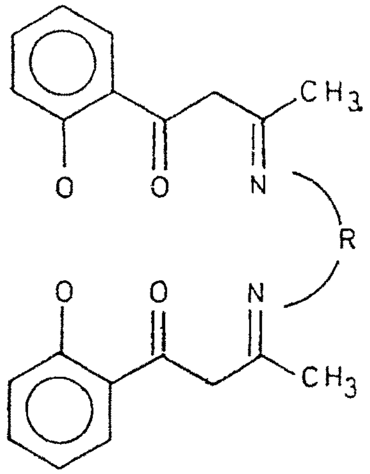
X = O,S with exogenous pyrazole, azaindole like bridges. [Ref. 5,56]



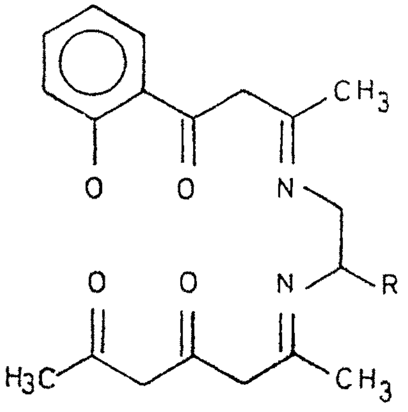
R = -CH$_3$, -C$_6$H$_4$, t-Bu [Ref. 58-60]



R = various bridging chains [Ref. 61,62]



[Ref. 63,64]



[Ref. 65]

Fig. 4.1.4a . Isolated donor sets within extandable macrocycles.

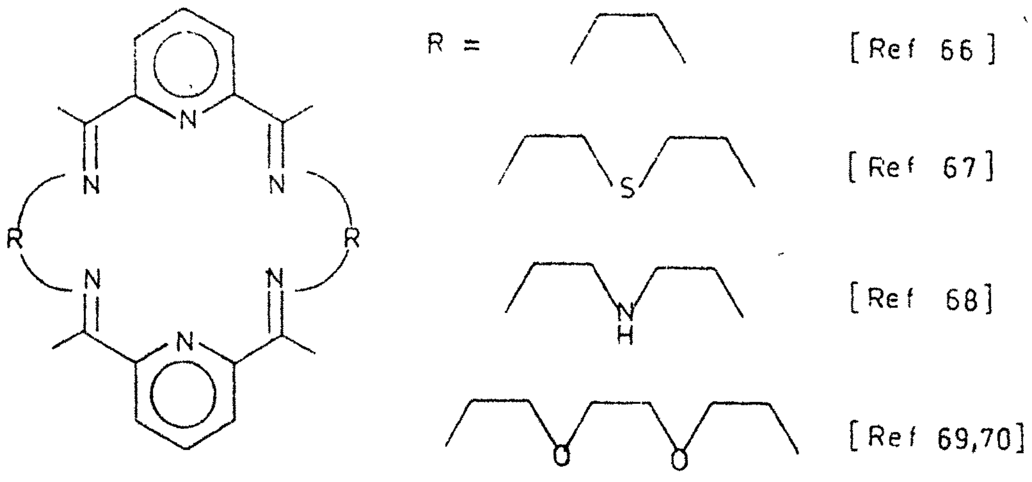


Fig. 4.1.4b : Isolated donor sets within extendable macrocycles [Ref. 71].

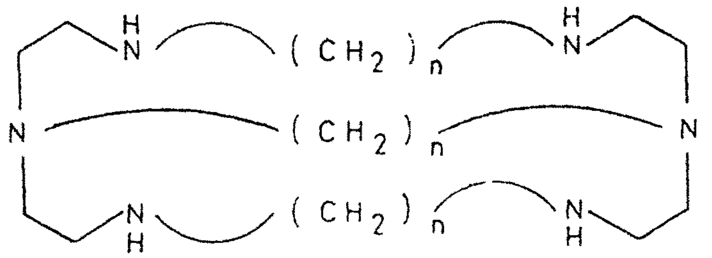
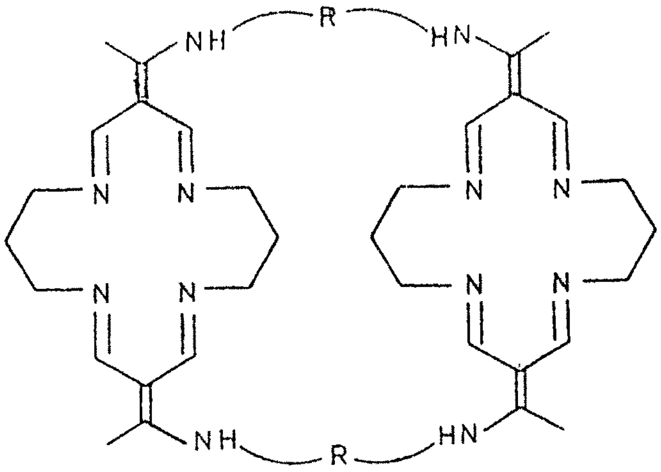


Fig. 4.1.4c Macrotricycles [Ref . 72].



R = m-xylyl

Fig. 4.1.4d Bis-macrocycles [Ref . 73].

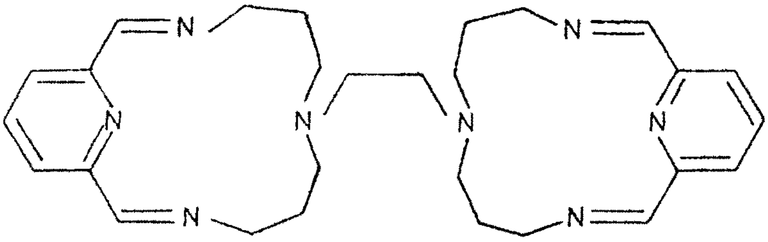


Fig. 4.1.4e . " Wish-bone " polypode [Ref . 74].

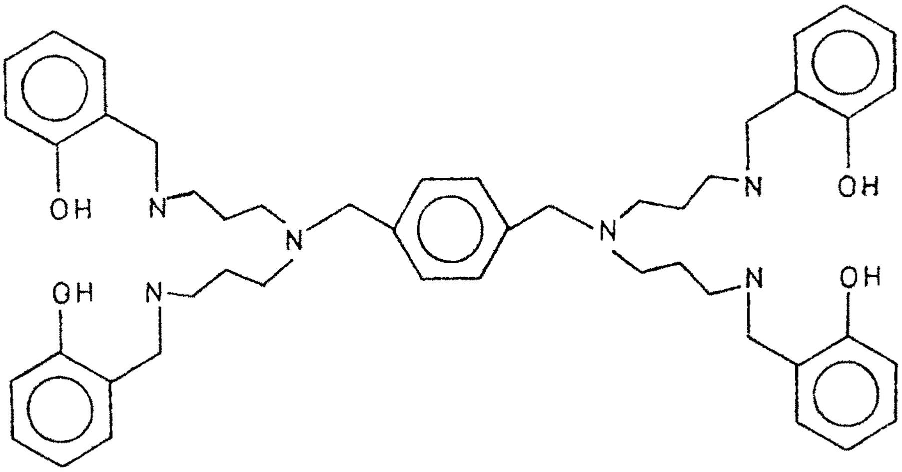
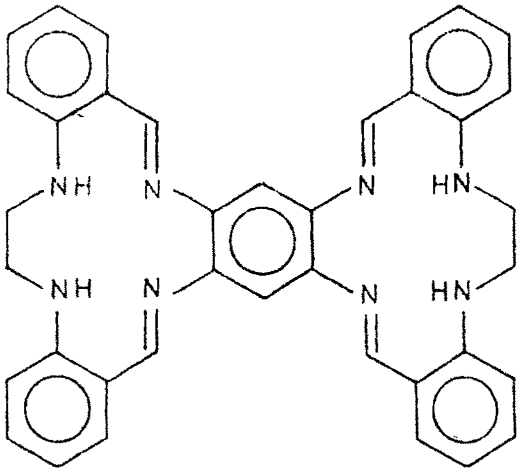
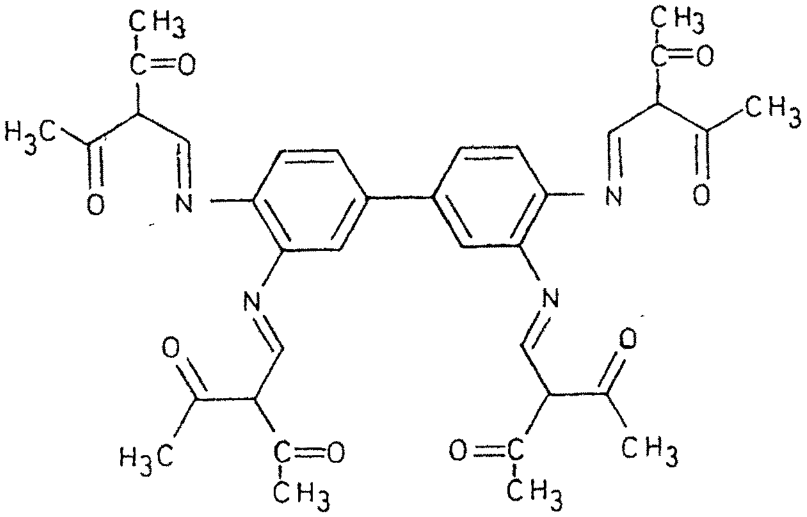


Fig. 4.1.4f Isolated donor sets separated by aromatic or other bridging functions.

