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STUDY OF THE RELATION BETWEEN THE STRUCTURAL DATA AND MAGNETIC INTERACTION IN OXO-BRIDGED BINUCLEAR COPPER(II) COMPOUNDS

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CONTENTS

ABBREVIATIONS

acsal	acetylsalicylate
bipy	2,2′-bipyridine
cbpb	*N*-n-butyl(5-chloro-α-phenyl-2-hydroxybenzylidene)-aminate
cha	cyclohexylamine
$C_{10}H_{10}N_2O_4$	condensation product of 3-aminopropanol with 3-nitrosalicylaldehyde
$C_{10}H_{10}NO_2Cl$	condensation product of 3-aminopropanol with 5-chlorosalicylaldehyde
$C_{11}H_{11}NO_2$	acetylacetone-mono(*o*-hydroxyanil)
$C_{12}H_{10}NO$	*N*-methyl-2-hydroxy-1-naphthaldiminate
$C_{14}H_{13}NO_2$	condensation product of 3-aminopropanol with 5,6-benzosalicylaldehyde
$C_{16}H_{14}N_2O_2$	*N*,*N*′-disalicylidene-ethylenediamine

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4 CH_3OpyNO	4-methoxypyridine-*N*-oxide
4 CH_3pyNO	4-methylpyridine-*N*-oxide
(CH_3sal)hfa	1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-(*N*-methyl-2-hydroxybenzylideneiminate)
2 Clpy	2-chloropyridine
dbaetO	2-dibutylaminoethanolate
deaeaprO	2-diethylaminoethyl-3-aminopropanolate
deaetO	2-diethylaminoethanolate
deaprO	1-diethylamino-2-propanolate
dmaep	2-(2-dimethylaminoethyl)pyridine
dmapraetO	2-dimethylaminopropyl-3-aminoethanolate
DMSO	dimethylsulfoxide
dox	1,4-dioxane
dpa	2,4-dichlorophenoxyacetate
eaep	2-(2-ethylaminoethyl)pyridine
eha	*N*,*N*′-ethylenebis(2-hydroxyacetophenimine)
es	*N*,*N*′-ethylenebis(salicylideneiminate)
(fsa)$_2$en	tetraanion of *N*,*N*′-bis(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane
hpmba	2-hydroxy-*N*-3-hydroxypropyl-α-methylbenzylideneaminate
hpnba	2-hydroxy-*N*-3-hydroxypropyl-5-nitrobenzylideneaminate
N-CH_3sal	*N*-methylsalicylaldiminate
N-chsal	*N*-cyclohexylsalicylaldiminate
N-Etsal	*N*-ethylsalicylaldiminate
8-OHquin	8-hydroxyquinoline
pia	dianion of $CH_3-CO-CH_2-C(CH_3)=N-(CH_2)_3-OH$
2 pic	2-picoline
3 pic	3-picoline
picprO	*N*-(picolinoyl)-3-amino-1-propoxide
1,3-ps	*N*,*N*′-propylenebis(salicylideneiminate)
py	pyridine
pyNO	pyridine-*N*-oxide
pz	pyrazine
quin	quinoline
sal	salicylate
suc	succinate
tcp	2,4,6-trichlorophenolate
teen	*N*,*N*,*N*′,*N*′-tetraethylethylenediamine
tmeen	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
tpok	2,2,5,5-tetramethyl-pyrroline-1-oxide-3-carboxylate

A. INTRODUCTION

This manuscript represents a brief survey of the structural and magnetic behaviour of oxo-bridged binuclear copper(II) compounds. The systems to be discussed include (Section B) a series of copper(II) carboxylates; (Section C) a series of di-μ-hydroxo-bridged copper(II) compounds of the general formula $[CuL(OH)]_2X_2$, where L is a bidentate amine such as bipy, eaep, dmaep, tmeen, teem or a monodentate such as cyclohexylamine; (Section D) a series of di-alkoxo-bridged copper(II) compounds of the general formula $[Cu(LO)X]_2$, where L is bidentate, mostly *N*-substituted aminoethanol or an aminopropanol; (Section E) a series of di-aryloxo-bridged copper(II) compounds of the general formula $Cu(LO)X_2$ or $Cu(LO)_2X_2$, where L is a pyridine-*N*-oxide or a substituted pyridine-*N*-oxide; and (Section F) a series of di-oxo-homo- and heterobinuclear Schiff's base compounds. In the last few years, progress in understanding the mechanism of super-exchange coupling has been considerable. We try to show whether or not some correlation exists between X-ray and magnetic data in such copper(II) compounds.

B. X-RAY AND MAGNETIC DATA FOR BINUCLEAR COPPER(II) CARBOXYLATES

In Table 1 are collected structural and magnetic data for copper(II) carboxylates with a bridged binuclear structure (Fig. 1). This list is complete up to the end of June 1980. Although the nature of the magnetic interaction in binuclear copper(II) carboxylates has been a subject of much discussion, no clear picture has yet emerged of the factors which determine the magnetic behaviour of such compounds [54–56]. The existence of (isolated) pairs of copper(II) atoms was confirmed from a study of the EPR spectrum of copper(II) acetate monohydrate [57], and a year later by an X-ray crystal structure analysis [19]. Up to 1953 a few tens of crystals had been prepared and their X-ray crystal structures studied (Table 1).

We can see some trends in Table 1. In general the Cu–Cu distance is increased when the acid strength increases, but at the same time there is movement of the copper atom out of the basal plane of its square pyramidal coordination polyhedron. The Cu–Cu and Cu–basal plane distances are increased from 2.61 and 0.19 Å (1 Å = 0.1 nm = 10^{-10} m) in $Cu(CH_3COO)_2 \cdot H_2O$ to 2.89 and 0.32 Å in $Cu(F_3CCOO)_2$quin, respectively. Data for the compounds are included in the plot of copper–copper distance vs. Cu–basal plane distance, shown in Fig. 2. These data are also listed in Table 1. If the data for $Cu(CH_3COO)_2$pz are omitted then the best line through the available values has a slope of −0.9103 and an intercept of 0.4252 Å with an *R* coefficient of −0.9419.

TABLE I

Structural and magnetic data for binuclear copper(II) carboxylates

Compound	Cu–Cu (Å) [a]	Cu–O (basal) (Å)	Cu–L (apical) (Å)	
$Cu(C_2H_5COO)_2(dox)_{0.5}$	2.563 (4)	1.953 (2)	O [b]	2.227 (2)
$Cu(CH_3(CH_2)_2COO)_2$	2.565	1.982	O	2.245
$Cu(C_6H_5COO)_2(dox)_{2.5}$	2.569 (3)	1.963 (8)	O	2.178 (9)
$Cu(CH_3COO)_2pz$ [c]	2.576 (1)	1.964 (4)	N	2.167 (5)
$Cu(C_2H_5COO)_2$	2.578 (4)	1.94 (1)	O	2.28 (1)
$Cu(HCOO)_2(dox)_{0.5}$	2.58 (1)	1.96 (2)	O	2.26 (2)
$Cu(CH_3COO)_2 \cdot CH_3COOH$	2.582 (1)	1.971	O	2.195 (6)
$Cu(CH_3COO)_2pz$ [d]	2.583 (1)	1.964 (5)	N	2.171 (4)
$Cu(CH_3COO)_2 \cdot CH_3OH$	2.597 (1)	1.961	O	2.159 (7)
$Cu(C_6H_5COO)_2(CH_3OH)_2$	2.606 (3)	1.95 (2)	O	2.24 (1)
$Cu(suc)_2 \cdot H_2O$	2.610 (1)	1.926 (7)	O	2.102 (7)
$Cu(CH_3COO)_2 \cdot H_2O$ [e]	2.614 (2)	1.969 (2)	O	2.161 (2)
$Cu(CH_3COO)_2 \cdot H_2O$ [f]	2.616 (1)	1.969 (3)	O	2.156 (4)
$Cu(acsal)_2$	2.617 (3)	1.962 (8)	O	2.241 (8)
$Cu(dpa)_2(dox)_{2.5}$	2.62	1.965	O	2.19
$Cu(2\text{-}BrC_6H_4COO)_2 \cdot H_2O$	2.624 (7)	1.99 (2)	O	2.17 (2)
$Cu(C_6H_5CH_2COO)_2$urea	2.623 (1)	1.963 (5)	O	2.155 (5)
	2.630 (1)	1.963 (5)	O	2.148 (5)
$Cu(CH_3COO)_2py$ [g]	2.630 (3)	1.981 (10)	N	2.126 (10)
$Cu_2(CH_3COO)_{2.25} \cdot (ClCH_2COO)_{1.75}urea_2$	2.631	1.97	O	2.12
$Cu(C_2H_5COO)_2$ 3 pic	2.6312 (4)	1.970 (2)	N	2.167 (2)
$Cu(CH_3COO)_2urea \cdot H_2O$ [h]	2.637	2.00	O	2.09
$Cu(4\text{-}OHC_6H_4COO)_2(DMSO)_3$	2.639 (3)	1.96 (1)	O	2.12 (1)
$Cu(sal)_2dox \cdot H_2O$ [i]	2.64	2.00	O	2.09
$Cu(C_2H_5COO)_2py$	2.642 (2)	1.96 (1)	N	2.17 (1)
	2.619 (2)	1.97 (1)	N	2.13 (1)
$Cu(CH_3COO)_2 \cdot (NCS)_2$	2.643 (3)	2.03	N	2.08 (2)
$Cu(ClCH_2COO)_2$urea	2.643	1.97	O	2.10
$Cu_2(tpok)_2(EtOH)_2 \cdot H_2O$ [j]	2.644	1.984	O	2.17
$Cu(CH_3COO)_2py$ [k]	2.645 (3)	1.955 (8)	N	2.186 (8)
$Cu(C_2H_5COO)_2$ 2 pic	2.647 (4)	1.97 (1)	N	2.21 (2)
$Cu(CH_3COO)_2$quin	2.652 (2)	1.977 (5)	N	2.224 (6)
$Cu(HCOO)_2$urea	2.657 (7)	1.952 (16)	O	2.114 (13)
$Cu(HCOO)_2py$	2.663	1.963	N	2.162
$Cu(FCH_2COO)_2$urea	2.665	1.974 (7)	O	2.102 (7)
$Cu(C_6H_5COO)_2$quin	2.671 (2)		N	
$Cu(CH_3COO)_2$ 2 pic	2.671	1.975 (10)	N	2.240 (12)
$Cu(ClCH_2COO)_2$ 3 pic	2.685 (2)	1.974	N	2.269 (4)
$Cu(HCOO)_2(NCS)_2$	2.716 (2)	1.983 (4)	N	2.093 (9)
$Cu(ClCH_2COO)_2$quin	2.724 (2)	1.973 (5)	N	2.211 (7)
$Cu(FCH_2COO)_2$quin	2.725 (1)	1.976 (2)	N	2.210 (3)
$Cu(ClCH_2COO)_2$ 2 pic	2.747 (3)	1.974 (9)	N	2.161 (10)
$Cu(Cl_3CCOO)_2 \cdot 2$ Clpy	2.766 (3)	1.957 (5)	N	2.145 (5)
$Cu(F_3CCOO)_2$quin	2.886 (2)	1.972 (6)	N	2.107 (6)

