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MONO-, BI-, TETRA- AND POLYNUCLEAR COPPER(II) HALOGENO-CARBOXYLATES

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CONTENTS

ABBREVIATIONS

A	1-phenyl-2,3-dimethyl-5-pyrazolone (antipyrine)
4 acpyNO	4-acetyl-pyridine N-oxide
an	aniline
4 Bran	4-bromoaniline
3 Brpy	3-bromopyridine
3,5 Br_2sal	3,5-$Br_2C_6H_2OHCOO^-$
5 Brsal	5-$BrC_6H_3OHCOO^-$
$C_4H_8O_2$	1,4-dioxane
$C_5H_8O_2$	acetylacetonate

$C_{10}H_{26}Cl_4N_4O_6$	reaction product of copper(II) dichloroacetate and 1,3-diamino-2-propanol
4 Clan	4-chloroaniline
2 Clpy	2-chloropyridine
4 ClpyNO	4-chloropyridine N-oxide
5 Clsal	$5\text{-}ClC_6H_3OHCOO^-$
$dipyO_2$	2,2-dipyridyl-N,N-dioxide
DMF	dimethylformamide
en	ethylenediamine
EPR	electron paramagnetic resonance
2 Etpy	2-ethylpyridine
5 Isal	$5\text{-}IC_6H_3OHCOO^-$
2,3-lut	2,3-lutidine
2,6-lut	2,6-lutidine
3,5-lut	3,5-lutidine
nic	3-(1-methyl-3-pyrrolidinyl)pyridine (nicotine)
4 NO_2pyNO	4-nitropyridine N-oxide
β-nquin	β-naphthoquinoline
Ph_3AsO	triphenylarsine oxide
Ph_3PO	triphenylphosphine oxide
2 pic	2-picoline
3 pic	3-picoline
4 pic	4-picoline
2 picNO	2-picoline N-oxide
3 picNO	3-picoline N-oxide
4 picNO	4-picoline N-oxide
1,2 pn	1,2-propanediamine
1,3 pn	1,3-propanediamine
py	pyridine
PyO	pyridine N-oxide
quin	quinoline
i-quin	isoquinoline
sal	$C_6H_4OHCOO^-$
3-tol	3-toluidine
4-tol	4-toluidine
TTA	thenoyltrifluoroacetate

A. INTRODUCTION

The solvated copper(II) carboxylates have been the subject of numerous publications [1—8]. Different possible coordination characteristics of the carboxyl group lead to the existence of mononuclear, binuclear or polymeric structures.

Copper(II) compounds have occupied a special place in the study of intramolecular magnetic exchange for a number of reasons. Magnetic susceptibility

measurements, particularly on copper(II) carboxylates, showed a large number of examples where the paramagnetic ions were antiferromagnetically coupled [1,8]. Potential problems such as orbital contributions, degenerate ground state and proliferation of accessible energy levels tend to be minimized in such systems, thus permitting concentration on the more fundamental aspects of the exchange process. Previous reviews of copper(II) carboxylates have concentrated on spectral and magnetic data mostly of copper(II) compounds with unsubstituted carboxylic acids.

We review herein the structural, magnetic and spectral properties of copper(II) halogenoacetates, copper(II) halogenopropionates, copper(II) halogenobenzoates and copper(II) halogenosalicylates. This work has been based on the premise that, despite the considerable literature on binuclear copper(II) compounds, no such review exists.

B. COPPER(II) HALOGENOACETATES

(i) Structural data—binuclear compounds

A large number of copper(II) carboxylates are binuclear. The most widely studied, and one of the simplest paramagnetic species, is copper(II) acetate monohydrate. Van Niekerk and Schoening's [9,10] investigation of the crystal structure of copper(II) acetate monohydrate has shown that the copper(II) ions occur in isolated pairs in the crystal. In copper(II) acetate monohydrate (Fig. 1) the metal—metal distance of 2.61 Å [11,12] (1 Å = 0.1 nm = 10^{-10} m) is only slightly longer than the 2.56 Å [13] separation in copper metal itself.

In Table 1 are collected structural data for some copper(II) halogenoacetates with the bridged binuclear structure. An attempt has been made to make this list complete to the end of 1978. The structure of copper(II) acetate monohydrate has been redetermined by independent X-ray [11] and neutron diffraction studies [12]. Results of both determinations, which

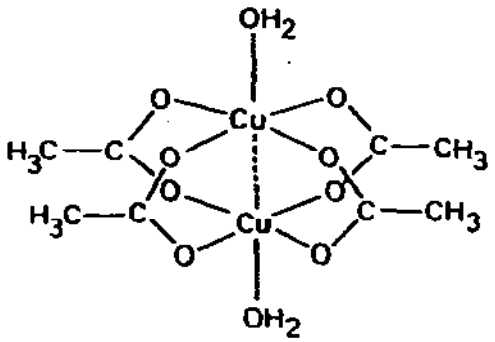

Fig. 1. A schematic view of the crystal structure of copper(II) acetate monohydrate [10].

TABLE 1

Structural data for binuclear copper(II) halogenoacetates and copper(II) acetate monohydrate

Compound	Cu—Cu (Å) [a]	Cu—O (basal) (Å)	Cu—L (apical) (Å)		O—C (Å)	Cu—Basal plane (Å)	Cu—O—C (deg.)	O—C—O (deg.)	Ref.
$Cu(CH_3COO)_2 \cdot H_2O$ [b]	2.614(2)	1.969(2)	O [c]	2.161(2)	1.259(2)	0.19	123.0(1)	124.9(1)	12
$Cu(CH_3COO)_2 \cdot H_2O$ [d]	2.616(1)	1.969(3)	O	2.156(4)	1.260(6)	0.19	123.1(3)	124.8(4)	10,11
$Cu_2(CH_3COO)_{2.25} \cdot (ClCH_2COO)_{1.75}\,urea_2$	2.631	1.97	O	2.12	1.26	0.21	123.6(2)	124.5(3)	52
$Cu(ClCH_2COO)_2$ urea	2.643	1.97	O	2.10	1.28	0.208	123.5	121.1	14
$Cu(FCH_2COO)_2$ urea	2.665	1.974(7)	O	2.102(7)	1.25	0.212		126.8	15
$Cu(ClCH_2COO)_2$ 3 pic	2.685(2)	1.974	N	2.269(4)	1.235	0.228	122.7(7)	127.8	16
$Cu(ClCH_2COO)_2$ quin	2.724(2)	1.973(5)	N	2.211(7)	1.24(1)	0.248	122.8(8)	128(1)	17
$Cu(FCH_2COO)_2$ quin	2.725(1)	1.976(2)	N	2.210(3)	1.252(2)	0.239		127.5(4)	18
$Cu(ClCH_2COO)_2$ 2 pic	2.747(3)	1.974(9)	N	2.161(10)	1.247(17)	0.26	123.8(8)	127.3	19
$Cu(Cl_3CCOO)_2$ 2 Clpy	2.766(3)	1.957(5)	N	2.145(5)	1.225	0.28	123.8	128.4	20
$Cu(F_3CCOO)_2$ quin	2.886(2)	1.972(8)	N	2.109(6)	1.242(10)	0.321	124.7(6)	129.3(8)	21

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

[b] Neutron diffraction results.

[c] The chemical identity of the apical atom is specified in this column.

[d] X-ray diffraction results.

agree exceedingly well with each other, are also included in Table 1 for comparison.

Some important trends can be seen in Table 1. The Cu—Cu distances are elongated when the acid strength increases. In this connection, however, it should be noted that the axial ligand also plays a role in determining the metal—metal distance [20]. In fact, longer distances have been found in binuclear compounds in which the axial ligand is more bulky and has some substitution in the neighbourhood of the donor atom.

However, the Cu—O (basal) distance is almost constant (1.97 Å) for all the copper(II) compounds listed in Table 1; moreover the sum of all interatomic distances in CuO_5 and CuO_4N (half the value of the Cu—Cu distances were also included in the sum of each chromophore) is almost constant and is approximately 11.33 Å and 11.42 Å, respectively.

The major structural change accompanying the elongated metal—metal distance is a movement of the metal ion out of the basal plane of its square pyramidal coordination polyhedron. The Cu-basal plane distance is also elongated from 0.19 Å in $Cu(CH_3COO)_2 \cdot H_2O$ to 0.32 Å in $Cu(F_3CCOO)_2$-quin. Other structural parameters show no discernible trends. Some variation exists in Cu—L (apical) distances, but this is not surprising.

(ii) Spectral and magnetic data—binuclear compounds

The short copper—copper distance in copper(II) acetate monohydrate has been recognized to be responsible for the unusual magnetic behaviour. A low molar susceptibility was recorded for this compound as early [22] as 1915. Bleaney and Bowers [23,24] on the basis of the EPR spectrum of copper(II) acetate monohydrate first recognized that the magnetic properties of this compound could be explained by including an additional spin-coupling term, $-JS_1S_2$, in the Hamiltonian used to describe the system. This term leads to a splitting J between the spin singlet and triplet states, obtained from two electrons constrained to different orbitals, of ca. 280 cm^{-1} such that, in this model, the coupling is antiferromagnetic.

Figgis and Martin [25], in their well-known discussion of the electronic structure of binuclear copper(II) acetate monohydrate discussed two models. The first was an extension of the treatment of Bleaney and Bowers [23] in which the two copper ions are regarded as weakly coupled. In the second model, Figgis and Martin, using arguments based on a theoretical treatment by Craig et al. [26], proposed a weak σ-bond to be responsible for the pairing of the paramagnetic electrons, in accord with the expectation that the unpaired electron will be in the $d_{x^2-y^2}$ orbital. More recent calculations by Ross [27] and by Boudreaux [28] have supported this σ-bond model. Recently, Goodgame et al. [29] compared the magnetic properties and geometries of the structurally similar $Cu(CH_3COO)_2 \cdot H_2O$ and $Cu(HCOO)_2(SCN)_2$ species and observed a direct rather than inverse relation between the Cu—Cu separation and the effective exchange coupling coefficient. They

TABLE 2

Spectral and magnetic data for binuclear copper(II) halogenoacetates with copper(II) acetate for comparison

Compound	$g_\perp$	$g_\parallel$	g_{av}	$\|D\|$ (cm^{-1})	$\mu_{eff}(T)$ (B.M.)	$-2J$ (cm^{-1})	Electr. sp. ($\tilde{\nu}_{max}$ (μm^{-1}))		Ref.
							I	II	
$Cu(CH_3COO)_2$	2.084	2.385	2.19	0.338	1.39(295)	302			33, 25
						300			34
$Cu(CH_3COO)_2 \cdot H_2O$	2.08	2.42	2.20	0.34	1.40(294)	300	1.43	2.70	23, 35—40
	2.08	2.35	2.17			299			40, 41
						286			25
	$g_x = 2.053$ $g_y = 2.093$	2.344	2.17			284			39, 34
	$g_x = 2.068$ $g_y = 2.085$	2.397	2.19 [a]						42
$Cu(FCH_2COO)_2$				<0.15	1.71(299)	149	1.38	2.78	33, 43
$Cu(FCH_2COO)_2 \cdot H_2O$	$g_x = 2.068$ $g_y = 2.072$	2.393	2.18 [d]	0.374	1.32(293)	366	1.37	2.80	43—45
$Cu(FCH_2COO)_2 \cdot C_4H_8O_2$	2.090	2.405	2.20 [d]	0.370	1.21(293)	424	1.47	2.74	44
$Cu(FCH_2COO)_2$ 2 Clpy	2.062	2.371	2.17	0.380	1.14(295)	471			46
$Cu(FCH_2COO)_2$ quin	2.095	2.397	2.20	0.395			1.44	2.85	33, 47
$Cu(FCH_2COO)_2$ 2 pic					1.26(294)	384	1.41	2.70	48
$Cu(FCH_2COO)_2$ py							1.37	2.72	48
$Cu(FCH_2COO)_2$ urea	2.080	2.375	2.183	0.367					49
$Cu(FCH_2COO)_2$ A	2.056	2.385	2.175	0.386			1.28	2.73	50
$Cu(FCH_2COO)_2Ph_3PO$	2.090	2.380	2.202	0.373	1.30(297)	360	1.31	2.70	51
$Cu(FCH_2COO)(CH_3COO) \cdot$ quin $\cdot 0.5\ CH_3OH$	2.08	2.37	2.18	0.362			1.46	2.79	47
$Cu(F_2CHCOO)_2$ 2 pic					1.48(297)	375	1.28	2.70	48

$Cu(F_3CCOO)_2$ quin	2.17	2.44	2.26	0.425	1.42(300)	310			53, 21
$Cu(ClCH_2COO)_2$	2.088	2.384	2.19 [d]	0.345	1.44(291)	292	1.09 1.38	2.70	33, 54–57
$Cu(ClCH_2COO)_2 \cdot H_2O$	2.13	2.38	2.21	0.350					58
$Cu(ClCH_2COO)_2 \cdot 2\,H_2O$					1.43(295)		1.45	2.69	59, 60
$Cu(ClCH_2COO)_2 \cdot 2.5\,H_2O$	$g_x = 2.077$ $g_y = 2.078$	2.385	2.18	0.346	1.45(300)	313	1.10 1.40	2.60	45, 55
						230			61
$Cu(ClCH_2COO)_2 \cdot 4\,H_2O$					1.45(287)				54
$Cu(ClCH_2COO)_2 \cdot (CH_3)_2CO$	2.106	2.370	2.197 [d]	0.355	1.41(295)		1.43	2.63	59, 62
$Cu(ClCH_2COO)_2 \cdot 0.75\,C_4H_8O_2$	2.095	2.337	2.178 [d]	0.342	1.40(296)	352	1.44	2.63	59, 62
$Cu(ClCH_2COO)_2 \cdot CH_3COC_2H_5$					1.39(298)	355	1.15, 1.43	2.72	57
$Cu(ClCH_2COO)_2$ A	2.055	2.427	2.187	0.365			1.27	2.70	50
$Cu(ClCH_2COO)_2Ph_3PO$	2.100	2.400	2.205	0.360	1.40(298)		1.32	2.75	51
$Cu(ClCH_2COO)_2$ py							1.35	2.72	48
$Cu(ClCH_2COO)_2$ 2 pic					1.39(294)	322	1.37	2.74	48
$Cu(ClCH_2COO)_2$ 2 Clpy	2.059	2.373	2.17	0.362	1.28(294)	331			46
$Cu(ClCH_2COO)_2$ quin	2.087	2.375	2.187	0.371					33
$Cu(ClCH_2COO)_2$ β-nquin	2.072	2.377	2.178	0.370					63
$Cu(ClCH_2COO)_2$ 4-tol	2.062	2.350	2.162 [d]	0.126 [b]					64
	2.068	2.230	2.123	0.115 [b]					65
$Cu(ClCH_2COO)_2$ 3-tol	2.069	2.330	2.159 [d]	0.127 [b]					64
$Cu(ClCH_2COO)_2$ 4 Clan	2.055	2.340	2.154 [d]	0.127 [b]					64
$Cu(ClCH_2COO)_2$ an	2.065	2.340	2.160 [d]	0.124 [b]		90			64
$Cu(ClCH_2COO)_2$ urea	2.073	2.352	2.170	0.350					49

(TABLE CONTINUED on next page)

TABLE 2 (continued)