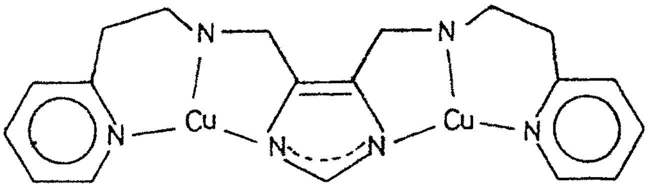
(1) · Linked-closed compartments [Ref . 75]



(2) Linked-open compartments [Ref . 76].



(3) . Linked-open chains [Ref . 77].



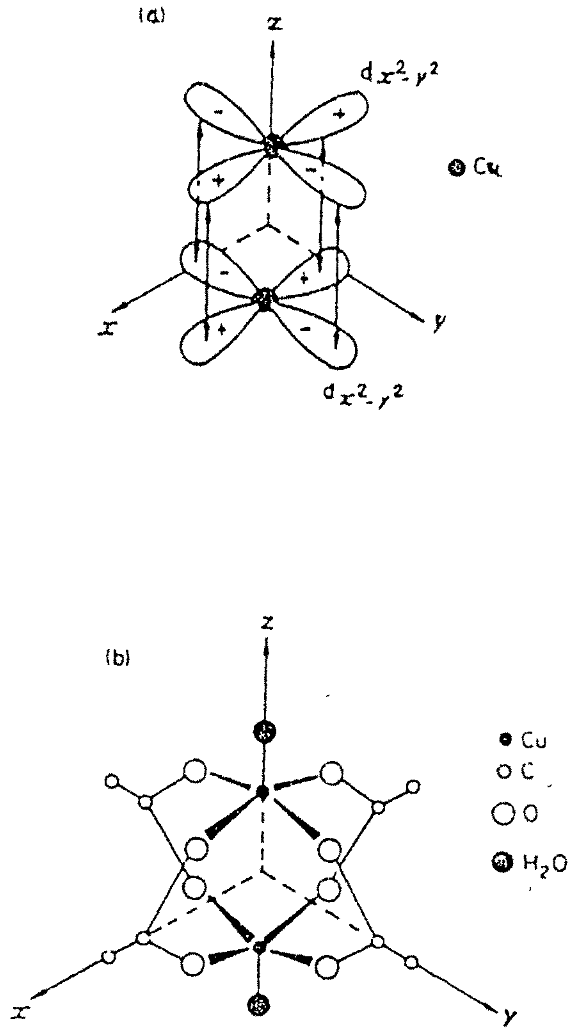


Fig. 4.1.5 (a) An illustration of the δ-bonding in and (b) the structure of copper (II) acetate monohydrate. (after Figgis and Martin [78]).

depends on a super exchange interaction propagated by carboxylate bridges. At this point the thinking had come full circle back to the original Bleaney and Bowers' view of weakly coupled chromophores [82]. Although, the possibility of considerable M-M interaction in copper acetate was turned down, the work of Cotton et al [83, 84] support the existance of a quadruple M-M bond in chromium acetate and molybdenum acetates leading, essentially, to a diamagnetic ground state. The single Rh-Rh bond in rhodium acetate also leads to a diamagnetic material.

2. Super exchange interaction :

The idea of "super-exchange interaction" [85, 86] was originally put forth by Anderson [85]. This involves an exchange of the spins over two paramagnetic centres mediated by the orbitals present over an intermediate anion. In this mechanism, in addition to the metal d orbitals, the filled orbitals of the intervening anion also take part. This can be explained with the help of Fig.4.1.6.

If, for example, a binuclear complex of a transition metal ion with a single unpaired electron involving O bridge is considered, in a linear M-O-M arrangement, the interaction may occur in two ways. There can be σ bonding or there can be π bonding as shown in Fig. 4.1.6 a and 4.1.6 b, respectively. If one metal ion has positive spin, it imposes negative spin of the electron in the oxygen orbital which is interacting with the metal orbital. The second electron in this bridging atom orbital should have positive spin. Overlap between this orbital and the orbital of the second metal ion with unpaired electron results in the antiparallel alignment of the electrons with two metal ions. This results in antiferromagnetism.

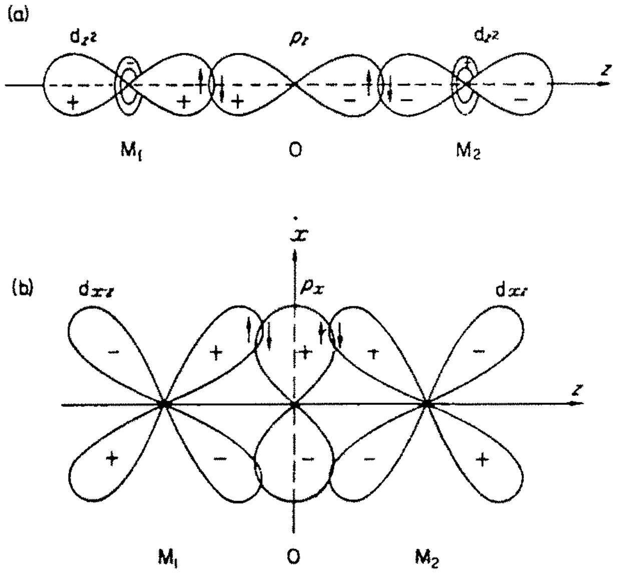
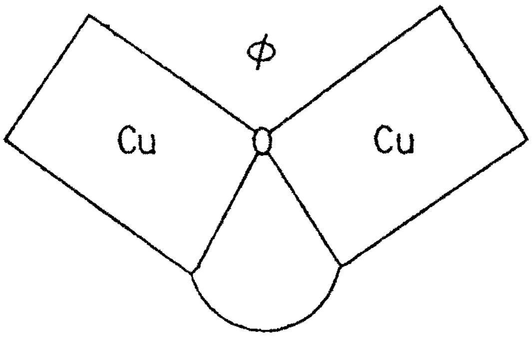


Fig. 4.1.6 : Superexchange in a linear M-O-M system. An example of superexchange via (a) σ -bonding , and (b) π -bonding.

Although, main interest lies in the O bridged binuclear copper (II) complexes, various complexes with halide or S bridges have been studied [87]. It has been pointed out that S or Br bridging in copper dimers should lead to stronger antiferromagnetism than O or Cl bridging, respectively [88]. The Cu-O-Cu bond angle (ϕ) dependence of the exchange interaction in various di- μ -hydroxo bridged copper dimers are very well evidenced [89-94]. A linear relationship was found to exist between 2J and ϕ [95]. In binuclear complexes with single hydroxy bridges, Thompson and coworkers could 'tune' Cu-O-Cu bridge angle by changing the size of the other bridging ligand [96-98]. They also found an approximately linear relationship between -2J and the Cu-O-Cu bridge angle for a related series of complexes with the same basic binuclear centre. Complementary and counter complementary effects of the orbitals in superexchange through heterobridges in binuclear copper (II) complexes have been described [99-101].

Studies on O bridged binuclear copper (II) complexes are mainly directed towards mimicing the active site in hemocyanin [44,45]. This is a coupled O-bridged (phenolato or alcoholato) copper (II) complex containing one or two atom exogenous bridging groups. The exogenous superexchange pathway plays a minimal role in these kinds of systems, the endogenous pathway being the most important and extremely dependent on both the geometry of the bridging O and on the relative dispositions of the Cu-ligand planes [1-2, 103], (Fig. 4.1 7). The angle between the two copper planes gives a measure of the extent of distortion and is found to exert a strong influence on the magnetic interaction [44, 104, 105]. A trigonal planar sp^2 geometry of the bridging atom, together with coplanarity of the adjacent Cu-ligand planes, leads to overall strong antiferromagnetic coupling. This is due to good overlap between the $d_{x^2-y^2}$ magnetic orbitals on Cu and the sp^2 orbitals on the bridging atom. As the geometry of the bridging atom approaches pyramidal (sp^3), usually with a dihedral angle concomitantly developing

Fig. 4.1.7 Cu-ligand planes in binuclear copper complex and angle ϕ .



between the adjacent Cu-ligand planes, the J value approaches zero or becomes overall positive. Any deviation of the bridging atom from the Cu-ligand best-plane will also lead to poor overlap with the Cu $d_{x^2-y^2}$ magnetic orbital, thus reducing the antiferromagnetic contribution.

Another interesting observation was made by Hendrickson and coworkers [106] in case of the transition metal complexes of the binucleating ligand formed by the condensation of 2, 6-diformyl-4-methyl phenol and 1, 3-diamino propane. The net antiferromagnetic interaction decreases monotonically in the series Cu (II) (J =-294 cm^{-1}) , Ni (II) (J = -27 cm^{-1}) , Co (II) (J =-9.3 cm^{-1}) and Fe (II) (J =-4.2 cm^{-1}) , and finally becomes a net ferromagnetic exchange interaction with the Mn (II) complex where J = + 0.2 cm^{-1}. They attributed the variation in J value across the series to (1) the changing number of unpaired electrons and associated exchange pathways and (2) the increasing M - ligand plane distance in going from Cu (II) to Mn (II).