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average e.s.d.'s for an individual distance or angle. [b] The chemical identity of the apical atom is specified in this column. [c] At

O–C (Å)	Cu–basal plane (Å)	Cu–O–C (deg.)	O–C–O (deg.)	$-2J$ (cm^{-1})	Ref.
			124.2 (1)	364	1, 2
1.243	0.19	123.8	123.3	322	3, 4
1.25 (1)			124.7 (8)		5a
1.259 (5)	0.28	122.5 (3)	124.8		6
1.28	0.22	130	113	300	7, 4
1.24 (4)	0.19	113	129 (3)	555	8, 9
1.257					10
1.248 (7)	0.26	122.7 (4)	125.3 (6)	325	6, 11
1.26					10
1.26			126 (2)		12
1.256 (10)	0.20	123.5 (11)	124.3 (9)	330	13–15
1.259 (2)	0.19	123.0 (1)	124.9 (1)	284	16, 17
1.260 (6)	0.19	123.1 (3)	124.8 (4)	284	18, 19
1.26 (1)	0.19	122.8 (7)	125.5 (10)	340	20, 21
1.26	0.19				22
1.26 (3)	0.20	123.5 (20)	124 (3)	250	21, 23
	0.204	125.3 (6)	124.8 (8)		24
	0.199	120.1 (6)	125.8 (8)		
1.239 (18)	0.22	123.4 (7)	125.1 (9)	325	25, 26
	0.21	123.6 (2)	124.5 (3)		27
1.25 (4)			124.2 (1)	364	28–30
1.25			119.9	270	31, 32
1.25 (2)			127 (2)		12
	0.206				33
1.26 (2)			125 (1)	350	34, 35
1.26 (2)			128 (1)		
1.24 (2)		123.0 (13)	126.2 (13)	305	36, 37
	0.208	123.5	121.1	311	38, 32
1.26			123		39
1.244 (18)	0.22	123.4	125.6		40
1.24 (2)		126 (1)		364	41
1.24 (1)	0.227	123.7 (7)	125.9 (8)	320	42–44
1.27 (2)	0.22	125.4 (13)	122.0 (18)		45
1.253 (4)			127.5 (3)	575	5b, 9
	0.212		126.8	355	36
					46
1.244 (14)	0.23	121.7 (10)	125.9 (14)	318	47
1.235	0.228	122.7 (7)	127.8		48
1.244 (8)		122.7 (3)	128.4 (5)	485	36
1.24 (1)	0.248	122.8 (8)	128 (1)	331	42, 32
	0.239		127.5 (4)	364	49, 32
1.247 (17)	0.26	123.8 (8)	127.3	321	50, 51
1.229 (3)	0.28	123.8	128.4	217	52
1.242 (11)	0.32	124.9 (6)	129.0 (9)	310	53

100 K. [d] At 300 K. [e] Neutron diffraction results. [f] X-ray diffraction results. [g] Monoclinic form. [h] Apical ligand is a urea oxygen atom. [i] Apical ligand is a water oxygen atom. [j] Apical ligand is an ethanol oxygen atom. [k] Orthorhombic form.

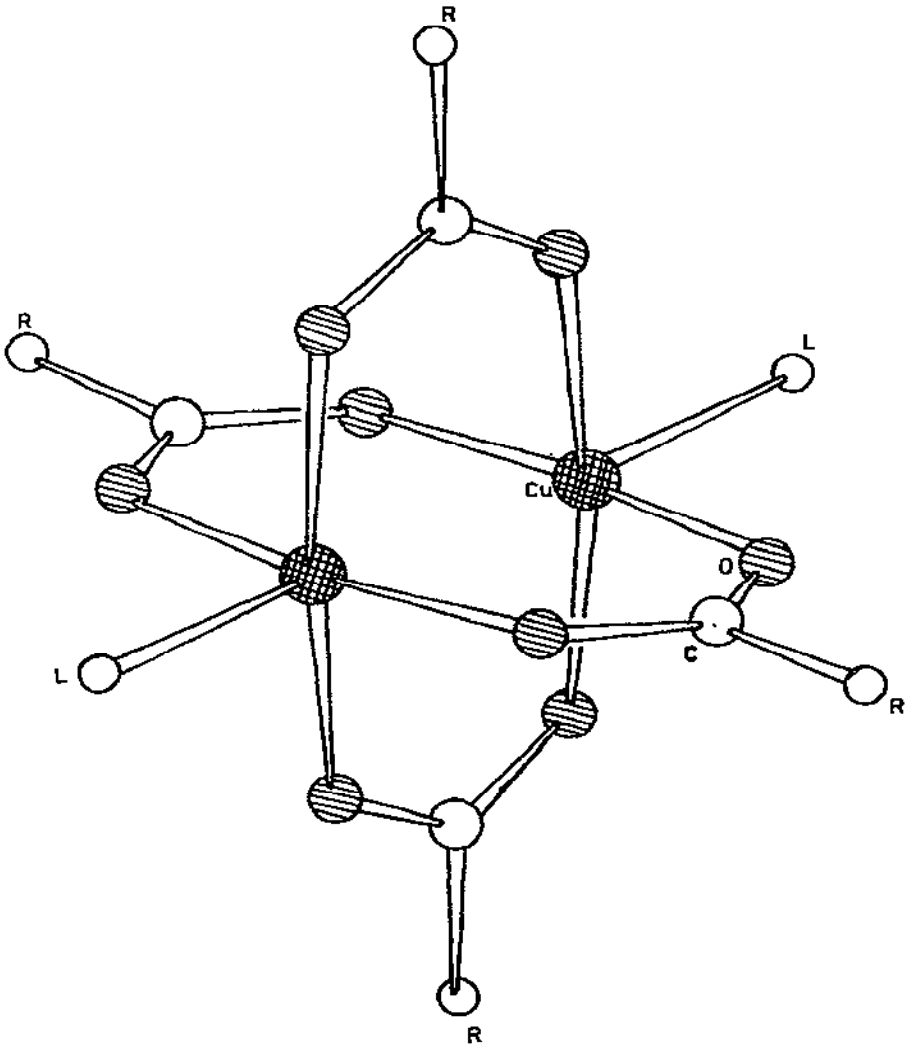


Fig. 1. A schematic view of the molecular structure of binuclear copper(II) carboxylate.

The coefficient of order correlation is much higher than its critical value on the significance level of 0.01 with $\nu = n - 2$ degrees of freedom, where n denotes the experimental data of the respective set ($n = 26$; $R_{crit} = 0.4869$), and thus the coefficient of order correlation is statistically significant [58].

The axial ligand also plays a role in determining both the Cu–Cu and Cu–basal plane distances. There exist some differences between the chromophore CuO_5 and CuO_4N, respectively. For instance, the sum of all interatomic distances in CuO_5 and CuO_4N (the half value of the Cu–Cu distances

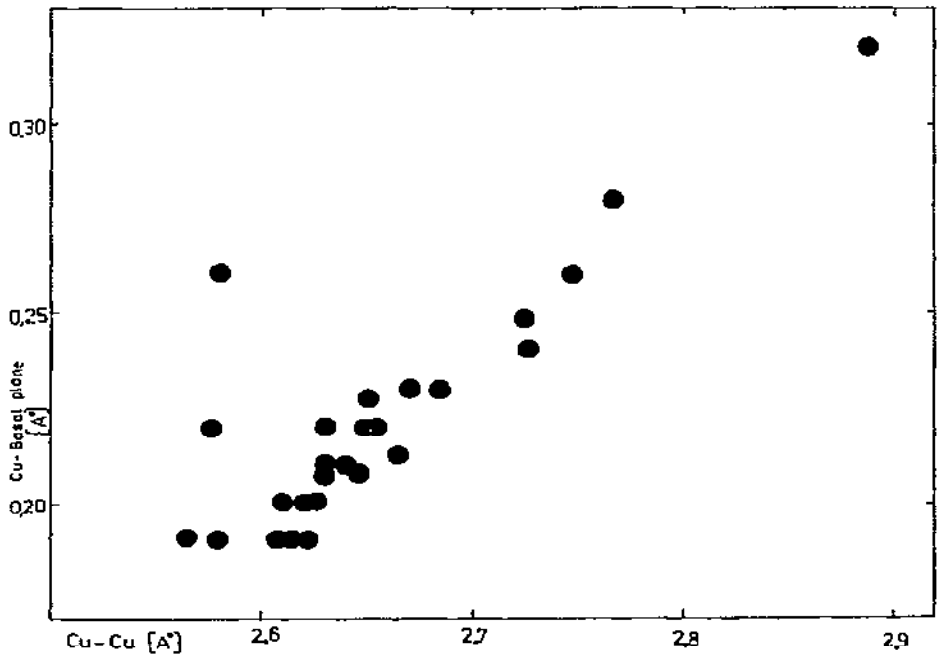


Fig. 2. A plot of the Cu–basal plane distance against the Cu–Cu distance of the copper(II) carboxylates (data are listed in Table 1).

were also included in the sum for each chromophore) is almost constant and is approximately 11.34 and 11.38 Å, respectively. The Cu–O (basal) distance is almost constant at 1.96 Å for the CuO_5 chromophore and 1.97 Å for the CuO_4N chromophore. On the other hand the O–C and Cu–L (apical) distances are somewhat longer in the CuO_5 chromophore than in the CuO_4N chromophore and are approximately 1.26 and 2.16 Å for the former, but 1.24 and 2.11 Å for the latter. The bridging Cu–O–C–O–Cu distances also show a small variation and were found to be almost constant at 6.44 Å for the CuO_5 chromophore and 6.42 Å for the CuO_4N chromophore.

While the out-of-plane copper–oxygen bond distances are in the range of 2.09–2.28 Å in both the chromophores, the displacement of the copper atom from the basal plane toward the apical ligand is more variable in the CuO_4N chromophore (0.22–0.32 Å), than in the CuO_5 chromophore (0.19–0.22 Å) (Table 1).

The Cu–O–C and O–C–O bridging angles are somewhat larger in the CuO_4N chromophore than in the CuO_5 chromophore and are approximately 124.7 and 125.6° for the former and 123.2 and 123.9° for the latter.