Compound	$g_\perp$	$g_\parallel$	g_{av}	$\|D\|$ (cm^{-1})	$\mu_{eff}(T)$ (B.M.)	$-2J$ (cm^{-1})	Electr. sp. ($\tilde{\nu}_{max}$ (μm^{-1}))		Ref.
							I	II	
$Cu(ClCH_2COO)(CH_3COO)$ · quin · 0.5 CH_3OH	2.07	2.38	2.178	0.357					47
$Cu(ClCH_2COO)(CH_3COO)$ · β-nquin · 0.5 CH_3OH	2.07	2.37	2.175	0.355					47
$Cu(ClCH_2COO)$-$(C_6H_5CH_2COO)$ · 4 tol	2.074	2.24	2.130 [d]	0.116 [b]		66 [c]			65
$Cu(Cl_2CHCOO)_2C_4H_8O_2$	2.099	2.387	2.199	0.362	1.49(297)		1.45	2.63	62, 66
$Cu(Cl_2CHCOO)_2(CH_3)_2CO$	2.105	2.404	2.209 [d]	0.376	1.58(296)		1.44	2.63	62, 66
$Cu(Cl_2CHCOO)_2CH_3COC_2H_5$					1.49(298)		1.13 1.34	2.70	57
$Cu(Cl_2CHCOO)_2$ 2 pic					1.50(299)		1.27	2.85	48
$Cu(Cl_2CHCOO)_2$ 2 Clpy	2.066	2.380	2.18	0.379	1.25(295)	316			46
$Cu(Cl_2CHCOO)_2$ quin	2.094	2.394	2.19	0.389					33
$Cu(Cl_3CCOO)_2CH_3COC_2H_5$					1.68(298)		1.11 1.31	2.60	57
$Cu(Cl_3CCOO)_2$ 2 Clpy	2.070	2.394	2.183	0.366	1.61(295) 1.53(294)	217 179			67, 20 46
$Cu(Cl_3CCOO)_2$ β-nquin	2.080	2.380	2.184	0.362					63
$Cu(Cl_3CCOO)_2$ 2 pic					1.68(299)		1.21		48
$Cu(BrCH_2COO)_2$	2.106	2.362	2.195 [d]	0.344	1.49(296)	254	1.47	2.63	68–71
$Cu(BrCH_2COO)_2 \cdot H_2O$					1.54(299)	259 313	1.09 1.39	2.66	71, 57 72

$Cu(BrCH_2COO)_2 \cdot 0.5\,C_4H_8O_2$	2.088	2.346	2.177 [d]	0.355	1.42(296)	295	1.54	2.67	68—70
$Cu(BrCH_2COO)_2 \cdot CH_3COC_2H_5$					decomp.		1.16 1.41	2.66	57
$Cu(BrCH_2COO)_2 \cdot A$	2.058	2.427	2.188	0.360			1.27	2.68	50
$Cu(BrCH_2COO)_2 \cdot Ph_3PO$	2.108	2.404	2.211	0.355	1.20(296)	352	1.32	2.75	51
$Cu(Br_2CHCOO)_2 \cdot 0.75\,C_4H_8O_2$	2.079	2.378	2.182 [d]	0.349	1.49(296)	273	1.55	2.70	68—70
$Cu(Br_2CHCOO)_2 \cdot CH_3COC_2H_5$					1.40(298)		1.15 1.38	2.60	57
$Cu(Br_3CCOO)_2$	2.109	2.387	2.207 [d]	0.351	1.68(300)	185	1.45	2.63	68—70
$Cu(Br_3CCOO)_2 \cdot CH_3COC_2H_5$					1.69(298)		1.12 1.32		57
$Cu(ICH_2COO)_2$	2.116	2.362	2.200	0.333	1.42(293)	280	1.49	2.56	73
$Cu(ICH_2COO)_2 \cdot H_2O$					1.49(299)	274			71
$Cu(ICH_2COO)_2 \cdot 0.5\,C_4H_8O_2$	2.110	2.362	2.197	0.329	1.42(293)	280	1.52	2.53	73
$Cu(ICH_2COO)_2 \cdot A$	2.061	2.405	2.180	0.340			1.26	2.60	50
$Cu(ICH_2COO)_2 \cdot Ph_3PO$	2.108	2.412	2.214	0.356	1.26(295)	339	1.29	2.80	51
$Cu(I_2CHCOO)_2$					1.69(300)	215			71
$Cu(I_2CHCOO)_2 \cdot H_2O$					1.66(299)	215			71

[a] By γ-irradiation of the parent compound. [b] At 77 K. [c] From EPR data. [d] Mononuclear impurity (species).

interpreted this to indicate the predominance of a super-exchange rather than of a direct mechanism of the coupling. It was demonstrated by Gerloch and Harding [30] that the antiferromagnetic exchange coupling in a binuclear copper(II) acetate is dominated by a super-exchange mechanism via the carboxylate π-bonds. A similar process was demonstrated in the case of the structurally analogous binuclear cobalt carboxylate [31,32]. The proposed super-exchange mechanism is made possible not via spin-orbit mixing of (xy) and $(x^2 - y^2)$ states but via configurational mixing of such functions caused by the close proximity of the second model atom.

Although a large number of papers have been devoted to the magnetic study of copper(II) acetate, no clear picture has yet emerged for the factors which determine the magnetic properties of the compound.

The effects of the introduction of one, two or three halogeno atoms in the methyl group of acetic acid and of axial donor ligands upon the exchange coupling constant, $-2J$, a measure of the magnitude of the copper—copper interaction are collected in Table 2.

The first copper(II) halogenoacetates were prepared by Bateman and co-workers [74,75]. All the hydrated and anhydrous copper(II) mono-, di- and trihalogenoacetates were prepared and found to be stable, except copper(II) triiodoacetate which was unstable [71]. From Table 2 we see that while only monohydrates of copper(II) monofluoro-, monobromo- and monoiodoacetate were prepared, copper(II) monochloroacetate was prepared in four hydrated forms [76]. Compounds of general formula $Cu(ClCH_2COO)_2L$ (L = cyclic N-oxide, triphenylphosphine oxide or triphenylarsine oxide) were first prepared by Paul et al. [77]. On the basis of effective magnetic moments, electronic and IR spectra, binuclear structures are predicted [77].

In an attempt to correlate the pKa values of the acids with magnetic data for copper(II) halogenoacetates, it was observed that a tendency for formation of mononuclear molecules is enhanced as the number of halogen substituents is increased [71]. This trend holds well within the series of anhydrous copper(II) fluoro-, chloro-, bromo- and iodoacetates (Table 3). The introduction of one, two or three halogeno atoms in the methyl group of acetic acid, results in an increase in the acid strength in the order $XCH_2COO^- < X_2CHCOO^- < X_3CCOO^-$ (X is F, Cl, Br or I) as a result of the σ-electron attracting effect of the halogen atom and produces a comparatively decreasing magnetic interaction by decreasing the electron density of the oxygen atoms, thus weakening the metal—oxygen covalent bond through which the demagnetisation operates. As shown in Table 3, copper(II) dibromoacetate does not appear to follow this trend. This observation and its specific causes is not yet clear.

It is interesting that the value of $-2J$ is almost the same in all copper(II) iodoacetates (Table 3) but in chloro-, bromo- and fluoroacetates it increases in the order anhydrous < hydrate < dioxane adduct. The biggest contribution to the $-2J$ value was found for the copper(II) fluoroacetate dioxane adduct; in the corresponding iodoacetate there was none. A similar trend can

TABLE 3

Values of $-2J$ (θ) and μ_{eff}, for copper(II) halogenoacetates and pKa values of the respective acids

Compound	$-2J$ (cm^{-1}) (θ (K))	μ_{eff} (T) (B.M.)	pKa	Ref.
$Cu(FCH_2COO)_2$	149	1.71(299)	2.66	43
$Cu(FCH_2COO)_2 \cdot H_2O$	366	1.32(293)		43
$Cu(FCH_2COO)_2C_4H_8O_2$	424	1.21(293)		44
$Cu(ClCH_2COO)_2$	292	1.44(291)	2.86	55
$Cu(ClCH_2COO)_2 \cdot 2.5\,H_2O$	313	1.45(300)		55
$Cu(ClCH_2COO)_2 \cdot 0.75\,C_4H_8O_2$	352	1.40(296)		59
$Cu(BrCH_2COO)_2$	254	1.49(296)	2.90	70
$Cu(BrCH_2COO)_2 \cdot H_2O$	313	1.54(298.5)		72
$Cu(BrCH_2COO)_2 \cdot 0.5\,C_4H_8O_2$	295	1.42(296)		70
$Cu(ICH_2COO)_2$	280	1.42(293)	3.17	73
$Cu(ICH_2COO)_2 \cdot H_2O$	274	1.49(299)		71
$Cu(ICH_2COO)_2 \cdot 0.5\,C_4H_8O_2$	280	1.42(293)		73
$Cu(F_2CHCOO)_2$	(−56)	1.75(298.6)	1.34	43
$Cu(F_3CCOO)_2$	(−15)	1.84(299.3)	0.2	43
$Cu(Cl_2CHCOO)_2$	(−68)	1.77(295)	1.36	55
$Cu(Cl_3CCOO)_2$		1.84(295.5)	0.515	55
$Cu(Br_2CHCOO)_2$	(−71.6)	1.88(296)	1.40	70
$Cu(Br_3CCOO)_2$	184.7	1.68(300)		70
$Cu(I_2CHCOO)_2$	215	1.69(299.5)		71

be seen in the values of the effective magnetic moments (Table 3). This can be explained in terms of steric hindrance which occurs in the iodoacetate compound. This steric hindrance reduces the contribution of dioxane to the $-2J$ value.

From Table 2 we can see that the singlet-triplet separation, $-2J$, in the case of the 2-chloropyridine adducts of copper(II) chloroacetates increases in the order $Cu(Cl_3CCOO)_2$(2 Clpy) < $Cu(Cl_2CHCOO)_2$(2 Clpy) < $Cu(ClCH_2COO)_2$(2 Clpy). This is in agreement with the early proposed relationships between the value of $-2J$ in the binuclear copper(II) compounds and the pKa value of the parent carboxylic acid [1,78].

Another important trend which has been noted for copper(II) carboxylates is for $-2J$ to increase 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 < picoline ~ SCN^- ~ ethanol < dioxane [78]. The data for the singlet-triplet separation presented in Tables 2 and 3 follow the general trends.

(iii) Tetranuclear compounds

The crystal structure of tetrakis(dichloroacetato)-tetra-μ-(2-diethylaminoethanolato)-tetracopper(II) has been reported by Smolander et al. [79a].

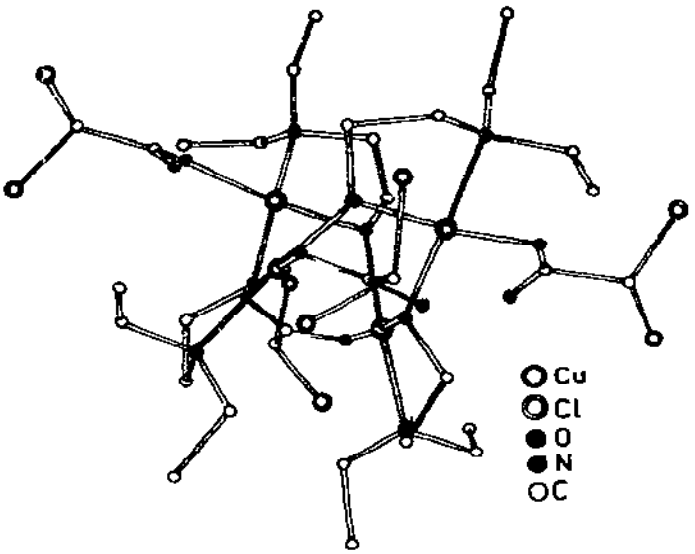

Fig. 2. Projection of the crystal structure of $[Cu(Cl_2CHCOO)(2\text{-diethylaminoethanolato})]_4$. (Reprinted with permission from [79a]. Copyright by the Slovak Technical University.)

This compound crystallizes in the triclinic space group $P\bar{1}$. The structure consists of discrete tetranuclear molecules as shown in Fig. 2. The tetranuclear array consists of an eight-membered Cu_4O_4 ring of cubane-type structure, though very distorted. Distances between copper atoms range from 3.176 to 4.024 Å and Cu—O—Cu angles from 108.3 to 120.0°. The coordination plane of each copper atom consists of two bridging ethanolato oxygen atoms, one carboxyl oxygen atom and one amino nitrogen atom, with Cu—O and Cu—N bonds ranging from 1.85 to 2.02 Å and from 2.05 to 2.11 Å, respectively (Fig. 3). While the coordination plane of the Cu-1 and Cu-2 is planar, Cu-3 and Cu-4 are not planar. The deviations of atoms from the least-squares plane is ≈0.20 Å.

The crystal structure of tetrakis(chloroacetato)-tetra-μ-(2-diethylaminoethanolato)-tetra-copper(II) [79b] is very similar to that of tetranuclear dichloroacetato(2-diethylaminoethanolato)copper(II) [79a]. The symmetry of the molecule in the chloroacetate compound is much higher than in the dichloroacetate compound. Smaller steric hindrance and favourable packing effects in passing from dichloroacetate to chloroacetate would seem to explain the higher symmetry [79b]. The distances between copper atoms range from 3.200 to 3.746 Å, and the value 111.0° of the Cu—O—Cu bridging angles in the eight-membered Cu_4O_4, are slightly shorter (smaller) than the mean values of these distances (angles) in the dichloroacetate compound.

Little et al. [80,81] reported the structural and magnetic characterization of the $[Cu_2OH(F_3CCOO)_3(quin)_2]_2$. This compound crystallizes in the triclinic space group $P\bar{1}$ similar to that of $[Cu(Cl_2CHCOO)(2\text{-diethylamino-}$

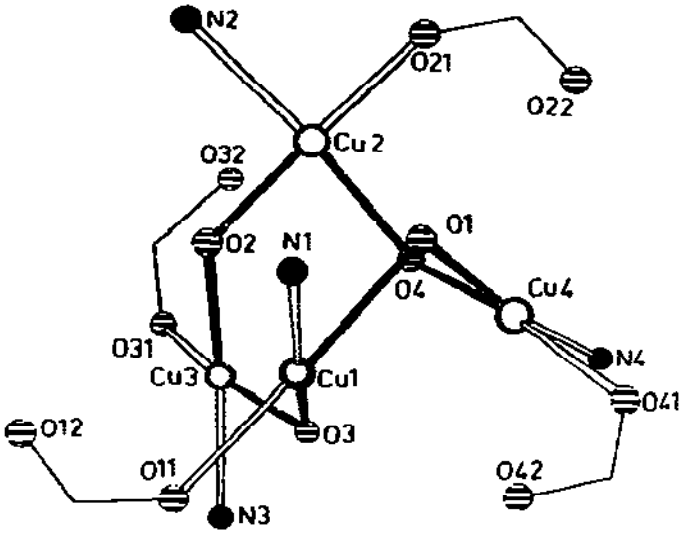

Fig. 3. A view of the copper(II) environments in [Cu(Cl_2CHCOO)(2-diethylaminoethanolato)]$_4$ [79a].

ethanolato)]$_4$ [79a]. A schematic view of the structure of one tetranuclear molecule is shown in Fig. 4. The crystal structure is comprised of centrosymmetric tetranuclear molecules in which copper(II) atoms are linked by carboxylate bridges and by triply bridging OH ions (Fig. 5). As is clearly

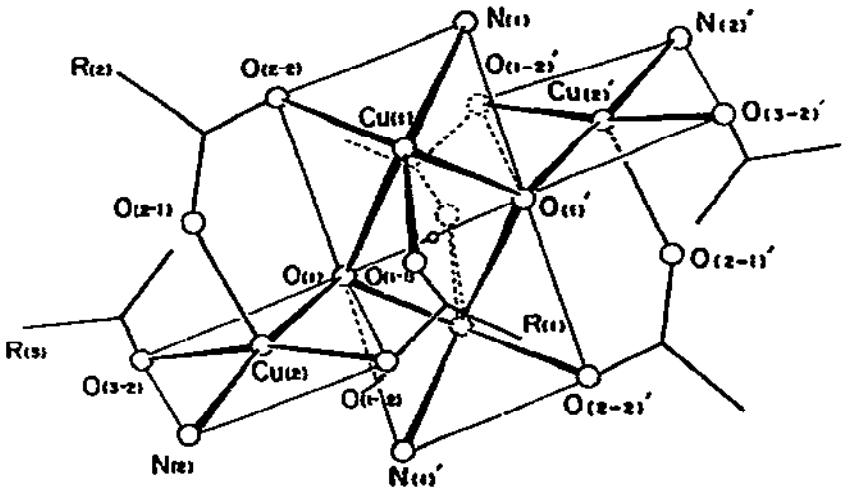

Fig. 4. A schematic view of the molecular structure of [$Cu_2OH(F_3CCOO)_3(quin)_2$]$_2$; CF_3 groups are represented as R and quinoline rings are not shown. (Reprinted with permission from [81]. Copyright by the Slovak Technical University.)