3. Magnetic exchange interactions propagated by multiatom bridges :

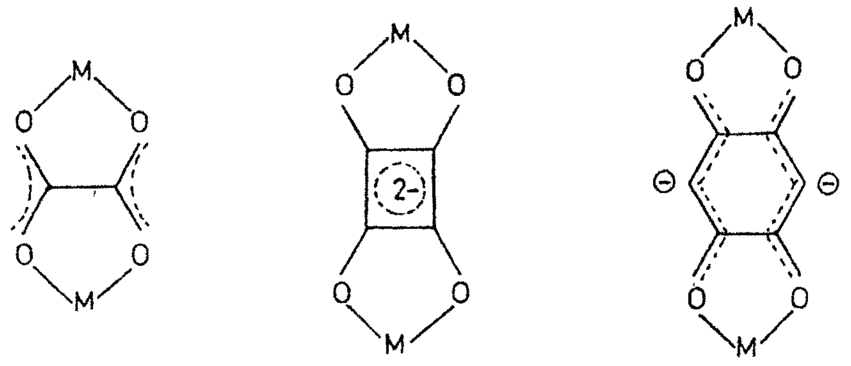
Apart from the two kinds of interactions mentioned above, magnetic exchange interactions have been observed to be taking place between metal centres bridged by more than one atoms. There can be at least four such instances [79] : (1) Polynuclear transition metal complexes with unsaturated bridges ; (2) Polynuclear transition metal complexes with saturated bridges ; (3) Transition metal complexes with a paramagnetic ligand and (4) Organic biradicals that are bridged by trnasition metal moieties.

Copper acetate is the very first member of a series of compounds synthesized with multiatom bridges. Studies on binuclear complexes with di - or tri-atomic bridges have been reviewed by Hendrickson [107].The basic mechanism of super-exchange i.e. the conveyance of the unpaired spin from one metal to the other through the orbitals of the bridging atoms can be considered to be applicable for the case of multiatom bridges also. If this would be the only criterian for the magnetic exchange, the extent of interaction would be dependent only on the distance between two metal centres or the number of the bridging atoms. In a series of binuclear copper (II) complexes bridged by oxalate [108-110], squarate [110] and the dianion of 2, 5-dihydroxybenzoquinones [111], as shown in Fig. 4.1.8, the largest exchange interaction is found for the μ-oxalate complex as expected on the basis of the Cu-Cu separation, but the next largest interaction is found for the dihydroxy benzoquinone complex and not the squarate complex [110, 111].

In di- μ -aqua-bis $\{\mu$- $\{$N,N'-bis (2-hydroxy ethyl) dithio oxamidato (2-) -N, O, S : N', O', S' $\}$ - bis $\{$ aqua copper (II) sulphato copper (II) $\}$ i.e. $[\,Cu\, S_2\, C_2\, (N\, (CH_2)_2\, OH_2)\, (H_2O)_2\,]\, SO_4$ (Fig. 4.1.9) the bridging of the dithiooxamide ligand results in very strong antiferromagnetic coupling ($J = 523\ cm^{-1}$) , despite the Cu . . . . Cu distance of 5.65 A^{o} [112]. By constrast, the planar bridging role of the 2,2'-bibenzimidazolate dianion in μ-2,2'-bibenzimidazolate bis (1, 1, 4, 7, 7 - pentamethyl diethylene triamine) dicopper (II) tetraphenylborate ($[\,Cu_2\, (Me_5dien)_2\, (biim)\,]\,[\,BPh_4\,]_2$) (Fig. 4.1.10) results in zero exchange coupling ($J \approx 0.5\ cm^{-1}$) between the copper (II) atoms sepated by 5.49 A^{o} [113].

Above examples indicate that the length of the bridge or the number of bridging atoms is not the only factor that decides the extent of exchange interaction. Studies have been carried out to establish various criteria for judging the viability of a particular single - atom or polyatomic bridging unit to support a magnetic exchange interaction between two paramagnetic metal ions [114].

Fig. 4.1.8



Oxalate squarate 2,5-dihydroxybenzoquinone

Fig. 4.1.9 $[CuS_2C_2(N(CH_2)_2OH_2)(H_2O)_2]SO_4$

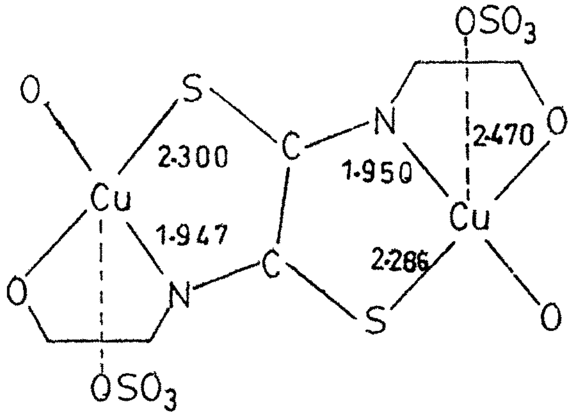
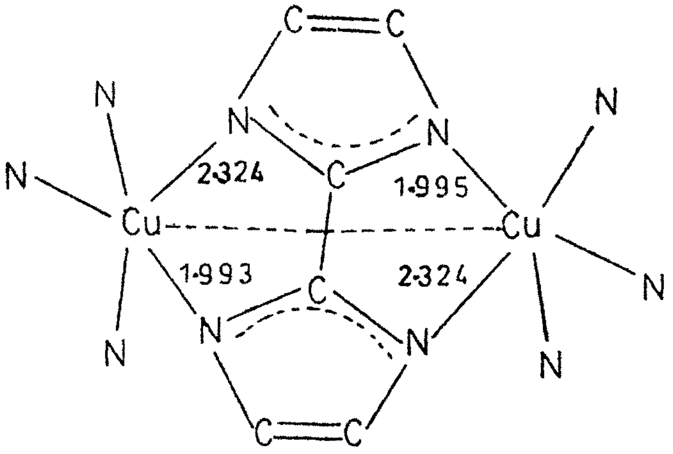


Fig. 4.1.10 $[Cu_2(Me_5dien)_2(biim)][BPh_4]_2$



Much of this work has been concerned with exchange interactions in binuclear or dimeric copper (II) complexes. Binuclear complexes with naphthazarin or quinizarin bridges have been studied [115]. It has been shown that penta - or hexa - coordinated complexes of these ligands do not undergo any magnetic exchange interaction because of the nonavailability of ligand orbitals with proper symmetry. To investigate further the effect of the geometry around the metal ion on the extent of spin exchange the complexes of the type [M_2 $(tren)_2$ DA $]^{4+}$ where tren = tris (aminoethyl) amine and DA is aromatic diamine have been synthesized and studied [116]. Investigations of some binuclear complexes with these diamines or their Schiff bases forming two bridges between the two paramagnetic centres have also been reported [117-120]. Studies with other compounds involving extensive organic systems as bridging groups include the complexes with the ligands obtained by the reaction of acetylacetone with 1, 2, 4, 5-tetra amino benzene or 3, 3', 4, 4' - tetra amino biphenyl [76]. Also a series of binuclear Schiff base complexes based on the ligands containing a bridging xylylene moiety has been reported [121, 122].

The observations [110, 111, 116, 123-126] have emphasized the importance of the symmetry and energy of the transition metal ground state relative to the highest occupied molecular orbitals of the bridging moiety in propagating an exchange interaction across a polyatomic bridging unit , i.e. the magnitude of interaction basically depends on two factors ·

1) The nature and the magnitude of the orbital overlap between the metal d orbitals containing the unpaired electrons and the ligand orbitals i.e. geometry around the metal centres.

2) The energy difference between the d orbitals containing the unpaired electrons and the exchange propagating orbitals of the bridging ligand.

Systematic studies of the exchange coupling in dinuclear copper (II) complexes with oxalato, oxamidato and oxamato ligands have been carried out [104, 106, 127–133]. The studies reveal that the antiferromagnetic coupling increases dramatically in the order oxalato < oxamato < oxamidato [132, 133]. An important achievement, by Kahn et al, is the synthesis of polymetallic systems with expected magnetic properties [130, 131, 134]. They have shown that the singlet-triplet energy gap J arising from the interaction between two copper (II) ions through the oxalato or oxamido bridge can be varied in a predictable manner by systematic variation in the geometry around the two metal centres. Recently [135], intramolecular antiferromagnetic exchange has been observed in binuclear copper (II) complexes bridged through 2, 5-dihydroxy 3, 6-di-X- substituted - 1, 4-benzoquinone where X = H, Cl, Br, I, NO_2 . The singlet-triplet energy gap ranges from -17.4 cm^{-1} for X = $-NO_2$ to -25.9 cm^{-1} for X = I with Cu . . . . Cu separation of 7.6 A^o. For the halo derivatives the magnitude of the interaction varies as I > Br > Cl. These observations further illustrate the remarkable dependance of spin exchange on factors other than the M . . . . M separation.

Scope of the present work :

In the present study reactions of the ternary complexes [Cu A L]. ClO_4 where A = bipy, phen or dpa and L = sal or A = dpa and L = naph, have been carried out with aromatic diamines. This would result in the formation of binuclear Schiff base complexes involving bridges with extended π systems. The compounds have been characterized by analysis and various spectral studies. Their magnetic properties have been studied.

The criterian for magnetic exchange , so far understood to be the availability of exchange propagating orbitals with suitable symmetry and energy, emphasizes the importance of unsaturated bridges.

The compounds considered in the present work are expected to have following three distinct features.