Structural and magnetic results (Table 1) confirm the insensitivity of the

singlet–triplet separation ($-2J$) to the Cu–Cu distance. This indicates the predominance of a super-exchange rather than of a direct mechanism for coupling [36,59]. The idea that the spin coupling proceeds predominantly by super-exchange via the carboxylate bridges has become increasingly favoured.

Binuclear compounds with the CuO_4N chromophore where the average distance and angle of bridging Cu–O–C–O–Cu are 6.42 Å and 175°, have an average value of $2J = -348$ cm^{-1} (the $-2J$ values of copper(II) formate adducts were not included in any chromophore); with the CuO_5 chromophore the values are 6.44 Å, 170° and -316 cm^{-1}, respectively. This indicates the sensitivity of the value of $-2J$ to the Cu–O–C–O–Cu bridge distance and angle, through which the demagnetization operates. The elongation of the Cu–O–C–O–Cu bridged distance, but contraction of the angle, is reflected in a decrease in the value of $2J$. This can be nicely illustrated with $Cu(HCOO)_2(NCS)_2$ and $Cu(CH_3COO)_2(NCS)_2$. While the Cu–O–C–O–Cu bridge angle and the distances of Cu–Cu and Cu–O–C–O–Cu in $Cu(HCOO)_2(NCS)_2$ are 173.8°, 2.716 and 6.45 Å, and $2J = -485$ cm^{-1}, the corresponding values in the acetate are 172.2°, 2.643, 6.54 Å and -305 cm^{-1}, respectively. On the other hand, note that the value of $2J = -217$ cm^{-1} found for $Cu(Cl_3CCOO)_2 \cdot 2$ Clpy, is the lowest in the series collected

TABLE 2

Structural and magnetic data for di-μ-hydroxo-bridged copper(II) compounds

Compound	Cu–Cu (Å) [a]	In-plane	
		Cu–O (Å)	Cu–N (Å)
$[Cu(bipy)OH]_2(NO_3)_2$	2.847	1.922 (1)	1.999 (2)
$[Cu(bipy)OH]_2(ClO_4)_2$	2.871 (1)	1.918 (2)	1.990 (3)
$[Cu(bipy)OH]_2SO_4 \cdot 5\,H_2O$	2.893 (3)	1.938 (5)	2.001 (6)
$[Cu(eaep)OH]_2(ClO_4)_2$	2.917 (5)	1.916 (7)	2.008 (9)
$[Cu(cha)_2OH]_2(ClO_4)_2$	2.934 (8)	1.941 (5)	2.007 (7)
β-$[Cu(dmaep)OH]_2(ClO_4)_2$	2.935 (1)	1.909 (3)	2.035 (3)
α-$[Cu(dmaep)OH]_2(ClO_4)_2$	2.938 (1)	1.941 (2)	2.036 (2)
$[Cu(tmeen)OH]_2(NO_3)_2$	2.954 (2)	1.902 (7)	2.023 (7)
$[Cu(tmeen)OH]_2(ClO_4)_2$	2.966 (3)	1.914 (8)	2.014 (9)
α-$[Cu(teen)OH]_2(ClO_4)_2$	2.978 (2)	1.903 (4)	2.018 (10)
β-$[Cu(teen)OH]_2(ClO_4)_2$	2.997 (2)	1.906 (6)	2.030 (6)
$[Cu(tmeen)OH]_2Br_2$	3.000 (4)	1.902 (3)	2.030 (10)

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average e.s.d.'s for an individual distance.

in Table 1, in spite of the fact that the bridging Cu–O–C–O–Cu distance of 6.37 Å is one of the shortest.

The apical ligands clearly play a role in determining the $2J$ value in binuclear compounds (Table 1). The value of $2J$ increase [54] as the terminal ligands become stronger electron donors. Thus, the $2J$ value tends to increase according to the series of terminal groups: aniline < water ≤ anhydrous < pyridine ~ picolines ~ SCN ~ ethanol < dioxane. Table 1 shows the series of terminal groups: water ≤ urea ≤ anhydrous < pyridine ~ pyrazole < quinoline ≤ picoline ~ NCS < dioxane.

Insufficient data are available in analogous copper(II) acetate monohydrate compounds to draw any precise conclusions regarding the nature of the interaction.

C. X-RAY AND MAGNETIC DATA FOR DI-μ-HYDROXO-BRIDGED BINUCLEAR COPPER(II) COMPOUNDS

Di-μ-hydroxo-bridged copper(II) compounds [73–75, 82, 83] have been extensively studied. Structural and magnetic data are given in Table 2.

From the structural point of view, the copper(II) compounds summarised

out-of-plane

Cu–O (Å)	Cu–basal plane (Å)	Cu–O–Cu (deg.)	O–Cu–O (deg.)	$2J$ (cm^{-1})	Ref.
2.379(2)	0.16	95.6 (1)	84.4	+172	60, 61
2.797(4)	0.053	96.94 (15)	83.06(14)	+93	62
2.225(5)	0.205	97.0 (2)	83.6(2)	+49	63–65
2.590(9)	0.12	99.2 (3)	80.8	−130	66–68
2.8	0.06	98.1 (2)	76.1(2)	−256	69
2.721(4)	0.08	100.4 (1)	79.6(1)	−200	70, 68
2.749(2)	0.045	98.35 (9)	81.65(9)	−4.8	71, 72
		101.9 (3)	78.1(3)	−367	73
		101.6 (4)	78.4(4)	−360	74, 75
		103.0 (3)	77.0	−410	60, 76, 77
		103.7 (3)	76.3(3)	−469	73
		104.1 (2)	75.92(17)	−509	78–80

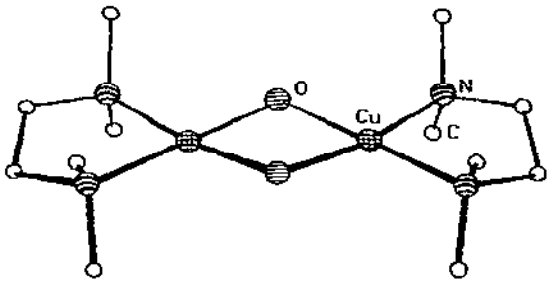


Fig. 3. A view of the copper(II) environments in $[Cu(tmeen)OH]_2^{2+}$ [74].

in Table 2 can be divided into three groups. The structures of $[Cu(tmeen)OH]_2(NO_3)_2$, $[Cu(tmeen)OH]_2(ClO_4)_2$, $[Cu(tmeen)OH]_2Br_2$, α- and β-$[Cu(teen)OH]_2(ClO_4)_2$ consist of binuclear four-coordinate $[CuLOH]_2^{2+}$ cations and discrete X^- anions (Fig. 3). In the structures of $[Cu(bipy)OH]_2(NO_3)_2$, $[Cu(bipy)OH]_2SO_4 \cdot 5\,H_2O$, $[Cu(eaep)OH]_2(ClO_4)_2$ and β-$[Cu(dmaep)OH]_2 \cdot (ClO_4)_2$, the copper(II) atoms are in a tetragonal pyramidal environment with monodentate anions occupying the axial positions, except $[Cu(bipy)OH]_2SO_4 \cdot 5\,H_2O$, where a water molecule is coordinated in the axial position to one copper and a sulfate anion to the other

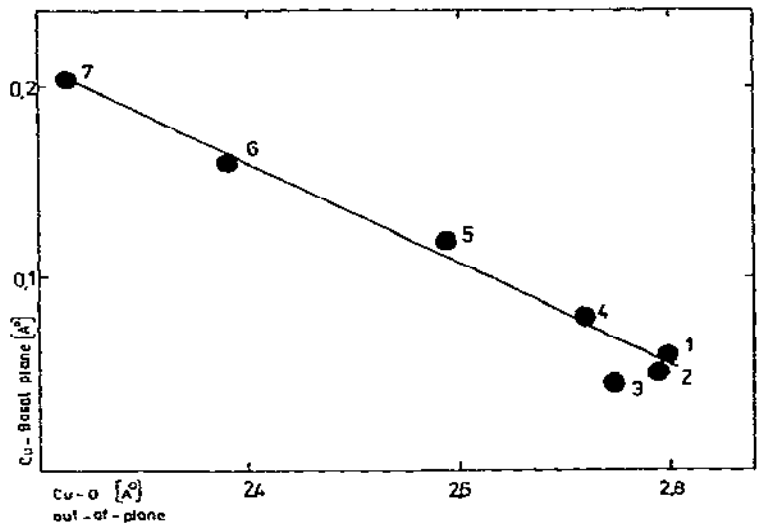


Fig. 4. A plot of the Cu–basal plane distance against the Cu–O distance (out-of-plane) of $[Cu(cha)_2OH]_2(ClO_4)_2$ (1), $[Cu(bipy)OH]_2(ClO_4)_2$ (2), α-$[Cu(dmaep)OH]_2(ClO_4)_2$ (3), β-$[Cu(dmaep)OH]_2(ClO_4)_2$ (4), $[Cu(eaep)OH]_2(ClO_4)_2$ (5), $[Cu(bipy)OH]_2(NO_3)_2$ (6) and $[Cu(bipy)OH]_2SO_4 \cdot 5\,H_2O$ (7).

copper. The geometry at each copper atom in $[Cu(bipy)OH]_2(ClO_4)_2$ and in α-$[Cu(dmaep)OH]_2(ClO_4)_2$ is distorted octahedral, the equatorial plane consisting of two hydroxo oxygen atoms and two nitrogen atoms from a dipy or dmaep ligand, while the axial coordination sites are occupied by perchlorate oxygen atoms.