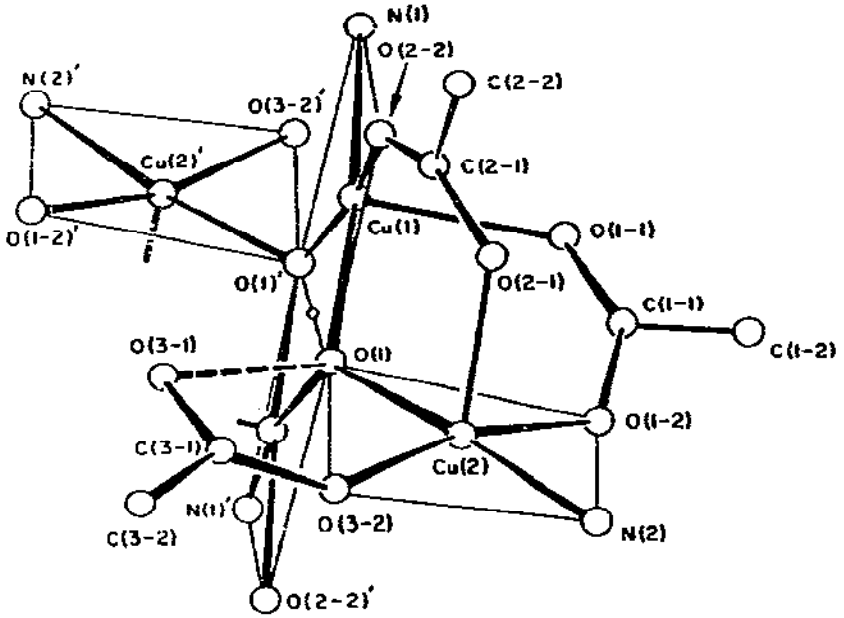

Fig. 5. A schematic view of the molecular structure of $[Cu_2OH(F_3CCOO)_3(quin)_2]_2$, illustrating the configuration of the bridging groups [81].

evident in Fig. 5, the bridging trifluoroacetate groups have the *syn, syn* configuration. Each of the two crystallographically independent Cu(II) ions is coordinated to four oxygen atoms and a quinoline nitrogen atom in a distorted square pyramidal configuration. Distances between copper atoms range from 2.996(4) to 3.502(5) Å and Cu—O—Cu angles from 98.6(2) to 124.8(3)°. The square pyramidal configuration of the copper atoms are quite similar. The three Cu—O(1) distances range from 1.963(6) to 1.990(6) Å and the Cu—N distances from 1.989(4) to 2.004(6) Å. Basal Cu—O (carboxylate) distances range from 1.936(7) to 1.990(6) Å; the apical Cu—O distances are Cu(1)—O(1-1) = 2.174(6) Å and Cu(2)—O(2-1) = 2.200(7) Å. The displacement of Cu(1) and Cu(2) from their basal coordination planes are 0.174 and 0.151 Å, respectively.

The magnetic moment for $[Cu_2OH(F_3CCOO)_3(quin)_2]_2$ is 1.60 B.M. at 300 K and decreases to 1.05 B.M. at 82.5 K implying a magnetically non-dilute system [81]. A least-squares fit to the observed magnetic susceptibility yielded the following values of the exchange integrals: $J_{11} = -90\ cm^{-1}$ and $J_{12} = -70\ cm^{-1}$. The results clearly demonstrate the presence of antiferromagnetic interaction.

Some Cu(II) compounds with the general formula $Cu_2OHX_3L_2$ (Table 4) were prepared and characterized [82]. On the basis of the room temperature magnetic moment and some spectral data [82] the compounds are proposed to be tetranuclear similar to $[Cu_2OH(F_3CCOO)_3(quin)_2]_2$.

TABLE 4

Magnetic moments and some spectral data for tetranuclear copper(II) halogenoacetates

Compound	μ_{eff} (T) (B.M.)	Electr. sp. ($\bar{\nu}_{max}$ (μm^{-1}))	IR (ν(N—O) (cm^{-1}))	Ref.
$[Cu_2OH(F_3CCOO)_3(quin)_2]_2$	1.60(300)			81
$Cu_2OH(Cl_2CHCOO)_3$-(2-CH_3-PyO)$_2$	1.77(297)	1.435	1215, 1204	82
$Cu_2OH(Cl_3CCOO)_3$-(2-CH_3-PyO)$_2$	1.76(297)	1.37	1208, 1203	82
$Cu_2OH(Cl_3CCOO)_3$-(2,6-$(CH_3)_2$-PyO)$_2$	1.82(297)	1.28	1203	82
$Cu_2OH(Cl_3CCOO)_3$-(2,4,6-$(CH_3)_3$-PyO)$_2$	1.74(299)	1.27	1206	82

(iv) Structural data—mono- and polynuclear compounds

Structural data for some mono- and polynuclear copper(II) halogenoacetates are given in Table 5. The crystals of *trans* $Cu(ClCH_2COO)_2(2\ pic)_2$ are triclinic [83]. The mononuclear molecule is strictly centrosymmetric and the copper(II) atom is surrounded by four atoms in a square-planar environment, with two Cu—N bonds from the 2-picoline ligands and two Cu—O bonds from the chloroacetate groups. The extremely tetragonally distorted octahedron is completed by two axial long bonds (Cu—O) (Table 5) from the remaining oxygen atoms of the chloroacetate groups.

The crystals of $Cu(Cl_2CHCOO)_2(2\ pic)_2$ are monoclinic [84]. The copper(II) atom in the mononuclear molecule has the form of an unsymmetrically axially distorted octahedron. The blue crystals of bis(chloroacetato)(N,N,N′,N′-tetramethylethylenediamine) copper(II) are monoclinic [85], in which the environment of the copper(II) ion is similar to that in $Cu(ClCH_2COO)_2$-(2 pic)$_2$ (Table 5) [83]. In the crystal structure of $Cu(Cl_3CCOO)_2$(N,N,N′,N′-tetramethylethylenediamine) · H_2O the copper(II) atom is in a square pyramidal environment [86]. The two diamine nitrogen atoms and one oxygen atom from each Cl_3CCOO^- group form a distorted square base. The copper atom is situated 0.16 Å above the mean basal plane and towards the apical water oxygen atom (Table 5).

In the infinite, left-handed, helical structure of catena-μ-trichloroacetato-acetylacetonatocopper(II), the coordination polyhedron has the form of a distorted octahedron [87]. The chromophore CuO_6 is built up from two oxygen atoms of the bidentate acetylacetonato ligand, two oxygen atoms from separate trichloroacetato ligands which bridge to neighbouring copper atoms in the spiral (Cu—Cu = 3.19 Å), and two which are atoms of the bidentate ligand of neighbouring copper atoms.

TABLE 5

Structural data for mono- and polynuclear copper(II) halogenoacetates

Compound	Z	Space group	Cu—O (Å)	Cu—N (Å)	Cu—O (Å) ('out-of-plane')	Cu—O (deg.) ('out-of-plane')	Ref.
$Cu(ClCH_2COO)_2(2\ pic)_2$	1	$P\bar{1}$	1.976(5)	1.989(6)	2.707(7)	36.1	83
$Cu(Cl_2CHCOO)_2(2\ pic)_2$ (blue)	4	$P2_1/n$	1.999(7) 2.017(7)	1.990(10) 2.032(10)	2.711(10) 2.493(9)	21.4	84
$Cu(ClCH_2COO)_2(N,N,N',N'\text{-}(CH_3)_4\ en)$	2	$P2_1$	1.977(3) 1.975(3)	2.039(3) 2.037(3)	2.627(3) 2.624(3)	25.6	85
$Cu(Cl_3CCOO)_2(N,N,N',N'\text{-}(CH_3)_4\ en)\cdot H_2O$	4	$P2_1/c$	1.992(10) 1.965(11)	2.010(12) 2.084(14)	2.302(12)		86
$Cu(Cl_3CCOO)_2(C_5H_8O_2)$	6	$P6_1$ and $P6_5$	1.85; 1.90 1.90; 1.94		2.48 2.66	22	87
$C_{10}H_{26}Cl_4CuN_4O_6$	8	*Cmca*		2.029(12) 2.022(13)	2.268(15)		88
$Cu(F_3CCOO)_2py_4$	2	$P\bar{1}$		2.039(4) 2.052(3) 2.037(4) 2.047(3)	2.361(4) 2.350(4)		89
[a] $Cu(TTA)_2py_2$ + [b] $Cu(F_3CCOO)_2py_4$	4	$P2/c$	2.067(5) [a]	2.053(9) [a] 2.098(10) [a] 2.043(10) [b] 2.056(11) [b] 2.047(7) [b]	2.143(6) [a] 2.343(6) [b]		89

[a] Distances in $Cu(TTA)_2py_2$. [b] Distances in $Cu(F_3CCOO)_2py_4$.

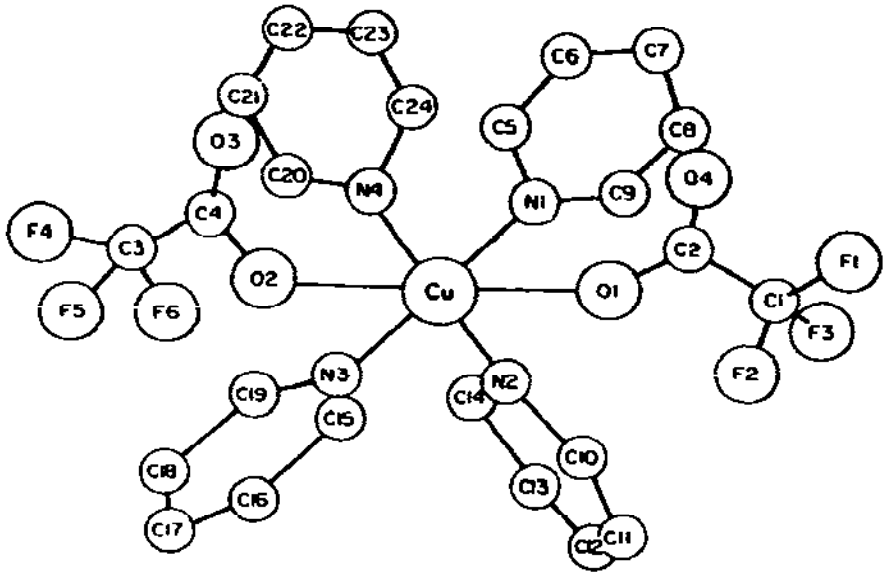

Fig. 6. Schematic illustration of the atomic numbering schemes in $Cu(F_3CCOO)_2py_4$ [89].

The crystals of the reaction product of copper(II) dichloroacetate and 1,3-diamino-2-propanol belong to the orthorhombic system with space group *Cmca* and eight formula units in the unit cell ($Z = 8$). The copper(II) atom is in the mirror plane and has a distorted square pyramidal coordination (Table 5) [88].

The tetrapyridine compounds exhibit very similar structures [89] in the crystal structures of pure $Cu(F_3CCOO)_2py_4$ (Fig. 6) and the mixed compound $Cu(TTA)_2py_2 + Cu(F_3CCOO)_2py_4$ (Fig. 7) (Table 5). The coordination polyhedron is a distorted octahedron. The copper(II) atom is coordinated by four shorter Cu—N bonds and by two longer Cu—O bonds (Table 5). Thenoyltrifluoroacetate (TTA) is bonded to Cu(II) as a chelate and the remaining two places are occupied by pyridine molecules.

(v) Spectral and magnetic data—mono- and polynuclear compounds

Spectral and magnetic data for non-binuclear copper(II) halogenoacetates are summarised in Table 6. The thermal decomposition of some copper(II) halogenoacetates was carried out by Obier et al. [105].