1. Presence of only one bridging unit, expected to remove the possibility of counter complementary interactions through the two bridges and hence extra complications in the exchange mechanism.
2. Complete conjugation of π system in bridging moiety allowing magnetic exchange through π orbitals also.
3. Variation in geometry around the metal ions is possible by changing the other bidentate ligand coordinated with the metal ion. Change in the energy of the M-L bonds can also be possible just by introducing substituents on the two ligands without affecting the bridging moiety.

4.2 Experimental :

Reactions of diamines with ternary complexes.

Chemicals : 2,2'-Bipyridine (bipy), 1, 10-phenanthroline (phen), (both E.MERCK), 1, 2-phenylene diamine (opd) (BDH), 1, 3-phenylene diamine (mpd) (Fluka) and 1, 4-phenylene diamine (ppd) were all A.R. grade and were used without further purification. All other chemicals were as described earlier.

Preparation of the ternary complexes :

The ternary complexes [Cu. dpa. sal]. ClO_4 and [Cu dpa naph]. ClO_4 were prepared as described in the previous chapter (Ch. 3). The complexes [Cu. bipy. sal]. ClO_4 and [Cu. phen. sal]. ClO_4 were prepared by a similar method, reported earlier from our laboratory [136].

Preparation of the binuclear complexes :

0.2 mmol of [Cu A L]. ClO_4 was treated with 0.1 mmol of the diamine in ethanolic solution and refluxed for 1 to 3 hrs. The resulting solid was filtered washed with ethanol and ether and air dried.

The methods and instrumentation used for the analyses of metal, C. H and N, and for conductivity, magnetic and spectral measurements are as detailed earlier in Ch. 3. Electronic spectra were recorded with methanolic solutions of the complexes and the IR spectra were recorded in KBr phase. The results of these studies are presented in Table 4.2.1 to 4.2.3.

ESR spectra of two representative compounds **1** and **2** at $5^{O}K$ have been obtained from TIFR, Bombay and room temperature ESR of compound **10** has been obtained from RSIC, IIT, Bombay. These are presented in Figs. 4.2.1 to 4.2.3 Variable temperature magnetic measurements on compounds **1** and **7** were done in TIFR, Bombay. (Fig. 4.2.4 and 4.2.5)

Table 4.2.1 Elemental analyses and magnetic moment values of binuclear complexes.

	Complex	% Cu	% N	% C	% H	μ_{eff}
1.	$[Cu_2(dpa)_2SB^1](ClO_4)_2$	12.87	11.69	49.36	3.38	1.47
		(12.94)	(11.40)	(48.87)	(3.26)	
2.	$[Cu_2(dpa)_2SB^2](ClO_4)_2$	13.58	11.19	48.77	3.25	1.72
		(12.94)	(11.40)	(48.87)	(3.26)	
3.	$[Cu_2(dpa)_2SB^3](ClO_4)_2$	12.77	11.66	48.09	3.53	1.69
		(12.94)	(11.40)	(48.87)	(3.26)	
4.	$[Cu_2(dpa)_2SB^4](ClO_4)_2$	12.18	10.27	53.60	3.36	1.59
		(11.74)	(10.35)	(53.21)	(3.33)	
5.	$[Cu_2(dpa)_2SB^5](ClO_4)_2$	12.26	9.99	53.68	3.86	1.69
		(11.74)	(10.35)	(53.21)	(3.33)	
6.	$[Cu_2(dpa)_2SB^6](ClO_4)_2$	11.65	9.86	52.70	3.62	1.61
		(11.74)	(10.35)	(53.21)	(3.33)	
7.	$[Cu_2(bipy)_2SB^1](ClO_4)_2$	13.21	9.02	49.94	3.51	1.49
		(13.35)	(8.82)	(50.41)	(3.15)	
8.	$[Cu_2(bipy)_2SB^2](ClO_4)_2$	13.04	8.41	48.10	3.20	1.52
		(13.35)	(8.82)	(50.41)	(3.15)	
9.	$[Cu_2(bipy)_2SB^3](ClO_4)_2$	13.23	9.17	49.89	3.61	1.41
		(13.35)	(8.82)	(50.41)	(3.15)	
10.	$[Cu_2(phen)_2SB^1](ClO_4)_2$	12.3	8.71	51.47	3.46	1.43
		(12.71)	(8.40)	(52.79)	(3.00)	
11.	$[Cu_2(phen)_2SB^2](ClO_4)_2$	12.8	8.39	50.46	3.13	1.65
		(12.71)	(8.40)	(52.79)	(3.00)	
12.	$[Cu_2(phen)_2SB^3](ClO_4)_2$	12.4	8.80	50.94	2.81	1.52
		(12.71)	(8.40)	(52.79)	(3.00)	

The values in parantheses are calculated theoretically from the formulae.

Table 4.2.2 : Electronic spectra of the binuclear complexes.

	Compound	$\bar{\nu}$ (1000 cm^{-1}). in methanol	$\bar{\nu}$ (1000 cm^{-1}). d.r.s.
1.	$[Cu_2(dpa)_2SB^1](ClO_4)_2$	45.0, 40.4, 36.88, 33.2, 31.68, 25.20, 19.0, 15.0	24.7, 14.93
2.	$[Cu_2(dpa)_2SB^2](ClO_4)_2$	45.2, 40.0, 37.0, 32.8, 25.3, 16.0	25.6, 19.6, 10.1
3.	$[Cu_2(dpa)_2SB^3](ClO_4)_2$	39.28, 37.44, 32.08, 29.0, 26.0, 24.0, 18.0	26.3, 23.1, 18.5
4.	$[Cu_2(dpa)_2SB^4](ClO_4)_2$	44.08, 40.1, 39.0, 33.2, 31.5, 24.32, 23.2, 18.6, 15.5	24.39, 18.0, 14.93
5.	$[Cu_2(dpa)_2SB^5](ClO_4)_2$	44.0, 39.84, 33.28, 31.6, 24.4, 16.0	24.6, 15.38
6.	$[Cu_2(dpa)_2SB^6](ClO_4)_2$	43.84, 40.25, 39.0, 33.2, 31.44, 25.6, 24.7, 21.5, 15.5	22.5, 14.5
7.	$[Cu_2(bipy)_2SB^1](ClO_4)_2$	46.0, 41.96, 38.6, 36.5 33.48, 32.36, 25.44, 19.8	20.2
8.	$[Cu_2(bipy)_2SB^2](ClO_4)_2$	46.0, 42.0, 38.6, 36.44, 33.4, 32.32, 25.56, 16.0	17.4

Table 4.2.2. Contd.

	Compound	$\bar{\nu}$ (1000 cm^{-1}). in methanol	$\bar{\nu}$ (1000 cm^{-1}). d.r.s
9.	$[Cu_2(bipy)_2\ SB^3](ClO_4)_2$	45.0, 42.0, 38.0, 35.0, 33.8, 32.25, 29.16, 24.04, 16.5	16.39
10.	$[Cu_2(phen)_2\ SB^1](ClO_4)_2$	43.0, 36.8, 34.16, 29.0, 25.36, 19.0	16.08
11.	$[Cu_2(phen)_2\ SB^2](ClO_4)_2$	43.0, 36.72, 34.12, 29.0, 25.0, 17.9	17.92
12.	$[Cu_2(phen)_2\ SB^3](ClO_4)_2$	43.0, 37.0, 34.08 29.16, 24.56, 17.0	14.10

Table 4.2.3 : Infrared absorption frequencies of the binuclear complexes.

	Complex	IR frequencies $\bar{\nu}$ in cm $^{-1}$
1.	$[Cu_2 (dpa)_2 SB^1] (ClO_4)_2$	3400 (m), 3200 (w), 3050 (w), 1640 (s), 1605 (s), 1590 (s), 1530 (s), 1480 (s), 1440 (s), 1380 (w), 1320 (m) 1240 (m), 1185 (w), 1140 (m), 1090 (s), 1020 (m), 930 (w), 890 (w), 840 (m) 770 (s), 660 (w).
2.	$[Cu_2 (dpa)_2 SB^2] (ClO_4)_2$	3330 (m), 3200 (w), 3020 (w), 1640 (s), 1610 (s), 1585 (s), 1530 (s), 1480 (s), 1440 (s), 1380 (m), 1360 (w), 1320 (m), 1280 (w), 1240 (m-s), 1200 (w), 1165 (m-s), 1150 (s), 1090 (s), 1020 (m), 970 (w), 930 (w), 910 (w), 870 (w), 850 (w), 815 (w), 770 (s), 700 (m), 665 (w).
3.	$[Cu_2 (dpa)_2 SB^3] (ClO_4)_2$	3320 (m), 3200 (w), 3020 (w), 1640 (s), 1600 (s), 1590 (s), 1530 (s), 1480 (s), 1440 (m), 1420 (m), 1380 (m), 1320 (w), 1270 (w), 1235 (m), 1185 (w), 1160 (m), 1120 (s), 1070 (s), 1015 (m), 960 (w), 930 (w), 905 (w), 870 (w), 840 (w), 770 (s), 660 (w).