Inspection of the data in Table 2 reveals that while the copper-bridging oxygen bond distances increase in the order of diamines: aliphatic < mixed aliphatic/aromatic < aromatic, the metal–metal distance is shortened in the order given. In the case of compounds composed of tetragonal pyramidal or distorted octahedral units a trend exists between movement of the metal atom from the basal plane toward the apical ligand with a decrease of the out-of-plane copper–oxygen bond distances (Fig. 4). The best line through

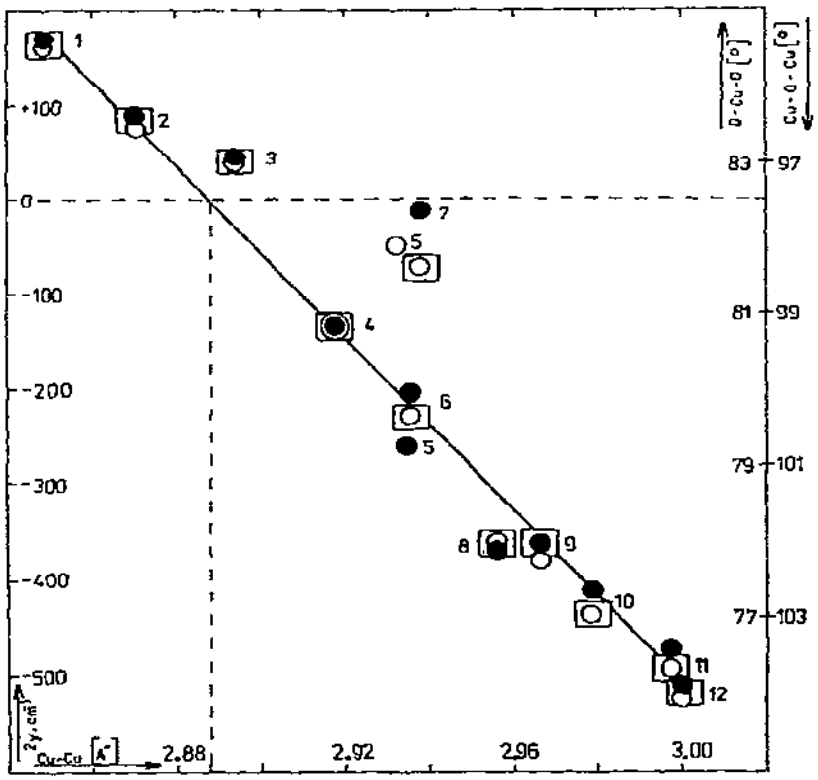


Fig. 5. The Cu–Cu distances plotted against the $2J$ values (●), Cu–Cu vs. Cu–O–Cu° (○) and Cu–Cu vs. O–Cu–O° (□) for $[Cu(bipy)OH]_2(NO_3)_2$ (1), $[Cu(bipy)OH]_2(ClO_4)_2$ (2), $[Cu(bipy)OH]_2SO_4 \cdot 5\,H_2O$ (3), $[Cu(eaep)OH]_2(ClO_4)_2$ (4), $[Cu(cha)_2OH]_2(ClO_4)_2$ (5), β-$[Cu(dmaep)OH]_2(ClO_4)_2$ (6), α-$[Cu(dmaep)OH]_2(ClO_4)_2$ (7), $[Cu(tmeen)OH]_2(NO_3)_2$ (8), $[Cu(tmeen)OH]_2(ClO_4)_2$ (9), α-$[Cu(teen)OH]_2(ClO_4)_2$ (10), β-$[Cu(teen)OH]_2(ClO_4)_2$ (11) and $[Cu(tmeen)OH]_2Br_2$ (12).

the seven available values of the Cu–O out-of-plane and Cu-basal plane distances has a slope of 0.7960 and an intercept of −0.2655 Å with an R coefficient of −0.98. The coefficient of order correlation is statistically significant; $|R| > R_{crit}$ (0.8745) [58].

The elongation of the Cu–Cu distance is reflected in simultaneous opening of the Cu–O–Cu bridging angle (Table 2).

Table 2 shows that compounds with 2,2′-bipyridine have a triplet ground state while the others have singlet ground states with the smallest $2J$ value of $-4.8\ cm^{-1}$ found for α-$[Cu(dmaep)OH]_2(ClO_4)_2$ in the order given.

There is an interesting correlation between the X-ray data and the singlet–triplet splitting [75]. When the Cu–Cu distance and Cu–O–Cu angle, Φ, increase the O–Cu–O angle Φ and the $2J$ value decrease. As the Cu–Cu separation increases from 2.847 Å in $[Cu(bipy)OH]_2(NO_3)_2$ to 3.000 Å in $[Cu(tmeen)OH]_2Br_2$, the singlet–triplet splitting changes from $+172\ cm^{-1}$ to $-509\ cm^{-1}$. In Fig. 5 the Cu–Cu distances are represented as a function of $2J$ values, Cu–Cu vs. Cu–O–Cu and Cu–Cu vs. O–Cu–O angles for all twelve compounds. The best least-squares line through the available values of the copper–copper separation and $2J$ has a slope of $-46r(Cu–Cu)/2J$ and an intercept of $13{,}389\ cm^{-1}$ with an R coefficient of 0.95. There is a similar correlation between the $2J$ values and Cu–O–Cu angle with the best least-squares fit yielding $2J = -77.6\Phi + 7{,}555\ cm^{-1}$ with an R coefficient of −0.95. The coefficient of order correlations is statistically significant; $|R| > R_{crit}$ (0.7079) [58].

The present correlation has been taken as evidence for a σ pathway, for spin-coupling and can be understood in terms of a simple molecular orbital model [83–85]. If the Cu–O–Cu–O ring is of approximate D_{2h} symmetry in these binuclear compounds, the X axis defined as the Cu–Cu direction and the y axis parallel to the O–O vector, then the two half-filled d_{xy} orbitals would interact with filled orbitals of the bridging groups. The pairs of p_x and p_y orbitals of the bridging oxygen would have identical overlap with the pair of d_{xy} orbitals, for a bridge angle of 90°. Thus these two different symmetry combinations would give molecular orbitals of equal energy, but if the Cu–O–Cu angle increases this accidental degeneracy is destroyed. However, if the s orbitals of the bridging oxygen interact with the molecular orbitals, then the interaction has u parity and the accidental degeneracy occurs at some angle other than 90°. Figure 5 can be used to illustrate a transition from paramagnetic to antiferromagnetic coupling. From the best-squares line calculations $2J$ equal to zero was observed at a Cu–O–Cu bridge angle of 97.7°. In these compounds the ground state is triplet if the Cu–O–Cu bridge angle is 90–97.7° and the p character of the oxygen bonding orbitals decreases. The ground state is singlet if the Cu–O–Cu bridge angle is $> 97.7°$; the increased value of this angle implies greater s character in the

bridging orbitals and produces increased antiferromagnetic coupling [71,77].

The value of $2J = -4.8\ cm^{-1}$ found for α-$[Cu(dmaep)OH]_2(ClO_4)_2$ [72] is lower than $-50\ cm^{-1}$, predicted on the basis of the observed Cu–O–Cu angle [75]. It is thought that the additional bridges either provide an additional pathway for super-exchange or that the coordination has a pronounced effect on the electronic structure of the interacting system [72]. On the other hand, the magnetic and structural correlation also hold for $[Cu(bipy)OH]_2(ClO_4)_2$ in spite of the fact there is additional bridge building by the perchlorate ion.

Iitaka et al. [81a] have studied the crystal structure of $[Cu(CH_3NH_2)_2OH]_2SO_4 \cdot H_2O$. This complex is the first example of a roof-shaped molecule with a dihedral angle of 132.9°. The crystal contains two kinds of crystallographically independent copper atoms. One of each kind has, as nearest neighbours, two nitrogen atoms of dimethylamine ligands at average Cu–N distances of 2.031(19) Å and two oxygen atoms of the bridging hydroxo groups at average Cu–OH distances of 1.965(15) Å with a Cu–Cu distance of 2.782(5) Å. The actual coordination of each copper atom is 4 + 1; one of them is bound to a water molecule ($Cu–OH_2 = 2.365(15)$ Å), the other is bound to the oxygen atom of a hydroxo bridge belonging to a nearest-neighbour molecule (Cu–OH = 2.403(15) Å). In this way a dimer ion of the composition $[Cu_2(CH_3NH_2)_4(OH)_2H_2O]_2^{4+}$ is formed. The singlet triplet separation, J, for the tetrakis(methylamine) di-μ-hydroxo-dicopper(II) sulfate monohydrate was found equal to $-7.9 \pm 0.5\ cm^{-1}$ [81b]. This result illustrates, in a very satisfying manner, the influence of bending on the exchange interaction in such binuclear copper(II) molecules [81b].

D. X-RAY AND MAGNETIC DATA FOR DI-ALKOXO-BRIDGED BINUCLEAR COPPER(II) COMPOUNDS

X-ray and magnetic data for di-alkoxo-bridged binuclear copper(II) compounds are summarized in Table 3. Three types of copper(II) compounds are included. In $[Cu(deaeprO)ClO_4]_2 \cdot H_2O$ both copper atoms are six coordinate. X-ray analysis [88] succeeded in explaining the non-equivalent environments of the copper(II) atoms in the dimer. In the binuclear structure the basal plane around each copper(II) atom is built up by two oxygen atoms and two nitrogen atoms of deaeprO, the copper(II) atoms are lying Cu(1) 0.19 Å and Cu(2) 0.25 Å out of the respective basal planes in the direction of the axial ligands and the two basal planes form a dihedral angle of 33°. One oxygen atom from a ClO_4^- ion coordinates to Cu(1) (Cu–O = 2.52(1) Å), while a water molecule coordinates to Cu(2) (Cu–O = 2.62(1) Å). The sixth coordinate position is occupied, in both copper atoms, by a hydrogen atom from a methyl group (Cu–H = 2.6 Å).

TABLE 3

Structural and magnetic data for di-alkoxo-bridged copper(II) compounds

Compound	Cu–Cu (Å) [a]	In-plane	
		Cu–O (Å)	Cu–N (Å)
$[Cu(deaprO)Cl]_2$	2.903 (3)	1.924 (9)	2.046 (11)
$[Cu(deaprO)Br]_2$	2.911	1.90	
$[Cu(picprO)H_2O]_2 \cdot 2\,H_2O$	2.948 (2)	1.948 (4)	1.919 (5)
$[Cu(deaeprO)ClO_4 \cdot H_2O]_2$	2.953 (3)	1.935 (6)	2.027 (7)
$[Cu(deactO)NO_2]_2$	2.976	1.910	
$[Cu(deaetO)SCN]_2$	2.981 (2)	1.925 (8)	1.941 (12)
$[Cu(OCH_3)(tcp)(quin)]_2$	3.004 (1)	1.920 (11)	2.001 (14)
α-$[Cu(dbaetO)Br]_2$	3.019 (4)	1.92 (2)	2.06 (2)
$[Cu(deaetO)Br]_2$	3.026 (2)	1.914 (8)	2.036 (8)
$[Cu(deactO)Br]_2$	3.033 (5)	1.911 (13)	2.021 (11)
$[Cu(dmapraetO)CH_3OH]_2 \cdot (ClO_4)_2$	3.034 (2)	1.930 (7)	2.010 (9)

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average e.s.d.'s for an individual distance. [b] The chemical identity of the atom is specified in this column. [c] O atom from water.