Copper(II) dichloroacetate forms one blue and one violet 1 : 2 addition compound with 2-picoline [48]. Only the crystal structure of the blue form has been reported [84]. The violet form is thermodynamically less stable than the blue form. However, it is not clear at present what influences the formation of the more stable blue form. Their effective magnetic moments are practically identical, but significant differences were found in the d—d band energies (Table 6), which suggests a difference in the stereochemistry

TABLE 6

Spectral and magnetic data for mono- and polynuclear copper(II) halogenoacetates

Compound	IR spectra (cm^{-1})		Electr. sp. ($\bar{\nu}_{max}$ (μm^{-1}))	μ_{eff} (T) (B.M.)	θ (K)	Ref.
	$\nu_{as}COO^-$	ν_sCOO^-				
$Cu(FCH_2COO)_2$(4 Bran) [a]						64
$Cu(FCH_2COO)_2$ py_2			1.615			48
$Cu(FCH_2COO)_2$(2 pic)$_2$			1.57, 1.85	1.87(295)		48
$Cu(F_2CHCOO)_2$	1660, 1600	1465, 1425sh		1.75(299)		43
$Cu(F_2CHCOO)_2 \cdot H_2O$	1670, 1620 1595	1540, 1470 1440		1.85(300)	−56	43
$Cu(F_2CHCOO)_2py_2$	1653		1.60	1.81(294)		48
$Cu(F_2CHCOO)_2$(2 pic)$_2$	1667	1454	1.50, 1.85	1.81(295)		48
$Cu(F_3CCOO)_2$	1693, 1655	1475, 1455		1.84(299)	−84	43
				1.81(297)	−42	90
	1715, 1690	1440				91
$Cu(F_3CCOO)_2 \cdot 3H_2O$	1660, 1650 1580	1465, 1445		1.95(300)	−15	43
$Cu(F_3CCOO)_2$(2 Clpy)	1715	1460				92
$Cu(F_3CCOO)_2$(3 Brpy)	1705	1470, 1455 1445				92
$Cu(F_3CCOO)_2$(pyNO)			0.95sh, 1.22	2.01(293)		93
$Cu(F_3CCOO)_2$(4 ClpyNO)			0.95sh, 1.23	1.95(301)		93
$Cu(F_3CCOO)_2py_2$	1701, 1667	1435	1.536	1.85(296)		48
$Cu(F_3CCOO)_2$(2 pic)$_2$	1678	1450	1.516wsh 1.70wsh 1.82			91
$Cu(F_3CCOO)_2$(3 pic)$_2$	1675	1435	1.43, 1.587			91

$Cu(F_3CCOO)_2(4\ pic)_2$	1700, 1681 1659	1440	1.418, 1.575sh			91
$Cu(F_3CCOO)_2(2\ Etpy)_2$	1680	1448	1.516, 1.82			91
$Cu(F_3CCOO)_2(2\ Clpy)_2$	1690	1455sh, 1450				91
$Cu(F_3CCOO)_2(3\ Brpy)_2$	1673, 1690sh	1447, 1455	1.47, 1.62			91
$Cu(F_3CCOO)_2(2,3\text{-lut})_2$	1678	1435	1.481, 1.818			91
$Cu(F_3CCOO)_2(2,6\text{-lut})_2$	1695	1475	1.429, 1.818			91
$Cu(F_3CCOO)_2(3,5\text{-lut})_2$	1690, 1672sh	1435				91
$Cu(F_3CCOO)_2(quin)_2$	1687, 1665	1445sh	1.429sh, 1.729			91
$Cu(F_3CCOO)_2(i\text{-quin})_2$	1705sh, 1665	1437				91
$Cu(F_3CCOO)_2(pyNO)_2$	1690	1430				92
$Cu(F_3CCOO)_2py_4$	1702, 1690	1440	1.55	1.87(294)		92, 48
$Cu(F_3CCOO)_2(3\ pic)_4$	1702sh, 1683	1455, 1462	1.44wsh, 1.613			91
$Cu(F_3CCOO)_2(4\ pic)_4$	1690, 1673		1.527sh, 1.637			91
$Cu(F_3CCOO)_2(3\ Brpy)_4$	1700	1450, 1425	1.45, 1.587wsh			91
$Cu(F_3CCOO)_2(3,5\text{-lut})_4$	1690, 1675sh	1442, 1436	1.429, 1.647			91
$Cu(F_3CCOO)_2(i\text{-quin})_4$	1695, 1675sh	1430				91
$Cu(F_3CCOO)_2$ en			1.587	1.90(296)		94
$Cu(F_3CCOO)_2en_2 \cdot H_2O$			1.818	1.86(296)		94
$Cu(F_3CCOO)_2en_3$ [b]			1.538	1.92(295)	−4.6	94, 95
$Cu(F_3CCOO)_2(1,2\ pn)$			1.587	1.89(294)		94
$Cu(F_3CCOO)_2(1,2\ pn)_2 \cdot H_2O$			1.852	1.86(297)		94
$Cu(F_3CCOO)_2(1,3\ pn)$			1.587	1.87(295)		94
$Cu(F_3CCOO)_2(1,3\ pn)_2$			1.785	1.86(296)		94
$Cu(F_3CCOO)_2 \cdot C_4H_8O_2 \cdot H_2O$ [c]			1.482, 2.66	1.79(293)	−48	96

(TABLE CONTINUED on next page)

TABLE 6 (continued)

Compound	IR spectra (cm^{-1})		Electr. sp. ($\bar{\nu}_{max}$ (μm^{-1}))	μ_{eff} (T) (B.M.)	θ (K)	Ref.
	$\nu_{as}COO^-$	$\nu_s COO^-$				
$Cu(ClCH_2COO)_2(2\ pic)_2$ [d]			1.50, 1.77 1.80, 1.87			97
			1.55, 1.86	1.80(293)		48
$Cu(ClCH_2COO)_2(4\text{-}tol)_2$ [e]						64
$Cu(ClCH_2COO)_2(4\ Clan)_2$ [f]						64
$Cu(ClCH_2COO)_2py_2$			1.59			48
$Cu(ClCH_2COO)_2en \cdot H_2O$			1.56	1.87(297)		98
$Cu(ClCH_2COO)_2en_2 \cdot 2\ H_2O$			1.818	1.85(297)		59
$Cu(ClCH_2COO)_2(1,2\ pn) \cdot H_2O$			1.49	1.92(295)		99
$Cu(ClCH_2COO)_2(1,2\ pn)_2 \cdot 3\ H_2O$			1.818	1.90(295)		99
$Cu(ClCH_2COO)_2(1,3\ pn)$			1.56	1.90(296)		99
$Cu(ClCH_2COO)_2(1,3\ pn)_2$			1.785	1.86(295)		99
$Cu(Cl_2CHCOO)_2$	1669, 1582	1435sh, 1415	1.33, 2.67	1.77(295)	−68	55, 100
				1.66(289)		54
$Cu(Cl_2CHCOO)_2 \cdot 4\ H_2O$	1660, 1642 1632	1410, 1400	1.10, 1.35, 2.78	1.82(298)		8, 57
				1.74(288)		54
$Cu(Cl_2CHCOO)_2py_2$	1660	1400, 1357	1.565	1.94(292)		101
	1663, 1623	1404, 1365	1.60	1.82(293)		48
$Cu(Cl_2CHCOO)_2(2\ pic)_2$ (blue)	1645, 1629	1394	1.60	1.82(295)		48
$Cu(Cl_2CHCOO)_2(2\ pic)_2$ (violet)	1657, 1643	1376	1.88, 1.53	1.81(298)		48
$Cu(Cl_2CHCOO)_2en$			1.61	1.86(297)		102

$Cu(Cl_2CHCOO)_2en_2$			1.818	1.82(297)	102
$Cu(Cl_2CHCOO)_2$(1,2 pn)			1.587	1.91(295)	102
$Cu(Cl_2CHCOO)_2$(1,2 pn)$_2$			1.818	1.86(296)	102
$Cu(Cl_2CHCOO)_2$(1,3 pn)			1.56	1.90(296)	102
$Cu(Cl_2CHCOO)_2$(1,3 pn)$_2$			1.785	1.92(294)	102
$Cu(Cl_2CHCOO)_2$(pyNO)			1.05sh, 1.32	1.51(301)	93
$Cu(Cl_2CHCOO)_2$(4 NO_2pyNO)			1.22	2.04(297)	93
$Cu(Cl_2CHCOO)_2$(pyNO)$_2$			1.30	1.85(room)	77
$Cu(Cl_2CHCOO)_2$(2 picNO)$_2$			1.30	1.72(room)	77
$Cu(Cl_2CHCOO)_2$(3 picNO)$_2$			1.30	1.85(room)	77
$Cu(Cl_2CHCOO)_2$(4 picNO)$_2$			1.30		77
$Cu(Cl_2CHCOO)_2$(dipyO_2)			1.30		77
$Cu(Cl_2CHCOO)_2Ph_3PO$			1.30	1.84(room)	77
$Cu(Cl_2CHCOO)_2(Ph_3AsO)_2$			1.30	2.00(room)	77
$Cu(Cl_3CCOO)_2$	1610	1385		1.84(295.5)	55
	1660, 1590	1340		1.65(298)	57
$Cu(Cl_3CCOO)_2 \cdot H_2O$ [g]	1629	1379	1.33, 2.67		103, 100
$Cu(Cl_3CCOO)_2 \cdot 3\ H_2O$	1620	1380		1.96(300)	55
			1.29	1.90(298)	57
			1.06	1.89(289)	54
$Cu(Cl_3CCOO)_2 \cdot 4\ H_2O$			1.33, 2.67	1.70(room)	100, 60
$Cu(Cl_3CCOO)_2(CH_3)_2CO$ [h]	1680, 1660	1370, 1340		1.75(296)	8, 66
$Cu(Cl_3CCOO)_2(C_4H_8O_2)_2$ [i]	1670	1375, 1342		1.85(296)	8, 66
$Cu(Cl_3CCOO)_2py_2$	1688, 1634	1375, 1345	1.545	1.83(297)	48
$Cu(Cl_3CCOO)_2$(2 pic)$_2$			1.50, 1.886	1.83(295)	48
$Cu(Cl_3CCOO)_2en$			1.587	1.89(297)	104

(TABLE CONTINUED on next page)

TABLE 6 (continued)

Compound	IR spectra (cm^{-1})		Electr. sp. ($\tilde{\nu}_{max}$ (μm^{-1}))	μ_{eff} (T) (B.M.)	θ (K)	Ref.
	$\nu_{as}COO^-$	ν_sCOO^-				
$Cu(Cl_3CCOO)_2en_2$			1.818	1.84(297)		104
$Cu(Cl_3CCOO)_2$(1,2 pn)			1.562	1.92(297)		104
$Cu(Cl_3CCOO)_2$(1,3 pn)			1.562	1.89(297)		104
$Cu(Cl_3CCOO)_2$(1,3 pn)$_2$			1.785	1.90(297)		104
$Cu(Cl_3CCOO)_2py_4$	1691	1317	1.54	1.82(293)		48, 92
$Cu(Cl_3CCOO)_2(pyNO)_2$	1670	1340				92
$Cu(Cl_3CCOO)_2$(pyNO)			0.98sh, 1.24	1.91(300)		93
$Cu(Cl_3CCOO)_2$(4 ClpyNO)			0.94sh, 1.24	1.91(300)		93
$Cu(Cl_3CCOO)_2$(4 NO_2pyNO)			1.19	1.95(299)		93
$Cu(BrCH_2COO)_2$(1,3 pn)			1.587	1.87(298.5)		68
$Cu(Br_2CHCOO)_2$ [j]	1654, 1576	1485		1.54(298)		57
	1606	1340		1.62(300)		71
	1648, 1570		1.492	1.88(296)	−71.6	68, 70
$Cu(Br_2CHCOO)_2$(1,3 pn)			1.587	1.94(297)		68
$Cu(Br_2CHCOO)_2 \cdot H_2O$ [k]	1645, 1571	1382, 1380		1.80(299)	−78	71
$Cu(Br_3CCOO)_2 \cdot 3H_2O$	1660, 1636	1358		2.03(299.4)	0	71
	1608					
$Cu(Br_3CCOO)_2 \cdot 2H_2O$ [l]	1635		1.439	1.99(300)	−6	68, 70
$Cu(Br_3CCOO)_2$(1,3 pn)			1.60	2.12(298)		68

w = weak; sh = shoulder.

[a] EPR of single crystal ($S = 1/2$) at 77 K, $g_x = 2.049$; $g_y = 2.135$; $g_z = 2.177$ [64]. [b] EPR of powdered sample ($S = 1/2$); $g_l = 2.11$ [95]. [c] EPR of powdered sample ($S = 1/2$); $g_l = 2.16$; ($S = 1$), $g_\perp = 2.07$; $g_\parallel = 2.31$; $|D| = 0.380$ cm^{-1} [96]. [d] EPR of single crystal ($S = 1/2$); $g_1 = 2.0546$; $g_2 = 2.0608$; $g_3 = 2.2659$; $d_{z^2} \rightarrow d_{x^2-y^2}$, 1.80 μm^{-1}; $d_{xy} \rightarrow d_{x^2-y^2}$, 1.50 μm^{-1}; $d_{xz} \rightarrow d_{x^2-y^2}$, 1.87 μm^{-1}; $d_{yz} \rightarrow d_{x^2-y^2}$, 1.77 μm^{-1} [97]. [e] EPR of powdered sample at 77 K, $g_1 = 2.044$; $g_2 = 2.061$; $g_3 = 2.320$ [64]. [f] EPR of powdered sample at 77 K, $g_1 = 2.044$; $g_2 = 2.059$; $g_3 = 2.267$ [64]. [g] EPR of single crystal ($S = 1/2$); $g_1 = 2.05$; $g_2 = 2.10$; $g_3 = 2.441$ [58]. [h] EPR of powdered sample ($S = 1/2$); $g_\perp = 2.048$; $g_\parallel = 2.386$; ($S = 1$), $g_\perp = 2.111$; $g_\parallel = 2.416$; $|D| = 0.368$ cm^{-1} [62]. [i] EPR of powdered sample ($S = 1/2$); $g_\perp = 2.036$; $g_\parallel = 2.394$ [62]. [j] EPR of powdered sample ($S = 1/2$); $g_l = 2.152$ [69]. [k] $J = 80$ cm^{-1} [72]. [l] EPR of powdered sample ($S = 1/2$); $g_\perp = 2.054$; $g_\parallel = 2.267$ [69].

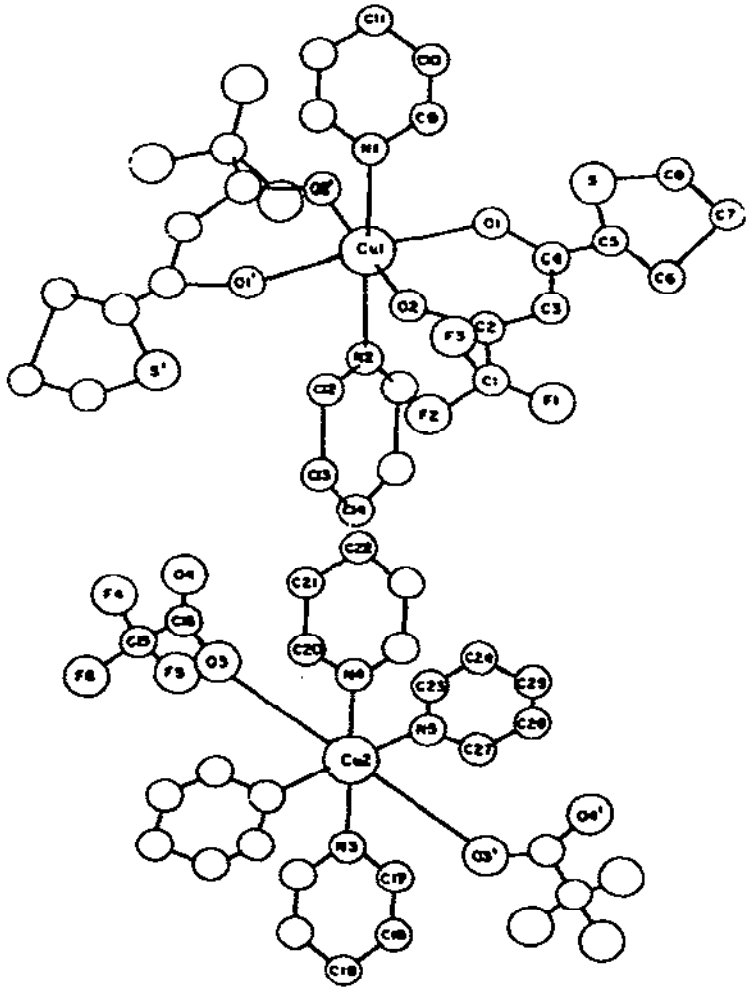

Fig. 7. Schematic illustration of the atomic numbering schemes in $Cu(F_3CCOO)_2py_4$ + $Cu(TTA)_2py_2$ [89].

of the copper(II) atom in these two compounds [48].