4.	$[Cu_2(dpa)_2\ SB^4]\ (ClO_4)_2$	3300(m), 1630 (s), 1620 (s), 1600 (s), 1580 (s), 1540 (s), 1500 (s), 1475 (s), 1430 (m), 1385 (m), 1370 (m), 1310 (w), 1240 (m), 1190 (s), 1165 (s-m), 1100 (s), 1060 (s), 990 (m), 930 (w), 900 (w), 835 (s), 775 (s), 750 (m), 660 (w).
5.	$[Cu_2(dpa)_2\ SB^5]\ (ClO_4)_2$	3300 (w), 3000 (w), 1650 (m), 1615 (s), 1580 (s), 1540 (s), 1600 (s), 1485 (s), 1460 (m), 1430 (m), 1400 (m), 1370 (m), 1340 (w), 1310 (w), 1270 (w), 1240 (m), 1190 (m), 1160 (m), 1140 (m), 1120 (s), 1080 (s), 1020 (m), 980 (w), 910 (w), 860 (w), 840 (m), 765 (s), 750 (m), 700 (w), 665 (w).
6.	$[Cu_2(dpa)_2\ SB^6]\ (ClO_4)_2$	3300 (w), 3000 (w), 1640 (m), 1615 (s), 1600 (s), 1580 (s), 1540 (s), 1480 (s), 1460 (s), 1440 (s-m), 1400 (s-m), 1370 (s), 1310 (w), 1280 (w), 1235 (w), 1190 (s), 1165 (m), 1140 (w), 1100 (s), 1020 (w), 980 (w), 910 (w), 855 (w), 830 (s), 770 (s), 745 (s), 650 (w).
7.	$[Cu_2(bipy)_2\ SB^1](ClO_4)_2$	3350 (m), 3050 (w), 1610 (s), 1575 (m), 1530 (s), 1500 (s), 1480 (m-s), 1470 (m-s), 1450 (s), 1435 (s), 1410 (s), 1315 (s), 1285 (w), 1260 (m), 1220 (w), 1190 (s), 1150 (s), 1100 (s), 1070 (s), 1035 (s), 930 (w), 900 (w), 860 (w), 840 (w), 770 (s), 730 (m), 665 (m).

8.	$[Cu_2(bipy)_2\ SB^2](ClO_4)_2$	3350 (w), 3050 (w), 1610 (s), 1580 (m), 1530 (s), 1500 (w), 1480 (m), 1470 (m), 1450 (s), 1435 (s), 1410 (s), 1315 (s), 1260 (m), 1215 (w), 1190 (s-m), 1150 (s), 1100 (s), 1070 (s), 1035 (m), 935 (w), 900 (m), 860 (m), 770 (s), 730 (m), 665 (m).
9.	$[Cu_2(bipy)_2\ SB^3](ClO_4)_2$	3400 (m), 3050 (w), 1605 (s), 1580 (s-m), 1560 (w), 1525 (m-s), 1480 (s), 1465 (s), 1450 (s), 1380 (m), 1315 (s), 1260 (s), 1190 (m), 1140 (m), 1090 (s), 980 (w), 930 (w), 860 (m), 800 (w), 770 (s), 730 (s), 665 (m).
10.	$[Cu_2(phen)_2\ SB^1](ClO_4)_2$	3350 (m), 3050 (w), 1610 (s), 1520 (s), 1460 (m), 1430 (s), 1405 (m), 1350 (w), 1320 (m), 1280 (w), 1220 (w), 1190 (m), 1150 (s), 1100 (s), 1065 (s), 930 (w), 900 (w), 875 (w), 850 (s-m), 765 (m), 720 (s), 665 (w), 630 (w), 620 (m), 600 (m).
11.	$[Cu_2(phen)_2\ SB^2](ClO_4)_2$	3350 (w),3030 (w), 1600 (s), 1520 (s), 1490 (w), 1450 (s), 1560 (s), 1430 (s), 1400 (m), 1340 (w), 1320 (m), 1250 (m), 1225 (w), 1140 (s), 1090 (s), 900 (w), 870 (m), 845 (s), 760 (m), 715 (s), 660 (w), 620 (m), 600 (m), 580 (w), 520 (w), 420 (w), 300 (w).

12	$[\mathrm{Cu_2(phen)_2SB^3}](\mathrm{ClO_4})_2$	3400 (w), 3050 (w), 1605 (s), 1580 (s), 1520 (s), 1480 (m), 1460 (s), 1445 (m), 1430 (s), 1400 (m), 1385 (m), 1345 (m), 1330 (m), 1315 (m), 1260 (m), 1225 (w), 1190 (m), 1150 (s), 1100 (s), 1050 (s), 980 (w), 930 (w), 900 (w), 870 (m), 845 (s), 805 (w), 760 (m), 750 (m), 715 (s), 660 (m), 650 (w), 620 (s), 600 (s), 570 (w), 545 (w), 520 (m), 495 (m), 430 (m), 390 (w), 360 (w), 305 (w-m).