In $[Cu(OCH_3)(tcp)(quin)]_2$ [91], $[Cu(deaetO)SCN]_2$ [89], $[Cu(picprO)H_2O]_2 \cdot 2\,H_2O$ [86] and $[Cu(dmapraetO)CH_3OH]_2(ClO_4)_2$ [96] the coordination geometry of each copper(II) atom is essentially five coordinate tetragonal pyramidal, in which the apical site is occupied by the chlorine atom of a trichlorophenolate anion (Cu–Cl = 2.983(6) Å) in the former; by the sulphur atom of SCN group (Cu–S = 2.851(4) Å) in the second; by the oxygen atom of water (Cu–O = 2.394(6) Å) in the third and by the oxygen atom of methanol (Cu–O = 2.348(10) Å) in the last. The deviation of the copper(II) atom being −0.045 Å, none, 0.16 and 0.22 Å, respectively, toward the apical site. Note the trend here; out-of-plane copper–ligand distances decrease with an increase in the displacement of the copper(II) atom from the basal plane toward the apical ligand, similar to the cases of copper(II) carboxylates and di-μ-hydroxo-bridged binuclear copper(II) compounds.

In the other compounds (Table 3) the coordination about copper is distorted square-planar. The structure of such binuclear copper(II) compounds is presented in Fig. 6.

The copper-bridging oxygen bond distances are all comparable and fall in the range 1.87–1.95 Å with the average bond distance being 1.92 Å. It is interesting that the average Cu–O distance is similar to the respective

Cu–X [b] (Å)		Out-of-plane Cu–X [b] (Å)		Cu–O–Cu (deg.)	O–Cu–O (deg.)	$-2J$ (cm^{-1})	Ref.
Cl	2.206 (5)			97.9 (4)	76.8 (4)	149	73
				100	75.5	338	73
N	2.010 (5)	O	2.394 (6) [c]	98.3 (2)	80.4 (2)	128	86, 87
O	2.57 (1)	O	2.52 (1) [d]	99.4 (2)	79.8 (2)		88
		O	2.62 (1) [c]				
				102.3	77.7	361	73
N	2.089 (11)	S	2.851 (4) [f]	101.5 (3)	78.5 (3)	250	89, 90
O	1.911 (11)	Cl	2.983 (6) [g]	102.9 (6)	77.1 (7)	756	91
Br	2.333 (4)			103.8 (7)	76.7 (6)		92
Br	2.239 (2)			104.5 (4)	75.5	799	93, 94
Br	2.356 (3)			105.0 (6)	75.0 (6)		95
N	2.052 (9)	O	2.348 (10) [h]	103.6 (3)	76.3 (3)		96

[d] O atom from ClO_4. [c] O atom from water. [f] S atom from SCN. [g] Cl atom from trichlorophenolate anion. [h] O atom from CH_3OH.

average distance in the series of di-μ-hydroxo-bridged copper(II) binuclear compounds (Table 2).

There is a correlation between the Cu–Cu separation and the value of $-2J$. As the Cu–Cu separation increases from 2.903 Å in $[Cu(deaprO)Cl]_2$ to 3.026 Å in $[Cu(deaetO)Br]_2$, the $-2J$ value also increases from 149 to 799 cm^{-1}. The best line through the six available values of the Cu–Cu separation and $-2J$ has a slope of -5012 cm^{-1} $Å^{-1}$ and an intercept of 14,421 cm^{-1} with an R coefficient of -0.8534. There is a similar correlation between the Cu–O–Cu bridge angle Φ and $-2J$, with the best least-squares fit yielding $2J = -101.52\Phi + 9830$ cm^{-1} and an R coefficient of -0.93.

But while in the case of di-μ-hydroxo compounds a linear relationship was observed between these quantities (Fig. 4), in the case of di-alkoxo compounds this is not the case. This was to be expected because different alkyl groups are bound to the bridging oxygen atoms and in some cases the Cu_2O_2 ring is strongly distorted from planarity. In the series of di-μ-hydroxo-bridged copper(II) compounds $2J$ was observed equal to zero at an angle of 97.7°. In other words, in di-alkoxo-bridged binuclear copper(II) compounds the coupling is more antiferromagnetic than in a compound of the OH-bridged series having the same Cu–O–Cu bridging angle. For instance, in $[Cu(deaprO)Cl]_2$ the angle is 97.9° and the value of $2J$ is -149 cm^{-1}. In

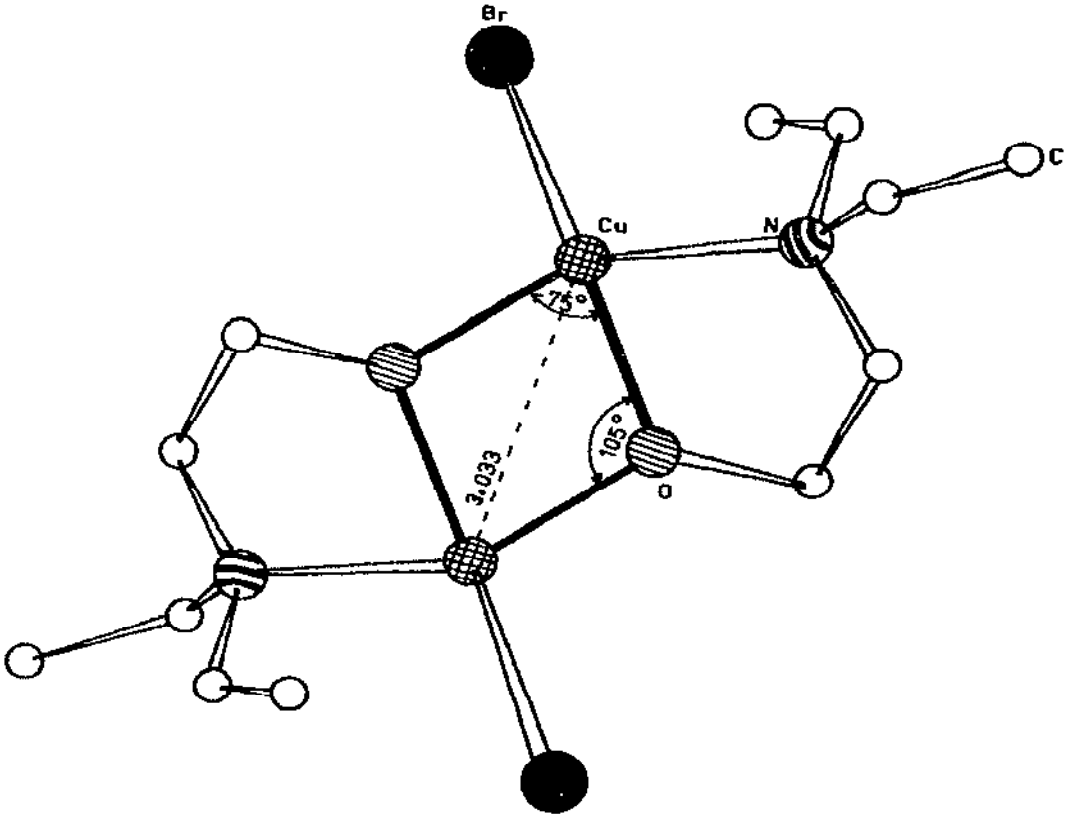


Fig. 6. Projection of the molecular structure of $[Cu(deactO)Br]_2$ [93].

di-alkoxo compounds, the bridging oxygen atoms are σ-bonded to the electronic systems of organic groups. The increase of $2J$ may be explained by the fact that a more negatively charged oxygen atom from the alkoxo-molecule is more inclined to σ-electron density transfer towards the copper(II) atom than is an oxygen atom from the OH group. The greater electron transfer causes the $3d_{\sigma}$ orbitals of the Cu(II) to increase in size, and consequently to overlap to a greater degree.

E. X-RAY AND MAGNETIC DATA FOR DI-ARYLOXO-BRIDGED BINUCLEAR COPPER(II) COMPOUNDS

X-ray and magnetic data for di-heterocyclic-*N*-oxide-bridged binuclear copper(II) compounds are collected in Table 4. In Figs. 7 and 8 we illustrate, as representative examples, the structure of $Cu(pyNO)Br_2$ [97] and $Cu(4\ CH_3pyNO)_2Cl_2$ [102]. The copper(II) atoms in $Cu(pyNO)Br_2$,

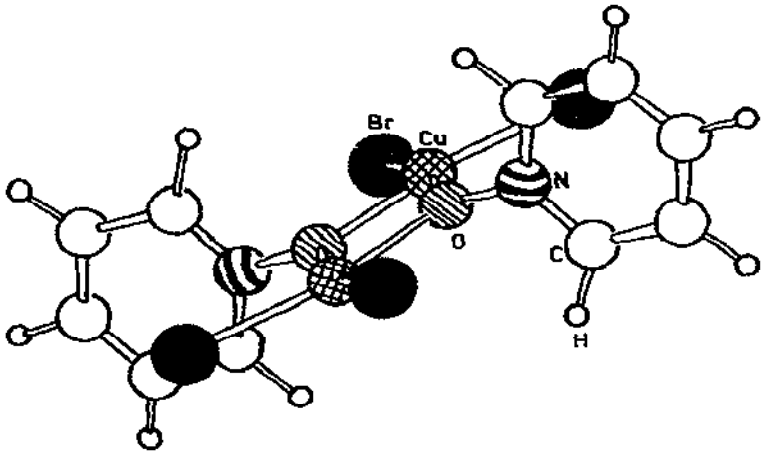


Fig. 7. A schematic view of the molecular structure of $[Cu(pyNO)Br_2]_2$ [97].

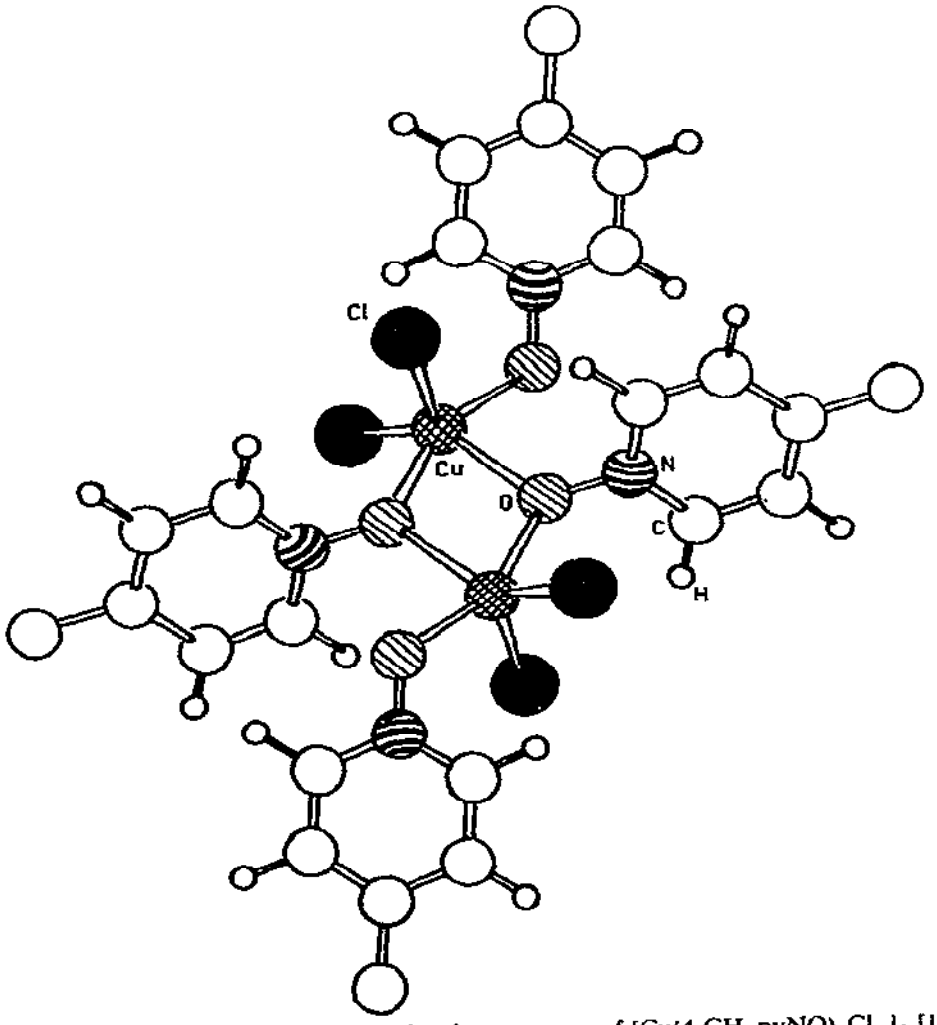


Fig. 8. A schematic view of the molecular structure of $[Cu(4\text{-}CH_3pyNO)_2Cl_2]_2$ [102].