On the basis of data presented in Table 6, the compounds are categorised as follows: compounds with stoichiometry CuL_4X_2 (L = pyridine or its derivatives) and CuL_2X_2 (L = ethylenediamine, 1,2- or 1,3-propanediamine) probably contain the copper(II) atom in an essentially tetragonal environment with the nitrogen ligands coordinated to form approximately square coplanar structures. The tetragonal positions are occupied by oxygen atoms from the monodentate halogenoacetate anions. Table 6 indicates that the band maxima of the electronic spectra for the bis(diamine) compounds are at appreciably higher energy (ca. 1.8 μm^{-1}) than those of CuL_4X_2 (ca. 1.6

μm^{-1}). This difference could be explained in terms of an increased tetragonal distortion in bis(diamine) compounds compared with CuL_4X_2.

Compounds with stoichiometry CuL_2X_2 (L = pyridine or its derivatives) and $CuLX_2$ (L = ethylenediamine, 1,2- or 1,3-propanediamine) are also six-coordinate, probably with bidentate halogenoacetate attached to the copper(II) atom.

The third class of compounds include anhydrous compounds with stoichiometry CuX_2L (L = monodentate ligand) which are thought to be polynuclear. In general, the electronic spectra of the third class have broad maxima which are at appreciably lower energies than those of corresponding compounds in the first two groups (Table 6).

From the stoichiometry of the diamine compounds we can also see (Table 6) that there is a tendency for the creation of hydrates dependent upon the p*Ka* value of the corresponding acid (as p*Ka* decreases, hydrates tend not to form) and also upon the coordinating diamine in the range 1,2-propanediamine > ethylenediamine > 1,3-propanediamine.

C. COPPER(II) HALOGENOPROPIONATES

(i) Spectral and magnetic data

An X-ray investigation of copper(II) propionate [106] shows a binuclear structure similar to the copper(II) acetate monohydrate [9—12]. A noteworthy feature of this structure is the Cu—Cu distance of 2.578(4) Å, shorter by 0.037 Å than the comparable distance in copper(II) acetate monohydrate (Table 1). On the basis of the results summarised in Table 1, we would expect a decrease in the distance of the Cu atom to its basal coordination plane with a shortening of the Cu—Cu distance. In spite of this fact, the distance of the Cu atom to its coordination plane in copper(II) propionate is 0.22 Å, which is longer by 0.03 Å than in copper(II) acetate monohydrate. The Cu—O distances range from 1.86(1) to 1.97(1) Å, with a mean value of 1.93(1) Å. The apical Cu—O distance is 2.28(1) Å.

Spectral and magnetic data of binuclear copper(II) propionates are given in Table 7. The spectral and magnetic data for anhydrous and monohydrated copper(II) propionates are very similar to those of the copper(II) acetates. The EPR spectra of the anhydrous copper(II) 2-halogenopropionates were extremely broad over 6000 Oe; the *g* values were found to be approximately 2.2. The molecules in the triplet state form clusters resulting in delocalization of the interacting unpaired electrons.

The introduction of a chlorine atom into propionic acid results in an increase in the acid strength in the order $ClCH_2CH_2COO^- < CH_3CHClCOO^- < CH_3CCl_2COO^-$. When the p*Ka* value of the respective acid increases the value of the exchange coupling constant also increases (Table 7). As the acid strength decreases the electron densities of the oxygen atoms increase, which leads to stronger covalent metal—oxygen bonds and thereby to an increased

overlap of the orbitals of the two unpaired electrons in the binuclear units. A similar correlation can also be seen in the case of copper(II) bromopropionates. The $-2J$ value decreases in the order $BrCH_2CH_2COO^- > CH_3CHBrCOO^- > BrCH_2CHBrCOO^-$.

From the data summarised in Table 7 it is also clear that the terminal ligands also influence these values. The $-2J$ value tends to increase along the following series of terminal ligands: antipyrine < water ≤ anhydrous < dioxane. The largest contribution to the $-2J$ value was found in the case of the dioxane adduct of copper(II) 3-fluoropropionate. Copper(II) fluoroacetate behaves similarly.

D. COPPER(II) HALOGENOBENZOATES

(i) Structural data—binuclear compounds

The structure of copper(II) 2-bromobenzoate monohydrate has been determined [126]. The Cu—O (basal), Cu—O (apical) and Cu—Cu distances in the compound were found to be 1.99(2), 2.17(2) and 2.624(7) Å, respectively. The distances are longer than those in copper(II) acetate monohydrate (Table 1). This can be explained in terms of the steric hindrance which occurs in the 2-bromobenzoate compound. This small elongation of the Cu—Cu distance in $Cu(2\text{-}BrC_6H_4COO)_2 \cdot H_2O$ is reflected in a small increase in the distance of the Cu atom from its basal coordination (0.20 Å), 0.01 Å more than the comparable distance in copper(II) acetate monohydrate. In spite of this the mean O—C—O bond angle in binuclear 2-bromobenzoate is smaller (124(3)° vs. 124.9(1)°), but the Cu—O—C angle was observed to be 123.5(20)°, larger by ≈0.5° than that in binuclear acetate.

(ii) Spectral and magnetic data—binuclear compounds

In Table 8 are summarised the spectral and magnetic data of the binuclear copper(II) halogenobenzoates. The introduction of a halogeno atom into the 2-, 3- or 4-position of benzoic acid results in a decrease in acid strength in the order $2\text{-}XC_6H_4COO^- > 3\text{-}XC_6H_4COO^- > 4\text{-}XC_6H_4COO^-$ (X = F, Cl, Br or I). Although the p*Ka* values of the halogenoarylcarboxylic acids increase, the tendency for the formation of mononuclear molecules increases too, which can be seen from the magnetic moments of their copper(II) hydrates (Tables 8 and 10). The opposite effect occurs in the case of copper(II) halogenoalkylcarboxylates (Table 3). It seems reasonable to seek the cause of this anomaly in the distinct bonding system of the carboxylate groups. Unpaired spin delocalization from the copper(II) atoms appears in the σ-bonding system of the carboxylate groups. This σ-bonding system is reduced in the case of halogenoarylcarboxylates because of finite spin densities appearing in the π-systems of the aromatic ring possibly via hyperconjugation.

TABLE 7

Spectral and magnetic data for binuclear copper(II) halogenopropionates and copper(II) propionates

Compound	$g_\perp$	$g_\parallel$	g_{av}	$\|D\|$ (cm^{-1})	μ_{eff} (T) (B.M.)	$-2J$ (cm^{-1})	Electr. sp. ($\bar{\nu}_{max}$ (μm^{-1}))		Ref.
							I	II	
$Cu(CH_3CH_2COO)_2$	2.04	2.30	2.13	0.340	1.36(289)	300			107, 34
$Cu(CH_3CH_2COO)_2 \cdot H_2O$	2.060	2.348	2.160	0.327	1.40(290)	300	1.43	2.70	34, 108–111
	g_x = 2.10, g_y = 2.09	2.365	2.18						110
	g_x = 2.095, g_y = 2.093	2.348	2.18						109
$Cu(CH_3CHFCOO)_2$			≈2.2		1.66(293)	167	1.45	2.63	112
$Cu(CH_3CHFCOO)_2 \cdot 0.5\ C_4H_8O_2$	2.112	2.395	2.213 [a]	0.376	1.30(293)	384	1.48	2.66	112
$Cu(ClCH_2CH_2COO)_2$					1.42(295)		1.49	2.66	113
$Cu(ClCH_2CH_2COO)_2 \cdot H_2O$	2.116	2.383	2.209 [a]	0.350	1.43(296)	322	1.48	2.70	113–115
$Cu(ClCH_2CH_2COO)_2 \cdot 0.5\ C_4H_8O_2$	2.069	2.362	2.172	0.337	1.36(296)	346	1.515	2.66	113,115,116
$Cu(ClCH_2CH_2COO)_2 \cdot A$	2.11	2.40	2.21	0.351	1.34(291)	292	1.33	2.66	117,118
$Cu(ClCH_2CH_2COO)_2 \cdot 4$ acpyNO	2.085	2.382	2.188 [a]	0.348	1.51(297)	280	1.40	2.60	119
$Cu(CH_3CHClCOO)_2$			≈2.2		1.48(294)	302	1.50	2.63	113,115,116
$Cu(CH_3CHClCOO)_2 \cdot 0.5\ C_4H_8O_2$	2.098	2.383	2.197	0.355	1.43(295)	326	1.50	2.66	113–115
$Cu(CH_3CHClCOO)_2 \cdot A$	2.11	2.41	2.21 [a]	0.370	1.46(291)	245	1.28	2.70	117,118

$Cu(CH_3CHClCOO)_2$ 2 picNO	2.114	2.425	2.222[a]	0.379			1.37	2.50	120
$Cu(CH_3CHClCOO)_2$· 4 acpyNO	2.070	2.401	2.186[a]	0.362	1.54(295)	258	1.35	2.60	119
$Cu(CH_3CHClCOO)_2Ph_3PO$	2.116	2.410	2.218	0.384	1.43(295)	314	1.29	2.60	120
$Cu(CH_3CCl_2COO)_2$	2.09	2.38	2.19	0.354	1.50(303)	252	1.46	2.66	121,122
$Cu(CH_3CCl_2COO)_2$ · 0.5 $C_4H_8O_2$	2.09	2.38	2.19	0.357	1.44(303)	267	1.47	2.63	121,122
$Cu(CH_3CCl_2COO)_2$ · A	2.11	2.43	2.22	0.375	1.60(293)	228	1.20	2.70	118
$Cu(CH_3CCl_2COO)_2$· 4 acpyNO	2.092	2.413	2.204	0.373	1.61(295)	230	1.30	2.60	119
$Cu(BrCH_2CH_2COO)_2$			≈2.2		1.43(296)		1.46	2.63	115,123
$Cu(BrCH_2CH_2COO)_2 \cdot H_2O$	2.114	2.374	2.204[a]	0.354	1.42(294)	340	1.47	2.63	114,115,123
$Cu(BrCH_2CH_2COO)_2 \cdot CH_3OH$	2.112	2.387	2.204[a]	0.356	1.43(295)	318	1.46	2.63	115,116,123
$Cu(BrCH_2CH_2COO)_2$ · 0.5 $C_4H_8O_2$	2.072	2.325	2.168[a]	0.332	1.40(296)	325	1.498	2.63	115,116,123
$Cu(CH_3CHBrCOO)_2$			≈2.2		1.45(292)	293	1.50	2.60	115,116,124
$Cu(CH_3CHBrCOO)_2$ · 0.5 $C_4H_8O_2$	2.100	2.370	2.194	0.349	1.44(294)	304	1.46	2.56	114,115,124
$Cu(BrCH_2CHBrCOO)_2$	2.080	2.354	2.175[a]	0.344	1.48(298)	286	1.50	2.63	115,116,125
$Cu(BrCH_2CHBrCOO)_2$ · $C_4H_8O_2$	2.097	2.382	2.196[a]	0.355	1.48(298)	292	1.51	2.66	115,116,125
$Cu(ICH_2CH_2COO)_2$	2.03	2.38	2.15	0.340	1.32(303)	254	1.48	2.63	122
$Cu(ICH_2CH_2COO)_2 \cdot C_4H_8O_2$	2.08	2.34	2.17	0.340	1.36(303)	265	1.50	2.66	122

[a] Mononuclear impurity.

TABLE 8

Spectral and magnetic data for binuclear copper(II) halogenobenzoates

Compound	$g_\perp$	$g_\parallel$	g_{av}	$\lvert D\rvert$ (cm^{-1})	$\mu_{eff}(T)$ (B.M.)	$-2J$ (cm^{-1})	Electr. sp. ($\tilde{\nu}_{max}$ (μm^{-1}))		Ref.
							I	II	
$Cu(2\text{-}FC_6H_4COO)_2 \cdot H_2O$	2.07	2.38	2.18 [a]	0.34	1.52(298)	260	1.43	2.63	127–129
$Cu(2\text{-}FC_6H_4COO)_2 \cdot C_4H_8O_2$	2.097	2.397	2.201 [a]	0.359	1.38(293)	316	1.36	2.65	130
$Cu(2\text{-}FC_6H_4COO)_2$ DMF	2.12	2.37	2.20	0.347	1.47(300)	334	1.36	2.65	131
$Cu(2\text{-}FC_6H_4COO)_2$ A	2.082	2.381	2.186	0.353	1.43(294)	303	1.30	2.60	130
$Cu(2\text{-}FC_6H_4COO)_2$ nic	2.093	2.362	2.186 [a]	0.375	1.45(293)	314	1.30	2.55	132
$Cu(2\text{-}FC_6H_4COO)_2Ph_3PO$	2.104	2.400	2.207	0.388	1.25(270)	354	1.34	2.60	133
$Cu(3\text{-}FC_6H_4COO)_2 \cdot 1.5\ C_4H_8O_2$	2.127	2.469	2.246	0.368	1.48(298)		1.515	2.63	128,129
$Cu(3\text{-}FC_6H_4COO)_2$ nic	2.085	2.346	2.175 [a]	0.366	1.405(293)	312	1.36	2.60	132
$Cu(2\text{-}ClC_6H_4COO)_2$					1.63(295.4)	167	1.39	2.37	134
$Cu(2\text{-}ClC_6H_4COO)_2 \cdot H_2O$	2.090	2.350	2.185 [a]	0.332	1.50(292.5)	245	1.40	2.37	134,135
$Cu(2\text{-}ClC_6H_4COO)_2 \cdot C_4H_8O_2$	2.086	2.354	2.179 [a]	0.342	1.46(295)	317	1.38	2.63	130,136
$Cu(2\text{-}ClC_6H_4COO)_2 \cdot$ DMF	2.09	2.38	2.19 [a]	0.369	1.41(293)	317	1.38	2.64	131
$Cu(2\text{-}ClC_6H_4COO)_2 \cdot$ A	2.090	2.393	2.195 [a]	0.365	1.27(296)	309	1.32	2.61	130
$Cu(2\text{-}ClC_6H_4COO)_2$ py	2.068	2.365	2.171	0.342	1.31(297)	312			134,137
$Cu(2\text{-}ClC_6H_4COO)_2$ an	$g_x = 2.024$ $g_y = 2.011$	2.247	2.175	0.337	1.54(295)	252			137
$Cu(2\text{-}ClC_6H_4COO)_2$ nic	2.103	2.358	2.191 [a]	0.375	1.60(293)	229	1.32	2.58	132
$Cu(2\text{-}ClC_6H_4COO)_2$ pyNO	2.082	2.385	2.187	0.364	1.27(297)	392	1.35	2.70	133
$Cu(2\text{-}ClC_6H_4COO)_2$ 2 picNO	2.087	2.344	2.176	0.362	1.60(295)	278	1.34	2.75	133
$Cu(2\text{-}ClC_6H_4COO)_2(3\ picNO)_{0.5}$	2.100	2.355	2.188 [a]	0.368	1.51(298)	270	1.36	2.65	133
$Cu(2\text{-}ClC_6H_4COO)_2(4\ picNO)_{0.5}$	2.103	2.364	2.193 [a]	0.370	1.60(295)	232	1.37	2.70	133