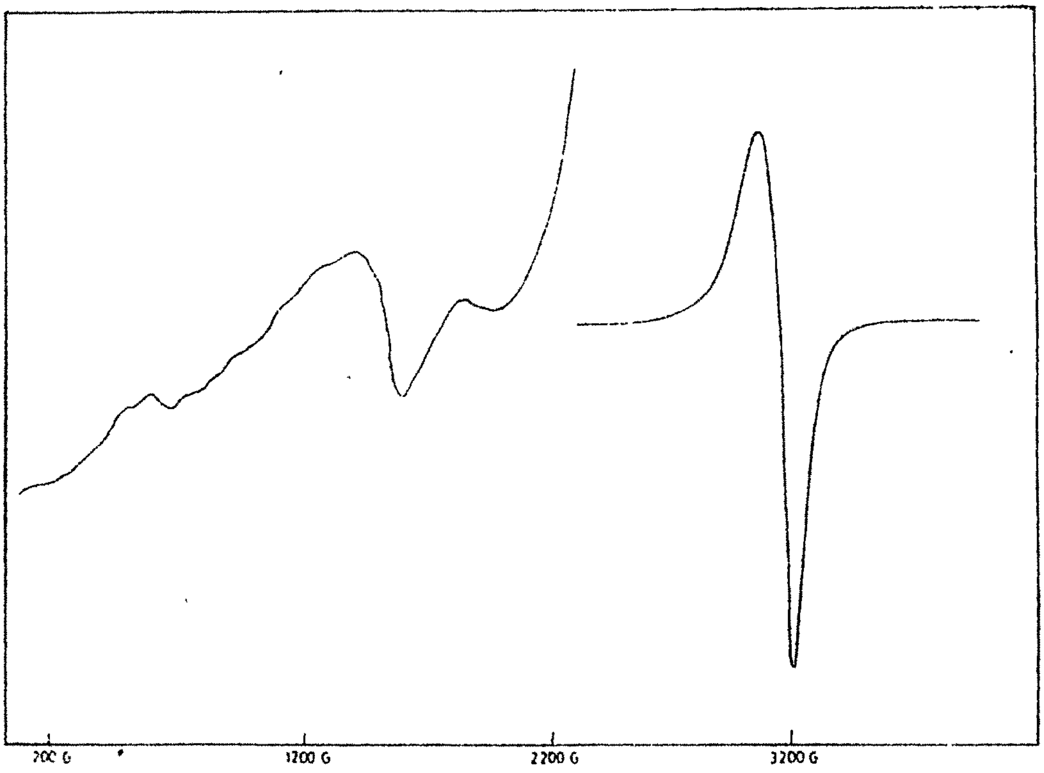


Fig. 4.2.1 : ESR spectrum of $[Cu_2(dpa)_2SB^1] \cdot (ClO_4)_2$ at 5°K

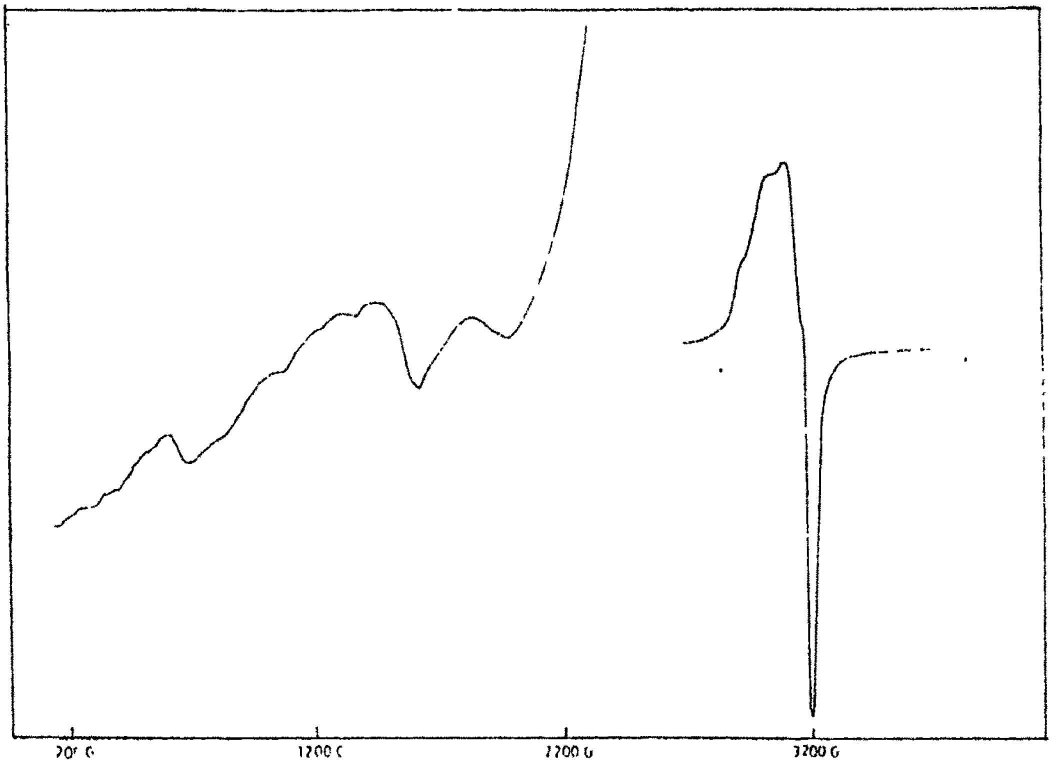


Fig. 4.2.2. : ESR spectrum of [Cu_2 $(dpa)_2$ SB^2]. (ClO_4) $_2$ at 5^oK

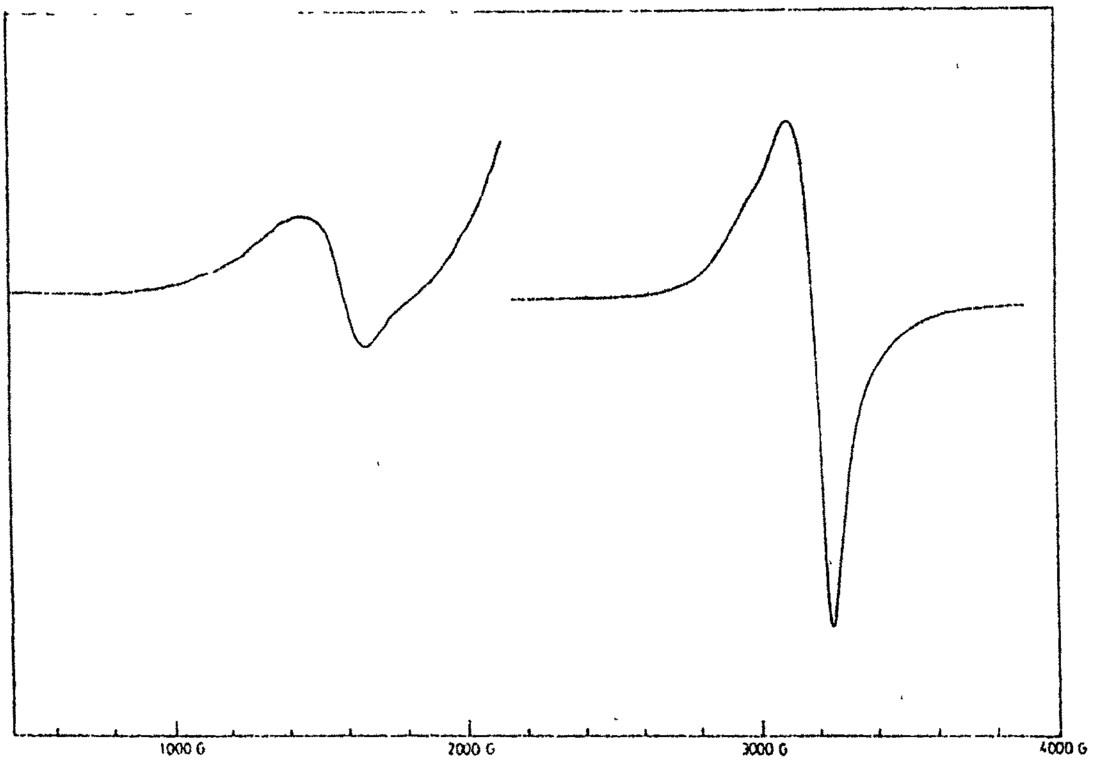


Fig. 4.2.3. · ESR spectrum of [Cu_2 $(phen)_2$ SB^1] . $(ClO_4)_2$

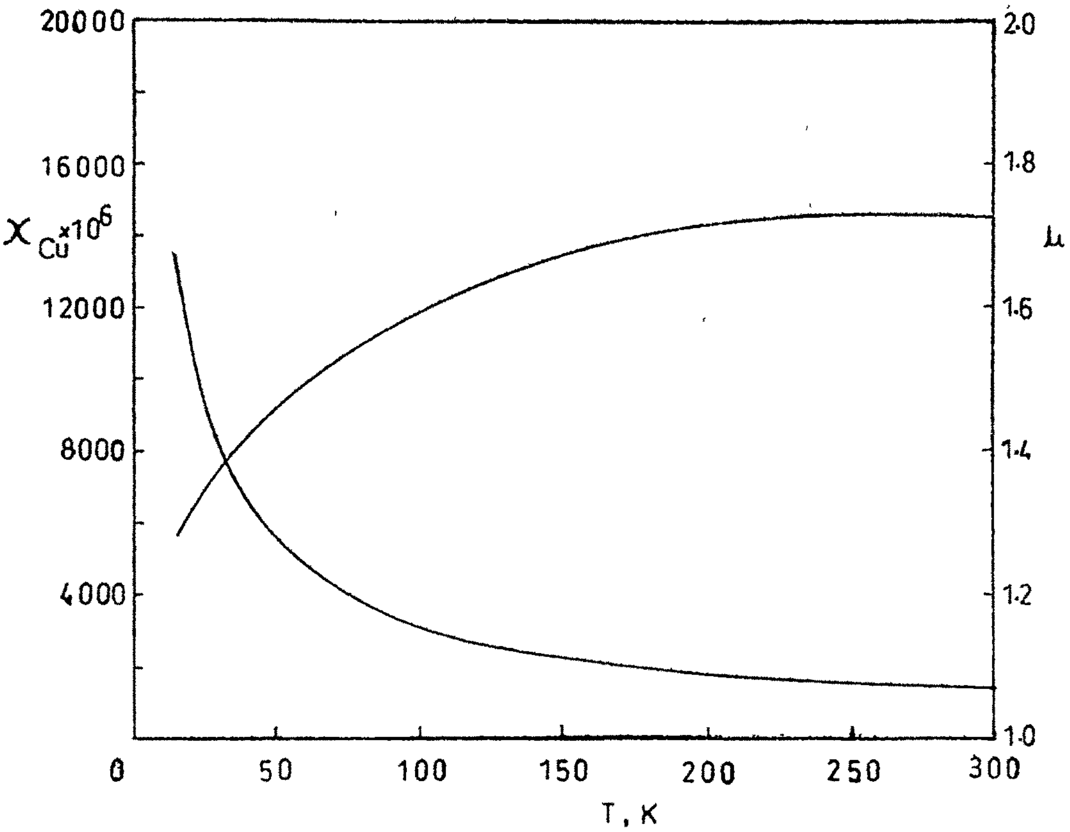


Fig. 4.2.4 : Temperature dependance of χ_{Cu} and μ in compound 1

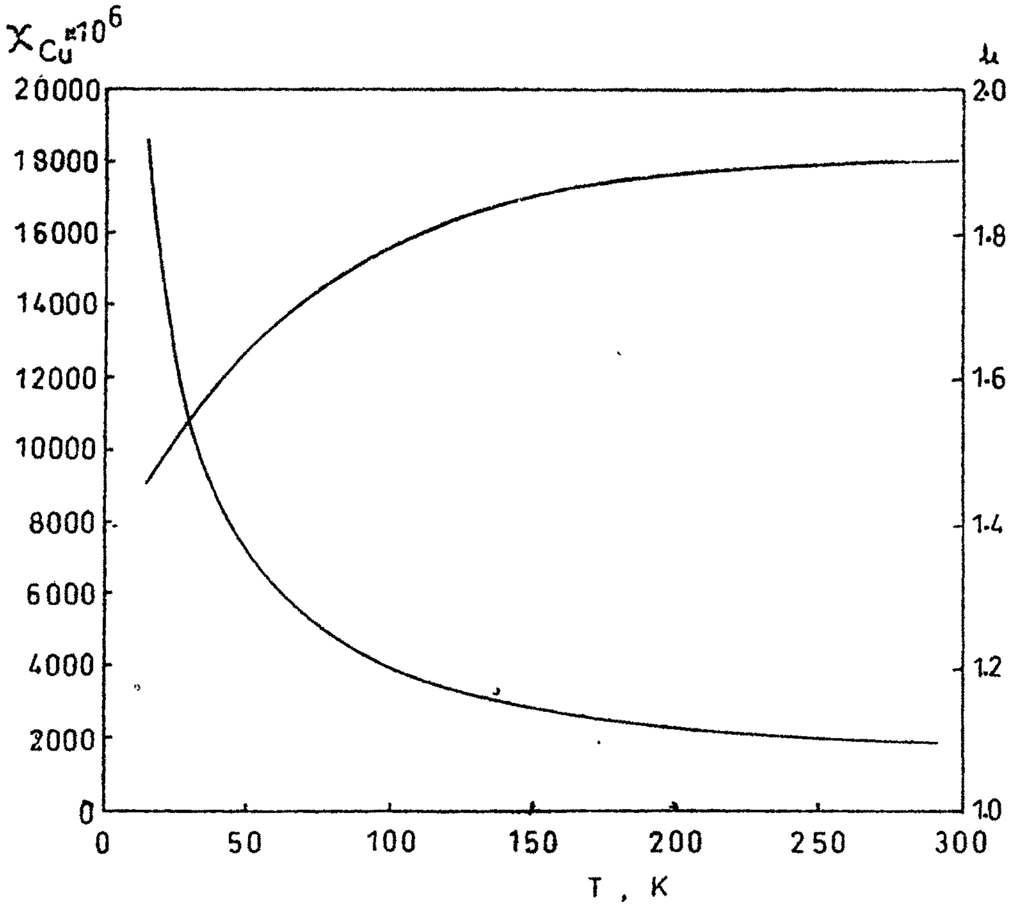


Fig. 4.2.5 : Temperature dependance of χ_{Cu} and μ in compound 7

4.3 Characterization of binuclear complexes and their magnetic properties.

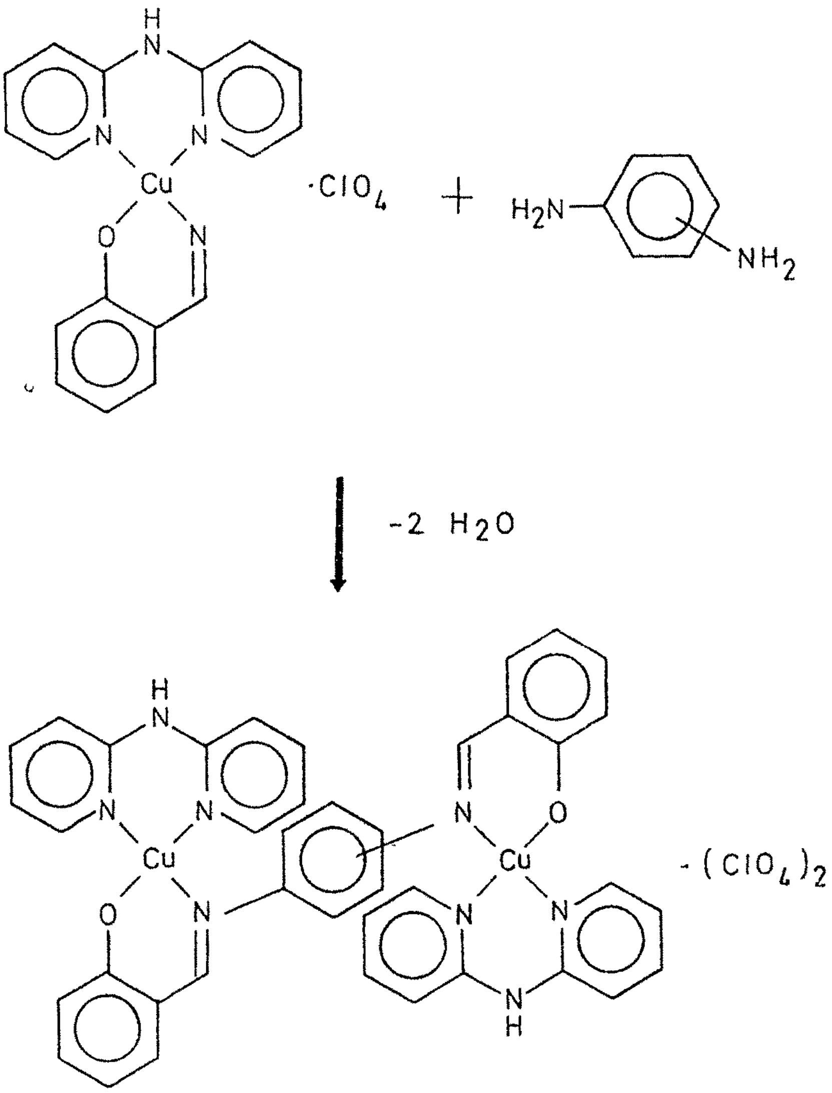
The analyses of the complexes (Table 4.2.1) correspond to the general formula [Cu_2 $(A)_2$ (SB)]. $(ClO_4)_2$ where H_2 SB are the Schiff bases,

H_2 SB^1 = N, N' - 1, 4-phenylene bis (salicylideneimine)
H_2SB^2 = N, N' - 1, 3-phenylene bis (salicylidene imine)
H_2SB^3 = N, N' - 1, 2-phenylene bis (salicylidene imine)
H_2SB^4 = N, N' - 1, 4-phenylene bis (2-hydroxy naphthalidene imine)
H_2SB^5 = N, N' - 1, 3-phenylene bis (2-hydroxy naphthalidene imine)
H_2SB^6 = N, N' - 1, 2-phenylene bis (2-hydroxy naphthalidene imine)

They are formed by the condensation of the respective diamines with coordinated salicylaldehyde or 2-hydroxy naphthaldehyde of two mixed ligand complex molecules [Cu A L]. ClO_4 . Reaction in a typical case with A = dpa can be shown as in Scheme **I**.