TABLE 4

Structural and magnetic data for di-heterocyclic *N*-oxide-bridged binuclear copper(II) compounds

Compound	Space group	*Z*	Cu–Cu (Å)	Cu–O (bridge) (Å)
$[Cu(pyNO)Br_2]_2$	$P2_1/c$	2	3.244 (2)	1.994 (6) 1.965 (9)
$[Cu(pyNO)Cl_2]_2$	$P2_1/b$	2	3.245 (4)	1.979 (11) 2.036 (11)
$[Cu(pyNO)_2Br_2]_2$	$P\bar{1}$	2	3.336	1.975 2.162
$[Cu(pyNO)(DMSO)Cl_2]_2$	$P2_1/c$	4	3.342 (3)	2.050 (7) 2.050 (6)
$[Cu(4\,CH_3pyNO)_2Cl_2]_2$	$P2_1/n$	2	3.348 (2)	1.957 (6) 2.153 (6)
$[Cu(pyNO)_2(NO_3)_2]_2$	$P2_1/n$	4	3.458	1.951 (5) 1.968 (5)
$[Cu(4\,CH_3OpyNO)_2(NO_3)_2]_2$	$P\bar{1}$	1	3.529	1.940 (6) 2.578 (5)

[a] The chemical identity of the coordinated atom is specified in this column. [b] The sum of length is defined as the mean of all five distances plus half value of Cu–Cu distance.

$Cu(pyNO)Cl_2$, $Cu(pyNO)_2Br_2$, $Cu(pyNO)(DMSO)Cl_2$, and $Cu(4\,CH_3pyNO)_2Cl_2$ are in a distorted square-based pyramidal and in $Cu(pyNO)_2(NO_3)_2$ and $Cu(4\,CH_3OpyNO)_2(NO_3)_2$ are in a distorted tetragonal pyramidal environment. Anions occupy the axial positions except for $Cu(pyNO)(DMSO)Cl_2$, $Cu(pyNO)_2(NO_3)_2$ and $Cu(4\,CH_3OpyNO)_2(NO_3)_2$, where DMSO, pyNO and $4\,CH_3OpyNO$ molecule coordinate in the axial position.

From the data in Table 4 we see that the oxygen bridging system contains unequal Cu–O bonds, except for $Cu(pyNO)(DMSO)Cl_2$. The distorted copper–oxygen bridging system is consistent with a reduction in the efficiency of the super-exchange mechanism. The elongation of the Cu–O bond reduces the overlap of the magnetic orbitals and leads to a reduction in

Cu–L [a] (Å)		Cu–O–Cu (deg.)	O–Cu–O (deg.)	$\Sigma(r)$ [b] (Å)	$-J$ (cm^{-1})	Ref.
Br	2.332 (2)	110.1 (4)	69.9 (3)	13.38	935	97, 98
Br	2.333 (2)					
Br	3.130 (3)					
Cl	2.206 (5)	107.8 (6)	72.2 (1.0)	12.90	616	99, 98
Cl	2.218 (5)					
Cl	2.836 (5)					
O	1.944	107.4		12.66	242	100, 98
Br	2.401					
Br	2.507					
Cl	2.243 (3)	109.2 (3)	70.8 (3)	12.55		101
Cl	2.260 (4)					
O	2.279 (6)					
O	1.925 (5)	109.0 (2)	71.0 (2)	12.32		102
Cl	2.258 (3)					
Cl	2.354 (3)					
O	1.966 (5)	102.9	77.1	12.02	15	103, 104, 107
O	1.967 (5)					
O	2.439 (6)					
O	1.930 (6)		78	12.17	2	105, 106
O	1.977 (7)					
O	1.982 (7)					

the magnitude of the exchange interaction. There exists the tendency for elongation of Cu–L (apical) bond length with the shortened Cu–Cu distance. While the Cu–Cu distance is shortened from 3.53 Å in $Cu(4CH_3OpyNO)_2(NO_3)_2$ to 3.24 Å in $Cu(pyNO)Br_2$, the Cu–L (apical) distance is extended from 1.98 to 3.13 Å, respectively. This is consistent with the "plasticity" of the copper environment [147].

It is interesting that while in the case of di-μ-hydroxo- and di-alkoxo-bridged binuclear copper(II) compounds antiferromagnetic coupling increases with increase of Cu–Cu distance as well as of Cu–O–Cu bridge angle (Tables 2 and 3), in the case of di-aryloxo-bridged binuclear copper(II) compounds. The opposite occurs (Table 4). Another factor of interest is the sum of all interatomic distances around copper(II), which simultaneously

decreased with increase in the Cu–Cu distances (Table 4). For instance, the Cu–Cu distance in $Cu(pyNO)Br_2$ is 3.24 Å and the sum of interatomic distances around copper(II) is 13.38 Å but the value of antiferromagnetic coupling is 935 cm^{-1}, in contrast to the value of 2 cm^{-1} observed for $Cu(4\,CH_3OpyNO)_2(NO_3)_2$, where the Cu–Cu distance is 3.53 Å and the sum of interatomic distances is only 12.17 Å. It seems that bigger values of the sum are consistent with a decrease of π bonding effects and consequent increase in the antiferromagnetic interactions [85]. Another factor which could be of interest is the value of Cu–O–Cu bridge angle which can have a large influence on the magnetic coupling; it seems that a large angle stabilizes antiferromagnetic coupling [85]. On the basis of the above discussion we can expect in $Cu(pyNO)(DMSO)Cl_2$ and $Cu(4\,CH_3pyNO)_2Cl_2$ a strong antiferromagnetic interaction with a singlet ground state. It is interesting that while in $Cu(4\,CH_3OpyNO)_2(NO_3)_2$ a singlet ground state was found, [106], in $Cu(pyNO)_2(NO_3)_2$ a triplet ground state [107,108] was observed.

The crystal and molecular structure of tetraaquobis(μ-hippurato-O)-bis(hippurato-O)dicopper tetrahydrate, $[Cu(C_6H_5CONHCH_2COO)_2 \cdot (H_2O)_2]_2 \cdot 4\,H_2O$ [109] reveals that the compound exists as a dimer (Cu–Cu = 3.33 Å) with each copper having distorted (4 + 1) tetragonal-pyramidal geometry. Each copper(II) atom is uniquely coordinated to one hippurate ion (Cu–O = 1.91 Å) and two water molecules ($Cu–OH_2$ = 2.00 Å) and shares coordination to two other hippurate ions which act as bridges in the dimer with Cu–O distances of 1.93 and 2.37 Å; the Cu–O–Cu bridge angle is 101.0°. The hippurate ions coordinate only through the terminal carboxyl oxygen in a monodentate arrangement. The value of the singlet–triplet splitting, $2J = -4.3$ cm^{-1}, [110], support the facts discussed above.

TABLE 5

X-ray and magnetic data for di-oxo-bridged binuclear Schiff base copper(II) compounds (type I)

Compound	Cu–Cu (Å)	Cu–O [a] (Å)	Cu–O (Å)	Cu–N (Å)
$[Cu(N\text{-}CH_3sal)Cl]_2$	3.041 (1)	1.992 (7)	1.915 (7)	1.94 (1)
$[Cu(N\text{-}Etsal)Br]_2$	3.05 (1)	1.96 (1)	1.89 (1)	1.95 (2)
$[Cu(cbpb)Br]_2$	3.019 (7)	1.95 (2)	1.96 (2)	2.01 (2)
$[Cu(N\text{-}Etsal)Cl]_2$	3.051 (1)	1.966 (3)	1.923 (3)	1.950 (4)

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average e.s.d.'s for an individual distance or angle.

Le May et al. [111] have investigated di-μ-(benzyloxo)-bis(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II) and found that the compound consists of discrete binuclear units well separated from one another with a Cu–Cu distance of 2.970(2) Å and a Cu–O–Cu bridge angle of 102.1(2)°. The geometry around the copper is approximately square planar, with Cu–O distances ranging from 1.883(5) to 1.910(5) Å. The four oxygen atoms coordinated to each copper and the copper atom lie approximately in a plane. The deviation from planarity, τ, is 10.2°. The compound exhibits an antiferromagnetic exchange interaction, $2J$, of -647 cm^{-1} [111]. This magnitude of $2J$ is much larger than that observed for analogous di-oxo-bridged compounds (Tables 2–4), and is taken as evidence in support of the conclusion that enhanced electron density at the bridge causes an increase in interaction [111].

F. X-RAY AND MAGNETIC DATA FOR BINUCLEAR COPPER(II) COMPOUNDS WITH DI-OXO-BRIDGING SCHIFF BASES, AND SOME RELATED LIGANDS

Figure 9 provides a stereoscopic view of a Schiff base binuclear copper(II) compound (type I) and Table 5 contains the X-ray and magnetic data for such compounds. All four structures contain well separated, neutral binuclear units with a crystallographic centre of symmetry which requires the two copper and two oxygen atoms to lie in a plane. In the binuclear structure the basal plane around each copper(II) atom is built up by two oxygen atoms, one nitrogen and one halogen atom. The non-planarity of the copper(II) environment $(CuNOX)_2$ (X = Cl or Br), is conveniently measured by the dihedral angle, τ, between the Cu_2O_2 plane and the plane of the remaining ligands (Fig. 10). τ ranges from 0 to 90° with distortion from a planar to a tetrahedral environment.