$Cu(2\text{-}ClC_6H_4COO)_2Ph_3PO$	2.095	2.352	2.184	0.364	1.41(292)	302	1.37	2.75	133
$Cu(3\text{-}ClC_6H_4COO)_2$(b)					1.32(298)	300	≈1.46		134,138
$Cu(3\text{-}ClC_6H_4COO)_2 \cdot C_4H_8O_2$	2.083	2.362	2.180	0.346	1.48(296)		1.47	2.66	136
$Cu(3\text{-}ClC_6H_4COO)_2py_{0.8}$					1.43(296)				140
$Cu(3\text{-}ClC_6H_4COO)_2py_{0.5}$					1.46(295)				140
$[Cu(4\text{-}ClC_6H_4COO)_2]_n$(a)					1.57(294.4)	210			134
$Cu(4\text{-}ClC_6H_4COO)_2$(b)					1.42(293)	195	1.54		127,134,138
$Cu(4\text{-}ClC_6H_4COO)_2$(c)	2.06	2.36	2.16[a]	0.34	1.43(292)	221	1.48	2.35	127,134,138
$Cu(4\text{-}ClC_6H_4COO)_2 \cdot C_2H_5OH$					1.50(299)				139
$Cu(4\text{-}ClC_6H_4COO)_2 \cdot 0.5\,C_4H_8O_2$	2.075	2.337	2.166	0.333	1.52(298)		1.48	2.66	136
$Cu(2,4\text{-}Cl_2C_6H_3COO)_2$	2.06	2.32	2.15[a]	0.35	1.51(299.5)	260			127
$Cu(2,5\text{-}Cl_2C_6H_3COO)_2$					1.73(301)	126			127
$Cu(2,4\text{-}Cl_2C_6H_3COO)_2 \cdot C_2H_5OH$					1.45(299.4)	300			127
$Cu(4\text{-}ClC_6H_4COO)_2py_{1.2}$					1.50(300)				140
$Cu(4\text{-}ClC_6H_4COO)_2py_{0.8}$					1.46(297)				140
$Cu(4\text{-}ClC_6H_4COO)_2py_{0.5}$					1.53(297)	294			140
$Cu(2\text{-}BrC_6H_4COO)_2$					1.66(299)	166			127
$Cu(2\text{-}BrC_6H_4COO)_2 \cdot H_2O$	2.06	2.34	2.15[a]	0.34	1.54(298.5)	250			127
$Cu(2\text{-}BrC_6H_4COO)_2py$	2.064 2.054	2.361	2.167	0.3727	1.45(301)	309			137
$Cu(2\text{-}BrC_6H_4COO)_2an$	2.076	2.357	2.166	0.3701	1.52(295)	274			137
$Cu(2\text{-}BrC_6H_4COO)_2DMF$	2.11	2.36	2.19	0.363	1.39(294)	300	1.39	2.65	131
$Cu(2\text{-}BrC_6H_4COO)_2$ $\cdot 0.5\,C_4H_8O_2$	2.091	2.378	2.191[a]	0.375	1.44(294)	331	1.39	2.62	130
$Cu(2\text{-}BrC_6H_4COO)_2 \cdot A$	2.120	2.395	2.215[a]	0.374	1.55(297)	306	1.33	2.60	130

(TABLE CONTINUED on next page)

TABLE 8 (continued)

Compound	$g_\perp$	$g_\parallel$	g_{av}	$\|D\|$ (cm^{-1})	$\mu_{eff}(T)$ (B.M.)	$-2J$ (cm^{-1})	Electr. sp. ($\tilde{\nu}_{max}$ (μm^{-1}))		Ref.
							I	II	
$Cu(2\text{-}BrC_6H_4COO)_2 \cdot$ nic	2.087	2.362	2.183 [a]	0.376	1.54(293)	280	1.33	2.55	132
$Cu(2\text{-}BrC_6H_4COO)_2$ pyNO	2.110	2.410	2.214	0.393	1.53(293)		1.35	2.55	133
$Cu(2\text{-}BrC_6H_4COO)_2$ 2 picNO	2.110	2.406	2.213	0.398	1.54(293)		1.35	2.55	133
$Cu(2\text{-}BrC_6H_4COO)_2 \cdot (3\ picNO)_{0.5}$	2.114	2.422	2.221	0.386			1.37	2.60	133
$Cu(2\text{-}BrC_6H_4COO)_2Ph_3PO$	2.108	2.423	2.218	0.390			1.32	2.60	133
$Cu(3\text{-}BrC_6H_4COO)_2$ py					1.50(295)	292			137
$Cu(4\text{-}BrC_6H_4COO)_2$	2.05	2.36	2.16 [a]	0.34	1.45(290)	286			127,141
$Cu(4\text{-}BrC_6H_4COO)_2C_2H_5OH$					1.41(290.5)	310			127,139
$Cu(4\text{-}BrC_6H_4COO)_2CH_3OH$	2.08(2)			0.345					141
$Cu(4\text{-}BrC_6H_4COO)_2C_4H_9OH$					1.45(298)	351	1.39	2.85	142
$Cu(2\text{-}IC_6H_4COO)_2$	2.06	2.34	2.15 [a]	0.35	1.48(299)	286			127
$Cu(2\text{-}IC_6H_4COO)_2 \cdot H_2O$					1.51(290)	260			127
$Cu(2\text{-}IC_6H_4COO)_2$ DMF	2.13	2.35	2.205	0.362	1.46(291)	292	1.38	2.63	131
$Cu(2\text{-}IC_6H_4COO)_2$nic	2.094	2.366	2.188 [a]	0.379	1.49(293)	292	1.29	2.70	132
$Cu(3\text{-}IC_6H_4COO)_2C_4H_9OH$	2.08(2)			0.357					141
$Cu(4\text{-}IC_6H_4COO)_2C_2H_5OH$					1.48(299)				139

[a] Mononuclear impurity

The value of $-2J$ is almost the same in all the copper(II) 2-iodobenzoates (Table 8). A similar observation was made in the case of the copper(II) iodoacetates (Table 3). Steric hindrance by the iodine atoms plays the major role.

The singlet-triplet separation ($-2J$) varies not only with the pKa values of the bridging acids [1,78] but also according to the terminal ligands, as is clearly demonstrated in Table 8. From Table 8 the tendency to increase the singlet-triplet separation ($-2J$) lies in the order anhydrous $<$ water $\leqslant$ aniline $<$ pyridine $\sim$ nicotine $\sim$ antipyrine $<$ dimethylformamide $\sim$ dioxan.

Three isomeric forms of $Cu(4\text{-}ClC_6H_4COO)_2$ were prepared [134]. According to the magnetic data form (a) is proposed to be a polynuclear structure with strong antiferromagnetic super-exchange interaction and the other two forms ((b) and (c)) are binuclear (Table 8).

Two isomers of $Cu(3\text{-}ClC_6H_4COO)_2$ ((a) and (b)) [134], differ in their magnetic data (Tables 8 and 10). On the basis of magnetic behaviour a polynuclear structure for form (a) and a binuclear structure for form (b), are proposed.

(iii) Tetranuclear compounds

The green $Cu(4\text{-}XC_6H_4COO)_2nic$ was obtained by drying $Cu(4\text{-}XC_6H_4\text{-}COO)_2nic_2$ (X = F or Cl; nic = nicotine) at 105°C [132]. The electronic spectra of both $Cu(4\text{-}FC_6H_4COO)_2nic$ and $Cu(4\text{-}ClC_6H_4COO)_2nic$ display a shoulder at about 2.60 μm^{-1} and bands at 1.35 and 1.33 μm^{-1}, respectively. Their EPR spectra exhibit absorption typical of a triplet in which $D > h\nu$. The compounds also display a line at $\approx$3209 Oe which can be attributed to a mononuclear impurity. The effective magnetic moments are 1.59 and 1.62 B.M. at 293 K and decrease to 1.13 and 1.025 B.M. at 93 K, respectively. On the basis of spectral and magnetic data [132] tetranuclear structures were proposed with a distorted square pyramidal configuration around each copper(II) atom.

(iv) Structural data—mononuclear compounds

Table 9 shows relevant crystallographic data for the bis(1,3-propanediamine)copper(II) benzoates. All the compounds crystallize in the monoclinic system, space group $P2_1/C$ (no. 14, C_{2h}^5), with 2 molecules per unit cell ($Z = 2$). In all the bis(1,3-propanediamine)copper(II) benzoates the 1,3-propanediamine molecules form a square-planar configuration around the copper(II) atom with four short bond lengths (Table 9, Fig. 3). The tetragonal environment is completed with two axial, longer bonds (Cu—O) from the monodentate anions. The compounds are all centrosymmetric.

The introduction of a halogen atom into benzoic acid results in an increase of the acid strength. The decrease in the electron density of the coordinated oxygen atom results in a decrease in the Cu—O bond strength (Table 9). However the distances between the coordinated oxygen atoms

TABLE 9

Crystallographic data for bis(1,3-propanediamine)copper(II) benzoates [a]

Compound	Cu—N (Å) (R_S)	Cu—O (Å) (R_L)	$R_L - R_S$	R_S/R_L	N—Cu—N (deg.)	N—Cu—O (deg.)	Ref.
$CuL_2(C_6H_5COO)_2$	2.055(20)	2.48(2)	0.425	0.828	88.5(7)	94.2(6)	143
$CuL_2(3\text{-}BrC_6H_4COO)_2$	2.05(1)	2.48(1)	0.43	0.826	89.2(4)	94.8(3)	144
$CuL_2(3\text{-}ClC_6H_4COO)_2$	2.04(1)	2.48(1)	0.44	0.822	87.6(3)	94.0(3)	145
$CuL_2(4\text{-}FC_6H_4COO)_2$	2.035(1)	2.50(1)	0.465	0.814	87.2(2)	96.2(2)	146
$CuL_2(4\text{-}BrC_6H_4COO)_2$	2.035(1)	2.50(1)	0.465	0.814	88.9(4)	93.4(4)	147
$CuL_2(4\text{-}ClC_6H_4COO)_2$	2.04(1)	2.53(1)	0.49	0.806	87.8(5)	95.8(5)	148
$CuL_2(4\text{-}IC_6H_4COO)_2$	2.015(20)	2.55(2)	0.535	0.790	89.1(8)	93.7(7)	149

[a] L = 1,3-propanediamine. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviation in parentheses are average e.s.d.'s for an individual distance. The mean value of interatomic distances in the equatorial plane (R_S); and in the axial direction (R_L).

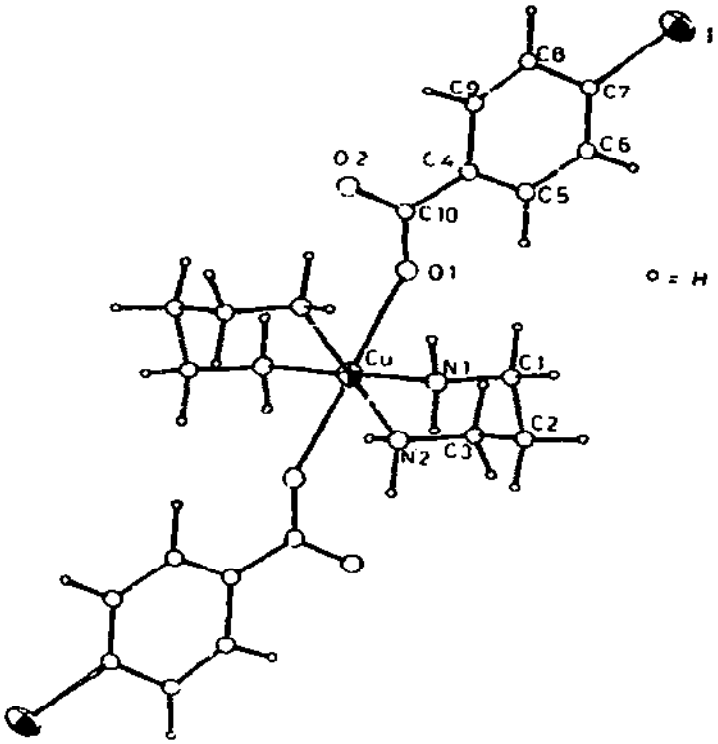

Fig. 8. A view of the bis(1,3-propanediamine)copper(II) 4-iodobenzoate molecule. (Reprinted with permission from [149]. Copyright by the Slovak Technical University.)

and the carbon atoms of the halogenocarboxylate groups range from 1.23 to 1.26 Å, shorter than the same distance, 1.30 Å, in the case of unsubstituted benzoate groups.

In Table 9 we see that while the value of R_S decreases the value of R_L increases. The value of $(R_L - R_S)$ is lowest in the case of $CuL_2(C_6H_5COO)_2$ but highest in $CuL_2(4\text{-}IC_6H_4COO)_2$. The ratio of R_S/R_L may be considered a measure of the relative tetragonal distortion [150—152].

These variations give some support to the suggestion that the axial distortions arise through a simultaneous elongation out-of-plane and contraction in-plane of the coordination polyhedron, and further indicate the plasticity of the coordination sphere of copper(II) [153].

The sum of all the interatomic distances Cu—N (4x) and Cu—O (2x) of bis(1,3-propanediamine)copper(II) benzoates (Table 9) is almost constant and is approximately 13.16 Å (±0.04 Å). The analogous sum for most examples [153] of the chromophores CuN_6 and CuO_6 are 14.3 and 12.6 Å, respectively. The sum of the chromophore CuN_4O_2 presented here lies almost between these two sums.

TABLE 10

Spectral and magnetic data for mono- and polynuclear copper(II) halogenobenzoates

Compound	$g_\perp$	$g_\parallel$	g_{av}	$\mu_{eff}(T)$ (B.M.)	θ (K)	Electr. sp. ($\tilde{\nu}_{max}$ (μm^{-1}))	Ref.
$Cu(4\text{-}FC_6H_4COO)_2$ [a]			2.13	1.78(300)		1.515	128
$Cu(4\text{-}FC_6H_4COO)_2 \cdot 2H_2O$	2.057	2.293	2.140	2.06(300)		1.49	128
$Cu(4\text{-}FC_6H_4COO)_2(1,3\ pn)_2$				1.95(300)		1.78	128
$\alpha\text{-}Cu(4\text{-}FC_6H_4COO)_2 nic_2$	2.072	2.264	2.138	1.84(293)	−4.4	1.70 1.36sh	132
$\beta\text{-}Cu(4\text{-}FC_6H_4COO)_2 nic_2$	2.069	2.237	2.126	1.90(293)	−13	1.48	132
$Cu(4\text{-}FC_6H_4COO)_2 nic_2 \cdot H_2O$			2.08	1.85(293)	−0.6	1.54 1.36sh	132
$[Cu(4\text{-}FC_6H_4COO)_2(OH)]_n$				1.96(299)			139
$Cu(2\text{-}FC_6H_4COO)_2 en$				1.91(299)		1.58	128
$Cu(2\text{-}FC_6H_4COO)_2 en_2 \cdot 2H_2O$				1.83(299)		1.82	128
$Cu(2\text{-}FC_6H_4COO)_2(1,2\ pn)$				1.91(299)		1.58	128
$Cu(2\text{-}FC_6H_4COO)_2(1,2\ pn)_2 \cdot 4H_2O$				1.94(299)		1.82	128
$Cu(2\text{-}FC_6H_4COO)_2(1,3\ pn)$				1.90(300)		1.64	128
$Cu(2\text{-}FC_6H_4COO)_2(1,3\ pn)_2$				1.93(300)		1.78	128
$Cu(2\ Cl\text{—}5\ NH_2C_6H_3COO)_2$	2.160	2.060	2.123	1.82(RT)			155
$Cu(3\text{-}ClC_6H_4COO)_2 \cdot 2H_2O$				1.90(294)	−10	1.45 2.65	134
$[Cu(3\text{-}ClC_6H_4COO)_2]_n$(A)				1.73(295.4)	−50	1.45	134
$Cu(4\text{-}ClC_6H_4COO)_2 \cdot H_2O$				2.00(292.4)	20	1.37 2.57	134
$Cu(4\text{-}ClC_6H_4COO)_2 nic_2$	2.066	2.236	2.123	1.83(293)	−11.5	1.50 1.36sh	132
$Cu(3\text{-}BrC_6H_4COO)_2 an$				1.67(295)			137
$Cu(4\text{-}BrC_6H_4COO)_2 an$				1.95(295)			137

[a] $g_\perp = 2.114$; $g_\parallel = 2.429$; $|D| = 0.354\ cm^{-1}$; sh = shoulder.