It is well known that Schiff base formation reaction is favoured in case of coordinated aldehydes because of the drift of electron density from ligand to metal. Such electron density shift is found to be still greater in complexes containing dpa, bipy or phen like tertiary diimines as primary ligands. Thus aromatic diamines which are known to be weak bases react with the coordinated aldehydes more easily to form Schiff bases than in absence of the metal ion. The reaction is expected to be more favoured in the ternary complex. The reactions were carried out on the mixed ligand complexes containing aldehyde rather than the imine form of the secondary ligand. This is because these ternary complexes can be obtained in the aldehyde forms at natural pH and hence it is not necessary

Scheme I



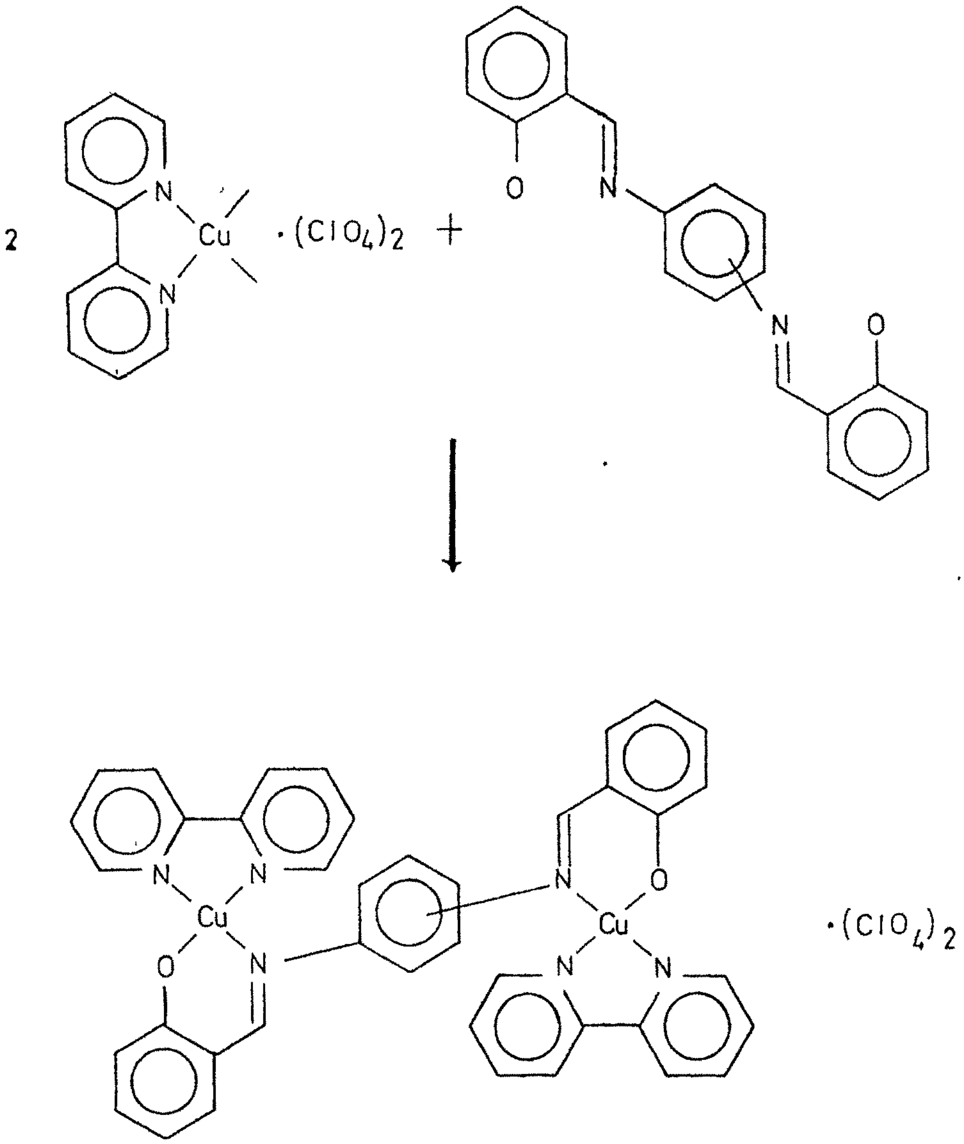
to get them in the imine form. Moreover , the reaction of the aldimines with diamines, involves amine exchange and is rather a slower process, specially with aromatic diamines. This could be avoided.

Another way of getting these binuclear complexes is treating the binary complex [Cu A] $(ClO_4)_2$ with preformed Schiff bases (Scheme II). In case of ppd and mpd the compounds obtained have reasonable agreement between experimental analyses and the values calculated from the molecular formulae. It has been observed that preformed Schiff base of opd and a bidentate aldehyde like sal reacts with [Cu bipy] $(ClO_4)_2$ or [Cu phen] $(ClO_4)_2$ to give a mononuclear [Cu (SB)] and [Cu A_2] $(ClO_4)_2$ (Scheme III). The tetradentate Schiff base displaces A from [Cu A] . However, the reaction of opd on the mixed ligand complex [Cu A sal] ClO_4 or [Cu A naph]. ClO_4 results in the formation of a binuclear complex having opd Schiff base as a bridging unit as in Scheme I.