Cu–X [b] (Å)		Cu–O–Cu (deg.)	O–Cu–O (deg.)	τ [c] (deg.)	$-J$ (cm^{-1})	Ref.
Cl	2.202 (4)	102.2 (2)	77.8 (2)	39.3	146	112, 113
Br	2.34 (3)	104.6 (2)	75.4 (2)	35.7	205	112, 113
Br	2.304 (6)	101.2 (9)	78.8 (8)	35.5	220	114
Cl	2.202 (1)	103.3 (2)	76.7 (2)	33.1	240	112, 113

[b] The chemical identity of the atom is specified in this column. [c] The degree of distortion between the plane of the Cu_2O_2 bridge and that of the remaining ligands.

The Cu–O bridging distances are in the range of 1.89–1.99 Å with the average bond distance being 1.94 Å, which is greater than those found in binuclear di-μ-hydroxo- and di-alkoxo-bridged copper(II) compounds (Tables 2 and 3), but smaller than those found in binuclear di-aryloxo-bridged

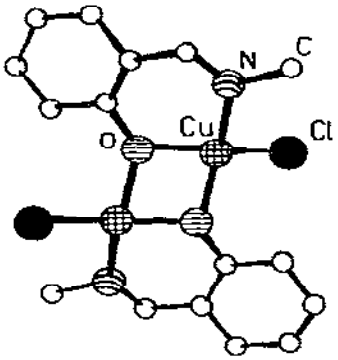
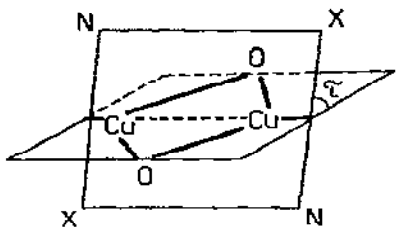


Fig. 9. A perspective view of the molecular structure of $[Cu(N\text{-}CH_3sal)Cl]_2$ (type I) [112].

copper(II) compounds (Table 4). From the data in Table 5 no systematic relation between the magnetic interactions and Cu–Cu distance and the Cu–O–Cu bridge angle in the compounds can be seen. This does not mean that this angle is unimportant, but merely that it does not vary enough to play a significant role.

Table 5 gives τ and J values, which demonstrate correlation between these two quantities [114,115]. The antiferromagnetic interaction is increased with decreased value of τ. The strength of antiferromagnetic interactions decreases, as distortion from planarity increases toward tetrahedral [116]; the data in Table 5 are consistent with this conclusion.

In Fig. 11 we illustrate, as a representative example of type II, the



X = O, Cl or Br

Fig. 10. A schematic view of the dihedral angle, τ, between the Cu_2O_2 plane and the plane of the remaining ligands.

structure of $[Cu(hpnba)]_2$ [117]. X-ray and magnetic data of such compounds are given in Table 6. The binuclear structures are held together by di-oxo-bridges between the copper(II) atoms, and the ligand environments of the metal are quite close to square planar.

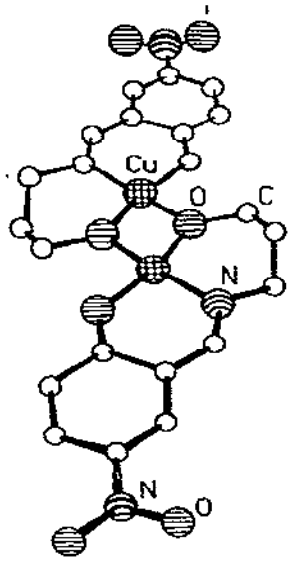


Fig. 11. A perspective view of the molecular structure of $[Cu(hpnba)]_2$ (type II) [117].

Inspection of the data in Table 6 reveals that the Cu–O bridging distances are in the range 1.89–1.925 Å with an average of 1.91 Å. which is smaller than those found in binuclear copper(II) compounds discussed in the sections above. The average Cu–O–Cu bridge angle is 104.6°, which is greater than those of 102.8° found in type I compounds (Table 5). From the comparison of data for type I and type II compounds large differences can be seen between the strengths of super-exchange interaction. Compounds of type II exhibit larger antiferromagnetic exchange interactions than those of type I. A few arguments can be presented. In the compounds of type II the value of τ is smaller than that found for type I, the average value of the Cu–O–Cu bridge angle in type II is larger, but the average value of the Cu–O bridge distance through which the demagnetization operates is smaller. than those observed for compounds of type I. These results demonstrate that while the correlation between the copper geometry and strength of antiferromagnetic interaction is quite well supported for compounds of type I (Table 5), for type II the correlation is not confirmed. It seems that the value of τ, at least in the range 7–14°, has no very important influence on the strength of magnetic interaction. Hence, as was noted above, smaller values

TABLE 6

X-ray and magnetic data for binuclear Schiff base copper(II) compounds (type II)

Compound	Cu–Cu (Å)	Cu–O [a] (bridge) (Å)	Cu–N (Å)	Cu–O (Å)	Cu–O–Cu (deg.)	O–Cu–O (deg.)	τ [b] (deg.)	$-J$ (cm^{-1})	Ref.
$[Cu(hpnba)]_2$	3.0	1.89 (3)	2.04 (2)	1.93 (2)	106.1 (10)	73.9 (10)	4.0	⩾500	117
$[Cu(hpmba)]_2$	3.0	1.922 (7)	1.978 (8)	1.871 (7)	104.2 (3)	75.8 (3)	7.0	⩾400	117
$[CuC_{10}H_{10}N_2O_4]_2$	3.0	1.917 (2)	1.939 (3)	1.892 (2)	103.4 (1)	76.6 (1)	9.6	⩾400	115, 118
$[Cu(pia)]_2$	3.026 (6)	1.89 (1)	1.83 (1)	1.96 (2)	106.4 (6)	73.6 (6)	10.0	[c]	119
$[CuC_{14}H_{13}NO_2]_2$	3.0	1.914 (4)	1.932 (6)	1.883 (4)	104.0	76	10.4	⩾400	115, 118
$[CuC_{10}H_{10}NO_2Cl]_2$	3.0	1.925 (1)	1.943 (2)	1.886 (1)	103.6	76.4 (1)	13.7	⩾400	115, 118

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. [b] The degree of distortion between the plane of the Cu_2O_2 bridge and that of the remaining ligands. [c] $\mu_{eff} = 0.41$ B.M., at room temperature.

TABLE 7

X-ray and magnetic data for binuclear Schiff base copper(II) compounds (type III)

Compound	Cu–Cu′ (Å)	Cu–O Cu–O′ (bridge) (Å)	Cu′–O Cu′–O′ (bridge) (Å)	Cu–N (Å)	Cu′–Cl (Å)	Cu–O–Cu′ Cu–O′–Cu′ (deg.)	O–Cu–O′ O–Cu′–O′ (deg.)	$-J$ (cm^{-1})	Ref.
(Cues)$CuCl_2$		1.89 (1) 1.92 (1)	2.30 (1) 1.98 (1)	1.90 (1) 1.91 (1)	2.288 (5) 2.240 (5)	95.3 (4) 105.7 (5)	85.0 (5) 73		120
(Cu-1,3-ps)$CuCl_2$		1.94 (1) 1.96 (1)	2.01 (1) 1.96 (1)	1.95 (1) 1.96 (1)	2.179 (5) 2.176 (5)	101.4 (5) 103.0 (5)	77.7 (5) 76.1 (5)	49	120, 121
$[Cu(N\text{-}CH_3sal)Cl]_2$	3.01	1.90 1.88	1.91 2.06	1.95 1.93	2.19 2.18		80 75	147	112, 122
(Cucha)$CuCl_2$	3.006	1.871 (6) 1.896 (6)	1.952 (7) 2.097 (6)	1.928 (8) 1.910 (7)	2.180 (3) 2.181 (3)	103.7 (3) 97.5 (3)	81.9 (3) 75.0 (3)	236	113, 121

of both τ and the Cu–O bridge, but a larger Cu–O–Cu bridge angle brings about an increase in the magnitude of J.

X-ray and magnetic data for binuclear copper(II) compounds derived

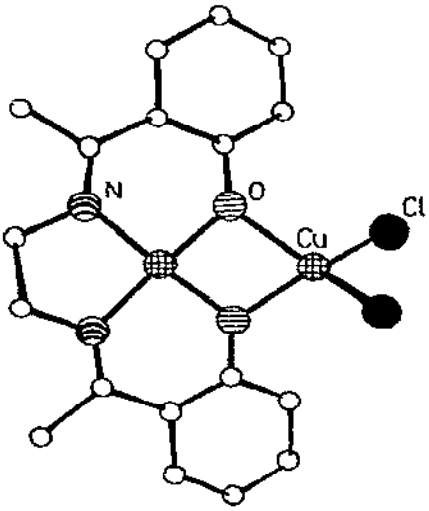


Fig. 12. A perspective view of the molecular structure of (Cueha)$CuCl_2$ (type III) [113].

TABLE 8

X-ray and magnetic data for binuclear pentacoordinated copper(II) compounds with Schiff bases and some related ligands

Compound	Cu–Cu (Å)	Cu–O [b] (bridge) (Å)		Cu–N (Å)
$Cu_2(fsa)_2en \cdot CH_3OH$	2.942	Cu (1)	1.913 (3)	1.901 (4)
		Cu (2)	1.919 (3)	
$[CuC_{11}H_{11}NO_2]_2$	2.989 (3)	Cu (1)	1.966 (9)	1.974 (11)
		Cu (2)	1.967 (9)	2.002 (9)
$[CuC_{16}H_{14}N_2O_2]_2$	3.18		2.22	2.01
$[Cu(CH_3sal)hfa]_2$	3.181		2.173 (4)	1.959 (4)
$[Cu(N\text{-chsal})]_2$ [a]	3.383 (3)		2.26 (1)	2.03 (1)
γ-$[Cu(N\text{-}CH_3sal)]_2$			2.17 (1)	1.96 (1)
γ-$[Cu(C_{12}H_{10}NO)_2]_2$			2.250 (4)	1.978 (4)
β $[Cu(8\text{-}OHquin)_2]_2$			2.372	1.973

[a] Green form. [b] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. [c] Cu–basal plane (Å). [d] $\theta = 4$ K.

from the tetradentate salicylaldimine derivatives are given in Table 7. While the binuclear compounds derived from the bidentate salicylaldimines have a so-called *trans* structure (type I, Fig. 9), the analogous tetradentate salicylaldimines have *cis* structures (type III, Fig. 12). In the *trans* structure each copper atom is uniquely coordinated, but the *cis* structure contains copper atoms with two different stereochemistries. There is a weaker antiferromagnetic interaction in the sequence (Cueha)$CuCl_2$ > [Cu(*N*-CH_3sal)Cl]$_2$ > (Cu-1,3-ps)$CuCl_2$. The distances and angles within the salicylaldimine bridges show no features which can be associated with such a trend in the magnetic interaction but provide a rational basis for the design of additional experiments.