$Cu(1,3\text{-propanediamine})_2(3\text{-}IC_6H_4COO)_2 \cdot H_2O$ crystallizes in the orthorhombic system in space group $P2_12_12$ (no. 18) with 4 molecules per unit cell ($Z = 4$) [154]. The 1,3-propanediamine molecules form an almost square-planar configuration around the copper(II) atom, where the Cu—N distances range from 2.01(3) to 2.08(8) Å. The axial positions of the octahedron are occupied by an oxygen atom of one 3-iodobenzoate anion (Cu—O = 2.67(3) Å) and by coordinating water ($Cu—OH_2$ = 2.51(5) Å). The second 3-iodobenzoate anion is bonded with hydrogen bonds to two water molecules and one 1,3-propanediamine via nitrogen atoms.

(v) Spectral and magnetic data—mono- and polynuclear compounds

On the basis of spectral and magnetic data (Table 10) mononuclear structures similar to those of the corresponding copper(II) alkylcarboxylates (see Sect. B.(v)) were proposed for the mono- and bis(diamine)copper(II) arylcarboxylates.

The violet-blue $\alpha\text{-}Cu(4\text{-}FC_6H_4COO)_2nic_2$ and blue $\beta\text{-}Cu(4\text{-}FC_6H_4COO)_2nic_2$ were found [132] to possess different spectral and magnetic data (Table 10). Both isomers are supposed to possess an axially distorted octahedron, with distortion somewhat greater in the case of α- than in the β-isomer. These may be distortion isomers of the type described for other copper(II) compounds [153].

A polynuclear structure was proposed for the anhydrous compounds (Table 10).

E. COPPER(II) HALOGENOSALICYLATES

(i) Spectral and magnetic data

The paramagnetic turquoise blue needles of $\alpha\text{-}Cu(C_6H_4OHCOO)_2 \cdot 4\ H_2O$, crystallise in the monoclinic space group $P2_1/c—C_{2h}^5$ with two formula units per cell ($Z = 2$) [156]. In the crystal structure the coordination number of copper(II) is six and the coordination polyhedron is elongated along the tetragonal axis. The plane around the Cu(II) atom is built up by two oxygen atoms of water in *trans* position at 1.92 Å and two oxygen atoms of the two carboxyl groups at 1.84 Å. Positions five and six are occupied by the oxygen atoms of two water molecules at 3.00 Å. Besides the two water molecules in the inner coordination sphere of the copper(II) atom, there are two water molecules in the crystal bonded only by hydrogen bonds and forming a crystal hydrate. The spectral and magnetic data of $\alpha\text{-}Cu(C_6H_4OHCOO)_2 \cdot 4\ H_2O$ (Table 11) are consistent with the crystal structure [156]. The other two isomeric forms β- and $\gamma\text{-}Cu(C_6H_4OHCOO)_2 \cdot 4\ H_2O$ were isolated and some data are collected in Table 11. For the β-isomer a binuclear structure similar to that of copper(II) acetate monohydrate was proposed; and for the γ-isomer a tetranuclear structure [160]. These results show the versatility of

TABLE 11

Spectral and magnetic data for copper(II) halogenosalicylates and copper(II) salicylate tetrahydrate

Compound	$g_\perp$	$g_\parallel$	g_{av}	μ_{eff} (T) (B.M.)	θ (K)	Electr. sp. [a] ($\tilde{\nu}_{max}$ (μm^{-1}))		Ref.
						I	II	
α-Cu(sal)$_2$ · 4 H$_2$O	2.06	2.31	2.15	1.92(294)	−6.4	1.50	1.82sh	157—160
β-Cu(sal)$_2$ · 4 H$_2$O [b]				1.44(293)		1.36	2.66	161, 157, 159
γ-Cu(sal)$_2$ · 4 H$_2$O [c]				1.58(296)		1.46	2.60	160
Cu(5 Clsal)$_2$	2.045	2.310	2.137	1.64(293)	−79	1.35	2.30	162
Cu(5 Clsal)$_2$ · 3 H$_2$O	2.040	2.332	2.141	1.78(291)	−6	1.52	2.50sh	162
α-Cu(5 Clsal)$_2$py$_2$	2.059	2.250	2.124	1.89(296)	9	1.66	1.39sh	162, 163
β-Cu(5 Clsal)$_2$py$_2$	2.063	2.261	2.131	1.95(295)	7	1.64	1.40sh	162, 163
Cu(5 Clsal)$_2$(2 pic)$_2$ · H$_2$O	2.014	2.204	2.078	1.91(294)	−6	1.78	1.43sh	164
Cu(5 Clsal)$_2$(3 pic)$_2$	2.066	2.253	2.130	1.81(293)	3.5	1.77	1.43sh	164
Cu(5 Clsal)$_2$(4 Clpy) · H$_2$O	2.041	2.332	2.142	1.89(300)	0	1.56	2.45	164

$Cu(5\ Brsal)_2$	2.041	2.384	2.160	2.05(294)	−37	1.36	2.20	165
$Cu(5\ Brsal)_2 \cdot 3\ H_2O$	2.066	2.349	2.170	2.07(294)	2.2	1.43	2.40	165
α-$Cu(5\ Brsal)_2py_2$	2.055	2.273	2.130	1.86(293)	14.3	1.70	1.41sh	163, 165
β-$Cu(5\ Brsal)_2py_2$	2.046	2.252	2.117			1.72	1.42sh 2.30	163, 165
$Cu(5\ Brsal)_2py_3$	2.028	2.248	2.103	1.86(293)	−0.1	1.56		163, 165
$Cu(5\ Brsal)_2(3\ pic)_2$	2.059	2.243	2.122	1.89(293)	−1.5	1.70	1.43sh	165
$Cu(5\ Brsal)_2en_{2.5}$			2.102	1.84(293)	−1.6	1.76	2.85	165
$Cu(5\ Brsal)_2C_4H_8O_2 \cdot H_2O$ [d]				1.50(293)		1.36	2.40	165
$Cu(3,5\ Br_2sal)_2$	2.040	2.380	2.150	1.90(297)	8	1.37br	2.25	164
$Cu(3,5\ Br_2sal)_2 \cdot 2\ H_2O$	2.066	2.310	2.150	2.03(293)	11	1.41	2.10	164
$Cu(3,5\ Br_2sal)_2en_{2.5}$	2.024	2.130	2.122	1.965(297)	−18	1.78	2.75	164
$Cu(5\ Isal)_2$	2.031	2.385	2.155	1.71(300)	−14	1.40br	2.25	164
$Cu(5\ Isal)_2 \cdot 3\ H_2O$	2.050	2.340	2.151	1.90(293)	−16	1.46	2.40	164

[a] sh = shoulder; br = broadening. [b] $g_\perp = 2.09$; $g_\parallel = 2.34$; $|D| = 0.330\ cm^{-1}$; $-2J = 308\ cm^{-1}$ [160]. [c] $g_\perp = 2.08$; $g_\parallel = 2.37$; $|D| = 0.359\ cm^{-1}$; $J_{12} = -147\ cm^{-1}$; $J_{14} = -7.9\ cm^{-1}$ [160]. [d] $g_\perp = 2.096$; $g_\parallel = 2.386$; $|D| = 0.355\ cm^{-1}$; $-2J = 333\ cm^{-1}$ [165].

coordination polymerism of copper(II).

Spectral and magnetic data for copper(II) halogenosalicylate compounds are given in Table 11. Two isomers of $Cu(5\ Clsal)_2py_2$ and $Cu(5\ Brsal)_2py_2$ were prepared and characterized with small differences in their spectral and magnetic data. The isomers are supposed to possess an octahedral stereochemistry with different tetragonal distortion around copper(II) and are another example of distortion isomerism in copper(II) [153].

In the case of $Cu(5\ Brsal)_2 \cdot C_4H_8O_2 \cdot H_2O$ the data are similar to those observed for copper(II) acetate monohydrate (Table 2). On the basis of such a similarity a binuclear structure for the dioxane adduct was proposed [165].

The $g_\parallel$ value increases and $g_\perp$ value decreases as the hydrates are dehydrated (except in the case of copper(II) 5-chlorosalicylates). The metal—oxygen bond length in the equatorial plane is expected, then, to be longer in the case of the anhydrous rather than the hydrated species. A possible reason for this is less electron delocalization in the anhydrous form due to less mixing of the metal wave functions with those of the anion ligands. This is in agreement with the results of Smith [166], i.e. the $g_\parallel$ value will tend to increase as the equatorial metal—ligand bond length increases. The effective magnetic moments of the hydrated forms are higher than those of the anhydrous. We can see (Table 11) that the magnetic super-exchange interaction decreases in the order $Cu(5\ Clsal)_2 > Cu(5\ Brsal)_2 > Cu(5\ Isal)_2 > Cu(3,5\ Br_2sal)_2$ probably as a result of steric hindrance.

F. CONCLUSIONS

The copper—copper distances in the binuclear structures are elongated when the p*Ka* value of the respective acid decreases but at the same time the Cu—L distances tend to contract. This elongation accompanies a movement of the metal ion out of the basal plane of its square pyramidal coordination polyhedron. In spite of this fact, the Cu—O (basal) distances, as well as the sum of all the interatomic distances around copper(II) ion are almost constant and are approximately 1.97 and 11.37 Å, respectively. These variations give some support to the suggestion that the asymmetric axial distortions observed in binuclear copper(II) halogenoacetates arise through a simultaneous elongation of the ellipsoidal electron cloud of the copper(II) ion. Although steric interactions of the terminal ligands undoubtedly play a role in stabilizing the binuclear structure, the primary factor determining the Cu—Cu distances is electronic behaviour of the carboxylate groups.

In copper(II) halogenocarboxylates the $-2J$ values vary according to the p*Ka* values of the bridging acids. In the case of anhydrous and hydrated copper(II) halogenoalkylcarboxylates the tendency for formation of mononuclear molecules is enhanced as the p*Ka* value of the respective acid decreases. The opposite effect occurs in the case of copper(II) halogenoarylcarboxylates.

In the copper(II) carboxylates, $-2J$ increases as the terminal ligands

become stronger electron donors [78]. Thus, the $-2J$ value tends to increase according to the series of terminal ligands: aniline < water ⩽ anhydrous < pyridine < picolines ~ SCN^- ~ ethanol < dioxane. Copper(II) halogenoalkylcarboxylates follow this trend, but copper(II) halogenoarylcarboxylates do not. These observations indicate that the variation of $-2J$ with the properties of the terminal ligands is not a simple function of the base strength of the ligands or of any other readily evident parameter. The significance, if any, of this observation cannot be definitively evaluated on the basis of existing experimental data. It does however suggest possible rational directions for further experiments. Further effort will be needed to clarify this situation.

From a wide range of EPR measurements of g_{av} and its anisotropic components two clear broad trends may be distinguished: (a) halogenoalkylcarboxylates: g (aniline and its derivatives) < g (pyridine and its derivatives) < g (dioxane) ~ g (H_2O) < g (O donor atom from organic compounds) ~ g (anhydrous); (b) halogenoarylcarboxylates: g (anhydrous) < g (aniline and its derivatives) < g (H_2O) < g (pyridine and its derivatives) < g (dioxane) < g (O donor atom from organic compounds). Binuclear copper(II) halogenoarylcarboxylates tend to exhibit rather smaller values of g than copper(II) halogenoalkylcarboxylates. This may correlate [78] partly with the stronger ligand fields and the presence of a rhombic coordination sphere for the aryl compounds. In general, such a situation will lead to the admixture of the $|z^2\rangle$ orbital with the ground state. For such a reason the average value of g will be reduced [167].

The general tendency to decrease the singlet—triplet separation ($-2J$) is in the order: halogenoacetates ⩾ halogenopropionates > halogenobenzoates. While the value of ($-2J$) is greatest in the case of copper(II) halogenoalkylcarboxylates, the value of the zero field splitting parameter $|D|$ is lowest, which is opposite to the case of copper(II) halogenobenzoates. Since the parameter $|D|$ includes a contribution from both exchange and dipole—dipole interaction and these effects are opposite in sign, this suggests that the dipole—dipole interaction provides the greatest contribution to $|D|$ in the first case and the least in the second case, and thereby the smallest reduction in the exchange interaction.

In the case of bis(1,3-propanediamine)copper(II) benzoates, the tendency to increase axial distortion lies in the order: unsubstituted benzoic acid < 3-halogeno- < 4-halogeno-substituted benzoic acid but the value of the dipole moment of the corresponding anion [151] decreases in the same order. These observations can be correlated with distortion of the umbrella configuration, which is formed by the halogeno atoms and benzene rings of different molecular groups. In the case of bis(1,3-propanediamine)copper(II) chlorobenzoates [145] the umbrella configuration is distorted considerably more for the 4-chlorobenzoate than for the 3-chlorobenzoate, and thereby the chlorine atoms are nearer the benzene rings in the 3-chlorobenzoate than in the 4-chlorobenzoate. In this fashion there arises a "new" situation to build σ—π

bonds between the chlorine atom and the benzene ring in the umbrella configuration. At the same time with distortion of the umbrella configuration the electron densities of the oxygen atoms decrease, leading to weaker covalent metal—oxygen bonds and therefore the axial distortion of bis(1,3-propanediamine)copper(II) benzoates increases in the order mentioned above.