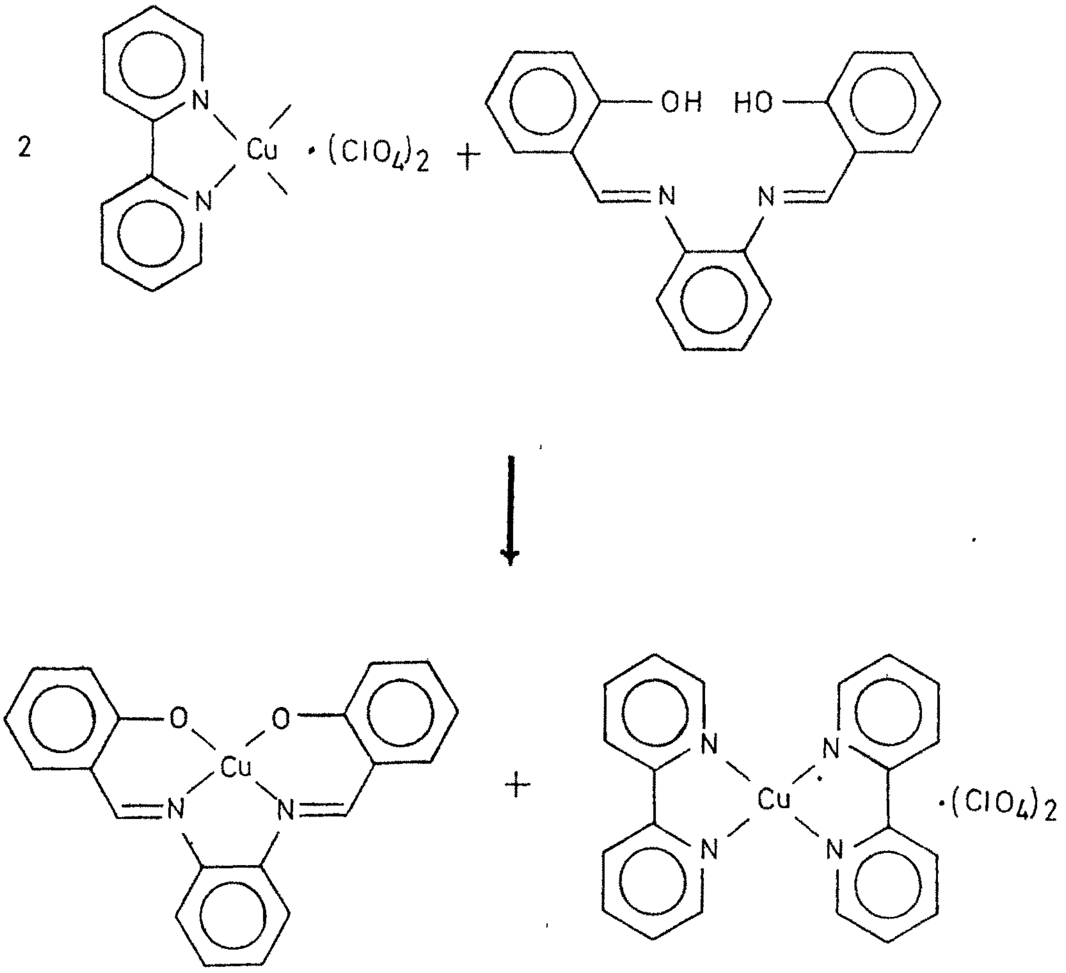
Electronic Spectra :

Each of these complexes exhibits an absorption band at ~ 41, 500 cm^{-1} (~ 240 nm) corresponding to the $\pi \rightarrow \pi^*$ transition in the bridging diamine. However, the $n \rightarrow \pi^*$ transition which occurs at ~ 35,000 cm^{-1} (285 nm) in the free diamine is lost because of the utilization of N lone pair for coordination with the metal ion. Other bands in the UV region are associated with the electronic transitions in the tertiary diimine and the o-hydroxy aldimine part of the complex. A doublet at ~ 33,000 cm^{-1} (303 nm) in the complexes of bipy, a band at ~ 37,000 cm^{-1} (~ 270 nm) in the complexes involving phen and the band at ~ 32,000 cm^{-1} (300-312 nm) in dpa containing complexes are characteristics

Scheme II



Scheme III.



of the respective diimines coordinated with a metal ion. All of these are red shifted because of coordination. A band in the visible region appears at ~ 25,000 cm^{-1} (~ 400 nm) which corresponds to Cu → N charge transfer transition. The ligand field band appears at ~ 17,000 - 18,000 cm^{-1} (590 - 555 nm). This is a broad band corresponding to the three transitions $A_{1g} \leftarrow B_{1g}$, $B_{2g} \leftarrow B_{1g}$ and $E_g \leftarrow B_{1g}$, possible in tetragonal copper (II) complexes. The nature of the spectrum is similar to that of the mononuclear complexes indicating that the two copper (II) centres are equivalent.

IR spectra :

The IR spectra of the complexes in the region 600 - 4000 cm^{-1} exhibit several bands corresponding to the stretching and bending modes of C-C , C-H , $C=N$ etc. Characteristic patterns associated with the coordinated tertiary diimines are also observed. In case of the complexes containing dpa, a band corresponding to ν_{N-H} is observed at 3350 cm^{-1} . The interesting IR features , however , are those associated with $C=N$ (imine) stretching, indicating condensation of diamine with aldehyde forming Schiff bases and bands due to perchlorate. Strong absorption corresponding to the $C=N$ stretching appears at ~ 1610 cm^{-1} i.e. at ~ 30 to 60 cm^{-1} lower energy compared to the normal range of this transition in free organic molecules. This is according to the expectation that coordination of the imine N with a metal ion having filled π orbitals should result in a shift towards lower energy region in $C=N$ [137]. Only one strong band at ~ 1100 cm^{-1} corresponding to asymmetric stretch of the perchlorate Cl-O is observed. Unsplit ν_{as} and absence of symmetric ν_{Cl-O} band at 920 cm^{-1} indicate that the perchlorates are not involved in coordination with the metal ion [137].

Magnetic exchange .

X band ESR spectra of compounds 1 and 2 at 5° K and that of compound 10 at room temperature have been shown in Fig. 4.2.1 to 4.2.3. They exhibit $\Delta M_s = 2$ transitions at g = 4.23 , 4.17 and 4.28 , respectively, indicating antiferromagnetic interaction between two copper (II) centres. Compounds 1 and 2 also exhibit weak singlet → triplet transitions , a rare feature of ESR. This allows calculation of |J| which is 0.119 cm^{-1} for compound 1 and 0.12 cm^{-1} for compound 2.

$\chi_M \longrightarrow T$ curves for compounds 1 and 7 do not exhibit any maxima. However, the room temperature magnetic moment values are observed to be less than the spin only value. This supports spin exchange interaction in all the binuclear complexes. However, the extent of lowering in magnetic moment value is less in case of mpd Schiff base complexes compared to their ppd and opd analogues. The reason for this inequality lies in different geometries of the bridging molecules. Understanding of the probable exchange mechanism and consideration of symmetries and energies of both σ and π orbital is essential. If the local symmetry around the metal ion is considered to be square planar the unpaired electron should be in the $d_{x^2-y^2}$ orbital. In a binuclear complex, they will give rise to two molecular orbitals with A_g and B_u symmetry.

$$\Phi_1 = d_{x^2-y^2} \quad (A) + d_{x^2-y^2} \quad (B) \qquad A_g$$

$$\Phi_2 = d_{x^2-y^2} \quad (A) - d_{x^2-y^2} \quad (B) \qquad B_u$$

These on the combination with σ and/or π MO's of the bridging ligand with appropriate symmetry and energy will lead to magnetic exchange between two metal centres through σ and/or π exchange pathway according to the availability of the orbitals.

Verification of the MO's of the bridging molecules clearly indicates that the highest energy orbital, comprising mainly of s and p_x orbitals of N and C , provides continuous bonding σ exchange pathway. Slight distortion in the square - planar geometry around the metal ion may allow $\sigma - \pi$ mixing which may provide additional path for exchange of unpaired electron - spins over the two metal ions through delocalized π orbitals over the bridge. MO calculations show that in case of mpd complexes the π - orbital having symmetry and energy suitable for exchange of unpaired spin with the metal ion has a nodal plane and hence it can not provide a continuous path for spin exchange.

In a qualitative way, the participation of π - orbitals is evidenced by the fact that the extent of exchange interation is less in case of bridge formed by condensation of mpd rather than that in case of Schiff bases of ppd and opd. Conventionally, it can be explained by the fact that the electronic effects at meta- position are less effective than at ortho - or para - positions.

A quantitative discussion of magnetic properties is not desirable in the absence of variable temparature magnetic data at required low temperature, as intermolecular spin exchange interaction can not be, directly, ruled out. It can, however, be seen that each copper (II) ion has four coordination sites occupied. Any intermolecular interaction will require coordination at an axial position, which is not preferred in copper (II) complexes. Absence of any lowering in magnetic moment (antiferromagnetism) in parent ternay complexes [136, 138] can be considered as an indirect evidence for the absence of intermolecular spin exchange in present binuclear complexes.

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