It is clear that the magnitude of the superexchange interaction through the oxygen bridges increases sensibly through the series: quadridentate Schiff base (type III) ≤ bidentate Schiff base (type I) < terdentate Schiff base (type II). This is not in good agreement with the proposal [123] that the magnitude of interaction increases in the order quadridentate Schiff base < terdentate Schiff base < bidentate Schiff base. Note that the proposal [123] included many examples without knowledge of their X-ray crystal structure data.

In Table 8 are summarized X-ray and magnetic data for di-oxo-bridged

Cu–O (Å)	Cu–O (axial) (Å)	Cu–O–Cu (deg.)	O–Cu–O (deg.)	$-J$ (cm^{-1})	Ref.
	2.266 (4)	99.9 (1)	80.0 (1)	650	124
1.878 (3)	(0.20) [c]	100.3 (1)	79.5 (1)		
1.880 (12)		97.1 (4)	78.3 (4)	298	125, 126
1.900 (10)	2.64	100.7 (4)	78.3 (4)		
	(0.036) [c]				
1.91	2.41	91	89	[d]	127–129
1.969 (4)	2.450 (4)	93.2 (1)	86.8 (1)	<4.2	130, 131
	(0.095) [c]				
1.90 (1)	2.62	95.3 (5)	80.1 (4)		132
1.88 (1)	2.44 (1)	100.4 (8)	79.6 (8)		133
	(0.12) [c]				
1.917 (4)	2.600 (1)	96.0 (2)	84.0 (1)		134
1.935	2.830			1	135, 136

binuclear copper(II) compounds, where copper(II) atoms are pentacoordinate, with Schiff bases and some related ligands. The structure of $Cu_2(fsa)_2en \cdot CH_3OH$ [124] and $[CuC_{11}H_{11}NO_2]_2$ is composed of non-symmetrical binuclear units in which one copper has a distorted square-pyramidal configuration whereas the other has a square-planar coordination. In the other compounds (Table 8) each copper atom is pentacoordinated in a distorted square-pyramidal configuration ($[CuC_{16}H_{14}N_2O_2]_2$, $[Cu(CH_3sal)hfa]_2$, $[Cu(N\text{-}chsal)]_2$, γ-$[Cu(N\text{-}CH_3sal)]_2$) or in a tetragonal pyramidal coordination (γ-$[Cu(C_{12}H_{10}NO)_2]_2$, β-$[Cu(8\text{-}OHquin)_2]_2$).

There is a similar trend, between the Cu–O (axial) distance and the displacement of the copper atom out of the basal plane, as in the earlier sections. While the Cu–O (axial) distance decreases, the displacement of the copper(II) atom from the basal plane increases in the direction of the axial ligand (Table 8). In spite of the fact that there are different kinds of ligands, there exists a relationship between X-ray data and magnetic interaction. Elongation of both the Cu–Cu and Cu–O bridge distances, as well as a larger distortion of the geometry around the copper(II) atom is reflected in a decrease in the magnetic interaction.

The crystal structure of Cu(glycyl-L-histidyl-glycine) $\cdot x H_2O$ was determined by Österberg and Sjöberg [137]. The structure of the compound consists of binuclear units with copper–copper distances of 3.5 Å. Each binuclear unit is surrounded tetrahedrally by four other such units. Each copper atom is five-fold coordinated to three nitrogen atoms (Cu–N = 1.97, 2.02 and 2.04 Å) and two oxygen atoms (Cu–O = 2.00 and 2.53 Å). The two

TABLE 9

X-ray and magnetic data for heterobinuclear compounds with $(fsa)_2en$

Compound	Cu–M (Å)	Cu–O [a] M–O (Å)	Cu–N M–O (Å)
$Cu^{II}Fe^{III}(fsa)_2en \cdot ClH_2O(CH_3OH)_2$		1.928 (6)	1.910 (8)
		2.028 (6)	1.930 (6)
$Cu^{II}Co^{II}(fsa)_2en \cdot 3\ H_2O$	3.025 (2)	1.909 (5)	1.915 (6)
		2.065 (4)	1.995 (5)
$Cu^{II}Co^{II}(fsa)_2en \cdot 6\ H_2O$		1.890 (4)	1.886 (5)
		2.000 (4)	1.947 (4)
$Cu^{II}Mg^{II}(fsa)_2en \cdot 3\ H_2O$	3.001 (4)	1.920 (3)	1.917 (3)
		2.049 (3)	
$Cu^{II}VO^{II}(fsa)_2en \cdot CH_3OH$			

[a] Where more than one chemically equivalent distance is present, the mean value is tabulated. [b] O atom from CH_3OH. [c] Atom from H_2O.

copper atoms are bridged together by two oxygen atoms of the carboxylic groups.

The study of homobinuclear compounds with paramagnetic metallic centers is still a very active field in coordination chemistry. The study of heterobinuclear compounds takes on increasing importance. Such compounds already have led to a more advanced understanding of the mechanism of exchange interaction. The first study focusing on the magnetic behaviour of a heterobinuclear compound with paramagnetic centers was by Okawa et al. [141]. The knowledge of the structure is often necessary and always useful to interpret the magnetic behaviour. To our knowledge, the first example of a crystal structure of a heterobinuclear compound with copper(II) and some other paramagnetic center dates only from 1978. The X-ray and magnetic data for such compounds are collected in Table 9. In these compounds the central atoms are bridged together by the phenolic oxygen atoms of $(fsa)_2en$. It is interesting that in all cases (Table 9) each copper(II) atom is located in the "inside" N_2O_2 site of the bichelating ligand and other central atoms in the "outside" O_2O_2 site. In recent papers [142,145] detailed discussions of the crystal structural data and an exchange interaction of the compounds have been presented and will not be considered here.

G. CONCLUSIONS

In a recent paper [146] it was shown that the copper–copper distances in the binuclear copper(II) halogenocarboxylates are increased when the pK_a

Cu–L (axial) (Å)		M–L (axial) (Å)		M (out-of-plane) (Å)		Cu–O–M (deg.)	J (cm^{-1})	Ref.
O[b]	2.277 (7)	Cl	2.303 (3)	Cu	0.212	100.7 (3)	−96.2	138
		O[c]	2.150 (7)	Fe	0.141	99.4 (3)		
		O[c]	2.137 (5)	Co	0.07	99.1 (2)	35	139–141
O[c]	2.784 (5)	O[c]	2.072 (5)	Cu	0.031	100.2 (4)		142
(O[c]	2.942	O[c]	3.2)	Co	0.268	99.8 (3)		
		O[c]	2.115 (3)			98.2 (1)		143
							118	144

value of the respective acid is decreased, but at the same time the Cu–L (axial) distances have the tendency to contract. Such a tendency can be seen in the copper(II) carboxylates presented here. When the Cu–Cu distance is increased there is a concomitant increase in the displacement of the copper atom out of the basal plane toward the apical ligand. Binuclear copper(II) carboxylates with the CuO_4N chromophore where the average distance and angle of bridging Cu–O–C–O–Cu are 6.42 Å and 175°, have the average value of $2J = -348$ cm^{-1}; with the CuO_5 chromophore these values are 6.44 Å, 170° and -316 cm^{-1}, respectively. This indicates the sensitivity of the value of $-2J$ to the Cu–O–C–O–Cu bridge distance and angle through which the demagnetization operates. The elongation of the Cu–O–C–O–Cu bridge distance, but contraction of the angle, is reflected in a decrease in the value of $-2J$. The apical ligands clearly play a role in determining the $2J$ value observed, which increases according to the following series of apical ligands: water ≤ urea ≤ anhydrous < pyridine ~ pyrazole < quinoline ≤ picoline ~ NCS < dioxane.

Inspection of the data for di-μ-hydroxo-bridged binuclear copper(II) compounds reveals that the copper-bridging oxygen bond distances increase in the order of diamines: aliphatic < mixed aliphatic/aromatic < aromatic, but the copper–copper distance is shortened in the same order. There exists a trend for a movement of the copper atom from the basal plane toward the apical ligand with a decrease of the out-of-plane copper–oxygen bond distances. There is a correlation between the structural data and the singlet–triplet splitting. The elongation of the Cu–Cu distance is reflected in a simultaneous opening of the Cu–O–Cu bridging angle and at the same time a transition from a ferromagnetic to antiferromagnetic coupling. The ground state is triplet if the Cu–O–Cu bridge angle is 90–97.7° and the p character of the oxygen bonding orbitals decreases. The ground state is singlet if the Cu–O–Cu bridge angle is > 97.7° ($2J$ equals zero at 97.7°) and an increased value of this angle implies greater s character in the bridging orbitals and this produces an increase of antiferromagnetic coupling.

In di-alkoxo-bridged binuclear copper(II) compounds, where the coordination geometry of the central atom is five coordinate tetragonal pyramidal, the displacement of the metal from the basal plane increases in the direction of the axial ligand with decrease of the out-of-plane copper–ligand distance, as in the case of di-μ-hydroxo-bridged binuclear copper(II) compounds. Also between the structural parameters and magnetic interaction in di-alkoxo-compounds there exists a similar trend as in the di-μ-hydroxo-compounds.

In the case of di-aryloxo-bridged binuclear copper(II) compounds antiferromagnetic coupling weakens with the extension of the copper–copper distance, opposite to the compounds discussed above. While in the di-μ-hydroxo- and di-alkoxo-compounds the sum of all interatomic distances

around copper(II) is almost constant, in the di-aryloxo-compounds the sum decreases with increase in the copper–copper distance. With increase of the value of the sum the antiferromagnetic interaction also increases.

In the binuclear copper(II) compounds with Schiff base the antiferromagnetic interaction strengthens with a lower value of τ. From the structural point of view a super-exchange interaction weakens in the order: type II (quadridentate Schiff base) $>$ type I (bidentate Schiff base) $\geqslant$ type III (terdentate Schiff base).

From the above it may generally be said that:

(1) Displacement of the copper atom from the basal plane usually increases in the direction of the axial ligand with decrease of the out-of-plane copper–ligand distance.

(2) There is insensitivity of the singlet–triplet separation to the copper–copper distance in the binuclear copper(II) carboxylates and Schiff base compounds.

(3) There is sensitivity of a super-exchange interaction to the copper–copper distance in the di-μ-hydroxo, di-alkoxo- and di-aryloxo-binuclear compounds.

(4) There is strengthening of magnetic interaction with shortening of the bridge distance but opening of the bridge angle through which the demagnetization operates.

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