REFERENCES

1 M. Kato, H.B. Jonassen and J.C. Fanning, Chem. Rev., 64 (1964) 99, and references therein.
2 R.L. Martin, in E.A.V. Ebsworth, A.G. Maddock and A.G. Sharpe (Eds.), New Pathways in Inorganic Chemistry, Cambridge University Press, Cambridge, 1968, Chap. 9, and references therein.
3 E. Sinn, Coord. Chem. Rev., 4 (1969) 313.
4 R.J. Doedens, Progr. Inorg. Chem., 21 (1976) 209.
5 P.W. Ball, Coord. Chem. Rev., 4 (1969) 361.
6 G.F. Kokoszka and R.W. Duerst, Coord. Chem. Rev., 5 (1970) 209, and references therein.
7 T.D. Smith, Coord. Chem. Rev., 13 (1974) 173, and references therein.
8 M. Melník, Acta Fac. Pharm. Com. Univ. Bratisl., 25 (1974) 37, and references therein.
9 J.N. Van Niekerk and F.R.L. Schoening, Nature (London), 171 (1953) 36.
10 J.N. Van Niekerk and F.R.L. Schoening, Acta Crystallogr., 6 (1953) 227.
11 P. de Meester, S.R. Fletcher and A.C. Skapski, J. Chem. Soc., Dalton Trans., (1973) 2575.
12 G.M. Brown and R. Chidambaram, Acta Crystallogr., Sect. B, 29 (1973) 2393.
13 L.E. Sutton (Ed.), Tables of Interatomic Distances and Configuration in Molecules and Ions, Spec. Pub. No. 18, Chem. Soc., London, 1965, Supplement.
14 V.I. Ivanov, Yu.A. Simonov, A.V. Ablov and L.N. Milkova, Krystallografiya, 19 (1974) 1286.
15 Yu.A. Simonov, V.I. Ivanov, A.V. Ablov, T.I. Malinovskii and L.N. Milkova, Koord. Chim. (USSR), 1 (1975) 716.
16 Yu.A. Simonov, L.N. Milkova, A.V. Ablov and T.I. Malinovskii, Dokl. Akad. Nauk SSSR, 229 (1976) 1134.
17 Yu.A. Simonov, V.I. Ivanov, A.V. Ablov, L.N. Milkova and T.I. Malinovskii, J. Struct. Chem. (USSR), 17 (1976) 516.
18 Yu.A. Simonov, A.A. Dvorkii, Yu.V. Jablokov, L.N. Milkova and A.V. Ablov, J. Struct. Chem. (USSR), 19 (1978) 175.
19 G. Davey and F.S. Stephens, J. Chem. Soc. A, (1970) 2803.
20 J.A. Moreland and R.J. Doedens, Inorg. Chem., 17 (1978) 674.
21 J.A. Moreland and R.J. Doedens, J. Am. Chem. Soc., 97 (1975) 508.
22 J. Lifschitz and E. Rosenbohm, Z. Elektrochem., 21 (1915) 499.
23 B. Bleaney and K.D. Bowers, Proc. R. Soc., Ser. A, 214 (1952) 451.
24 B. Bleaney and K.D. Bowers, Phil. Mag., 43 (1952) 372.
25 B.N. Figgis and R.L. Martin, J. Chem. Soc., (1956) 3837.
26 D.P. Craig, A. Maccoll, R.S. Nyholm, L.E. Orgel and L.E. Sutton, J. Chem. Soc., (1954) 322.
27 I.G. Ross, Trans. Faraday Soc., 55 (1959) 1057.
28 E.A. Boudreaux, Inorg. Chem., 3 (1964) 506.
29 D.M.L. Goodgame, N.J. Hill, D.F. Marsham, A.C. Skapski, M.L. Smart and P.G.H. Troughton, Chem. Commun., (1969) 629.

30 M. Gerloch and J.H. Harding, Proc. R. Soc., Ser. A, 360 (1978) 211.
31 P.D.W. Boyd, M. Gerloch, J.H. Harding and R.G. Woolley, Proc. R. Soc., Ser. A, 360 (1978) 161.
32 P.D.W. Boyd, J.E. Davies and M. Gerloch, Proc. R. Soc., Ser. A, 360 (1978) 191.
33 Yu.V. Jablokov, A.V. Ablov, L.N. Milkova and L.N. Romanenko, Dokl. Akad. Nauk SSSR, 180 (1968) 659.
34 R.L. Martin and H. Waterman, J. Chem. Soc., (1957) 2545.
35 B. Guha, Proc. R. Soc., Ser. A, 206 (1951) 353.
36 G. Foex, T. Karantassis and N. Perakis, C. R. Acad. Sci., 237 (1953) 982.
37 S. Yamada, H. Nakamura and R. Tsuchida, Bull. Chem. Soc. Jpn., 30 (1957) 953.
38 C.W. Reimann, G.F. Kokoszka and G. Gordon, Inorg. Chem., 4 (1965) 1082.
39 H. Abe and J. Shimada, J. Phys. Soc. Jpn., 12 (1957) 1255.
40 J. Lewis, F.E. Mabbs, L.K. Royston and W.R. Smail, J. Chem. Soc. A, (1969) 291.
41 T. Watanabe, J. Phys. Soc. Jpn., 16 (1961) 1677.
42 W. Sakaguchi, Y. Arata and S. Fujiwara, J. Chem. Phys., 53 (1970) 464.
43 K.S. Patel and J.A. Faniran, J. Inorg. Nucl. Chem., 38 (1976) 1001.
44 M. Melník, Finn. Chem. Lett., (1978) 255.
45 V.V. Gavrilov, Yu.V. Jablokov, V.F. Siškov, A.V. Ablov and L.N. Milkova, Dokl. Akad. Nauk SSSR, 194 (1970) 352.
46 L.N. Romanenko, V.V. Gavrilov, L.N. Milkova and A.V. Ablov, Dokl. Akad. Nauk SSSR, 188 (1969) 1332.
47 Yu.V. Jablokov, V.V. Gavrilov, L.N. Milkova and A.V. Ablov, Dokl. Akad. Nauk SSSR, 199 (1971) 159.
48 S.F.A. Kettle and J.P. Pioli, J. Chem. Soc. A, (1968) 1243.
49 A.V. Ablov, Yu.V. Jablokov, Yu.A. Simonov, L.I. Landa, T.I. Malinovskii and L.N. Milkova, Dokl. Akad. Nauk SSSR, 201 (1971) 599.
50 M. Melník, Finn. Chem. Lett., (1974) 142.
51 M. Melník and J. Mrozinski, Mater. Sci., in press.
52 V.I. Ivanov, Yu.A. Simonov, A.V. Ablov and L.N. Milkova, Dokl. Akad. Nauk SSSR, 220 (1975) 365.
53 J.A. Moreland and R.J. Doedens, J. Chem. Soc., Dalton Trans., (1974) 28.
54 M. Kondo and M. Kubo, J. Phys. Chem., 62 (1958) 1558.
55 K.S. Patel, J.A. Faniran and A. Earnshaw, J. Inorg. Nucl. Chem., 38 (1976) 352.
56 K.E. Hyde, G. Gordon and G. Kokoszka, J. Inorg. Nucl. Chem., 30 (1968) 2155.
57 M.F. Lundman-Obier, M. Dartiguenave and Y. Dartiguenave, J. Mol. Struct., 18 (1973) 123.
58 H. Abe and H. Shirai, J. Phys. Soc. Jpn., 16 (1961) 118.
59 R. Näsänen and M. Melník, Suom. Kemistilehti B, 42 (1969) 300.
60 M.D. Judd, B.A. Plunkett and M.I. Pope, J. Therm. Anal., 9 (1976) 83.
61 G.F. Kokoszka, H.C. Allen Jr. and G. Gordon, J. Chem. Phys., 47 (1967) 10.
62 R. Uggla and M. Melník, Suom. Kemistilehti B, 43 (1970) 496.
63 Yu.V. Jablokov, V.V. Gavrilov, A.V. Ablov and L.N. Milkova, Dokl. Akad. Nauk SSSR, 191 (1970) 1102.
64 Yu.V. Jablokov, V.V. Gavrilov, L.N. Milkova and A.V. Ablov, J. Struct. Chem. (USSR), 12 (1971) 237.
65 L.V. Mosina, Yu.V. Jablokov, L.N. Milkova and A.V. Ablov, Dokl. Akad. Nauk SSSR, 227 (1976) 904.
66 M. Melník and R. Näsänen, Suom. Kemistilehti B, 42 (1969) 413.
67 A.V. Ablov, V.V. Gavrilov, L.N. Milkova, L.N. Romanenko and Yu.V. Jablokov, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 1404.
68 M. Melník and A.M. Taiminen, Suom. Kemistilehti B, 44 (1971) 8.
69 R. Uggla and M. Melník, Suom. Kemistilehti B, 44 (1971) 6.
70 M. Melník, R. Näsänen and I.J. Seppälä, Suom. Kemistilehti B, 44 (1971) 95.

71 K.S. Patel and J.A. Faniran, J. Inorg. Nucl. Chem., 39 (1977) 1149.
72 M. Dartiguenave, R. Jesser, M.F. Obier, R. Schwaller and J. Wucher, C.R. Acad. Sci., 271 (1970) 981.
73 M. Melník, Acta Chem. Scand., 25 (1971) 3777.
74 W.G. Bateman and A.B. Hoel, J. Am. Chem. Soc., 36 (1914) 2517.
75 W.G. Bateman and D.B. Conrad, J. Am. Chem. Soc., 37 (1915) 2552.
76 I. Mukherjee, Indian J. Phys., 41 (1967) 776.
77 R.C. Paul, P.R. Sharma and S.L. Chadha, Indian J. Chem. A, 15 (1977) 27.
78 R.W. Jotham, S.F.A. Kettle and J.A. Marks, J. Chem. Soc., Dalton Trans., (1972) 428.
79 (a) K. Smolander, U. Turpeinen and M. Ahlgrén, Finn. Chem. Lett., (1978) 195.
(b) U. Turpeinen, R. Hämäläinen, M. Ahlgrén and K. Smolander, Finn. Chem. Lett., (1979) 108.
80 R.G. Little, D.B.W. Yawney and R.J. Doedens, J. Chem. Soc., Chem. Commun., (1972) 228.
81 R.G. Little, J.A. Moreland, D.B.W. Yawney and R.J. Doedens, J. Am. Chem. Soc., 96 (1974) 3834.
82 M. Žemlička and J. Krätsmár-Šmogrovič, Proc. 7th Conf. Coord. Chem., Smolenice-Bratislava, Czechoslovakia, 1978, p. 285.
83 G. Davey and F.S. Stephens, J. Chem. Soc. A, (1971) 1917.
84 G. Davey and F.S. Stephens, J. Chem. Soc. A, (1971) 2577.
85 M. Ahlgrén, R. Hämäläinen and U. Turpeinen, Acta Chem. Scand. A, 32 (1978) 57.
86 U. Turpeinen, M. Ahlgrén and R. Hämäläinen, Cryst. Struct. Commun., (1978) 617.
87 P.R. Ireland, B.R. Penfold and W.T. Robinson, J. Chem. Soc., Chem. Commun., (1970) 486.
88 R. Kivekäs, Finn. Chem. Lett., (1977) 252.
89 J.A. Pretorius and J.C.A. Boeyens, J. Inorg. Nucl. Chem., 40 (1978) 1745.
90 R.C. Thompson and D.B.W. Yawney, Can. J. Chem., 43 (1965) 1240.
91 C.A. Agambar and K.G. Orrell, J. Chem. Soc. A, (1969) 897.
92 S. Amasa, D.H. Brown and D.W.A. Sharp, J. Chem. Soc. A, (1969) 2892.
93 M. Žemlička and J. Krätsmár-Šmogrovič, Proc. 7th Conf. Coord. Chem., Smolenice-Bratislava, Czechoslovakia, 1978, p. 291.
94 M. Melník, Suom. Kemistilehti B, 43 (1970) 256.
95 M. Melník and R. Uggla, Suom. Kemistilehti B, 43 (1970) 327.
96 R. Uggla and M. Melník, Suom. Kemistilehti B, 45 (1972) 16.
97 G. Davey, R.J. Dudley and B.J. Hathaway, J. Chem. Soc. A, (1971) 1446.
98 M. Melník and R. Näsänen, Suom. Kemistilehti B, 43 (1970) 18.
99 R. Näsänen and M. Melník, Suom. Kemistilehti B, 42 (1969) 300.
100 S. Yamada, H. Nishikawa and R. Tsuchida, Bull. Chem. Soc. Jpn., 33 (1960) 1278.
101 A.B.P. Lever and D. Ogden, J. Chem. Soc. A, (1967) 2041.
102 R. Näsänen and M. Melník, Suom. Kemistilehti B, 42 (1969) 263.
103 A.V.R. Warrier and R.S. Krishnan, Spectrochim. Acta, Part A, 27 (1971) 1243.
104 R. Näsänen and M. Melník, Suom. Kemistilehti B, 42 (1969) 485.
105 M.F. Obier, M. Dartiguenave and Y. Dartiguenave, Bull. Soc. Chim. Fr., (1971) 2520.
106 Yu.A. Simonov and T.I. Malinovskii, Kristallografiya, 15 (1970) 370.
107 Yu.V. Jablokov and A.V. Ablov, Dokl. Akad. Nauk SSSR, 144 (1962) 173.
108 G.F. Kokoszka, M. Linzer and G. Gordon, Inorg. Chem., 7 (1968) 1730.
109 H. Abe, Phys. Rev., 92 (1953) 1572.
110 H. Abe, J. Phys. Soc. Jpn., 13 (1958) 987.
111 S. Yamada, H. Nakamura and R. Tsuchida, Bull. Chem. Soc. Jpn., 30 (1957) 953.
112 R. Uggla and M. Melník, Acta Chem. Scand., 25 (1971) 1790.
113 M. Melník, Acta Chem. Scand., 24 (1970) 3243.
114 R. Uggla and M. Melník, Suom. Kemistilehti B, 43 (1970) 492.

115 M. Melník, R. Näsänen and I.J. Seppälä, Acta Chem. Scand., 25 (1971) 2081.
116 M. Melník and R. Uggla, Suom. Kemistilehti B, 44 (1971) 5.
117 M. Melník, Finn. Chem. Lett., (1974) 189.
118 M. Melník and J. Mrozinski, J. Mol. Struct., 31 (1976) 269.
119 M. Melník and J. Mrozinski, J. Mol. Struct., 48 (1978) 79.
120 M. Melník, J. Mol. Struct., in press.
121 M. Melník, Acta Chem. Scand., 26 (1972) 697.
122 M. Melník and R. Uggla, Acta Chem. Scand., 26 (1972) 4166.
123 M. Melník and R. Näsänen, Suom. Kemistilehti B, 42 (1969) 387.
124 M. Melník and R. Näsänen, Suom. Kemistilehti B, 42 (1969) 298.
125 M. Melník, Suom. Kemistilehti B, 44 (1971) 175.
126 W. Harrison, S. Rettig and J. Trotter, J. Chem. Soc. A, (1972) 1852.
127 J. Lewis, F.E. Mabbs, L.K. Royston and W.R. Smail, J. Chem. Soc. A, (1969) 291.
128 M. Melník, Suom. Kemistilehti B, 44 (1971) 97.
129 M. Melník and R. Uggla, Suom. Kemistilehti B, 44 (1971) 95.
130 M. Melník and J. Mrozinski, J. Mol. Struct., 57 (1979) 135.
131 M. Melník and J. Mrozinski, J. Mol. Struct., 35 (1976) 133.
132 M. Melník, J. Inorg. Nucl. Chem., 41 (1979) 779.
133 M. Melník and J. Mrozinski, J. Mol. Struct., in press.
134 J. Lewis, Y.C. Lin, L.K. Royston and R.C. Thompson, J. Chem. Soc., (1965) 6464.
135 M. Melník, Suom. Kemistilehti B, 46 (1973) 323.
136 M. Melník and R. Uggla, Suom. Kemistilehti B, 43 (1970) 499.
137 F.G. Herring, B. Landa, R.C. Thompson and C.F. Schwerdtfeger, J. Chem. Soc. A, (1971) 528.
138 S. Yamada, H. Nishikawa and S. Miki, Bull. Chem. Soc. Jpn., 37 (1964) 576.
139 R. Whyman, W.E. Hatfield and C.S. Fountain, Inorg. Chim. Acta, 1 (1967) 429.
140 Y.C. Lin and R.C. Thompson, Can. J. Chem., 46 (1968) 557.
141 Yu.V. Jablokov, V.V. Zelentsov and L.N. Romanenko, Teor. Eksp. Khim., 4 (1968) 407.
142 W.E. Hatfield, C.S. Fountain and R. Whyman, Inorg. Chem., 5 (1966) 1855.
143 R. Uggla and M. Klinga, Suom. Kemistilehti B, 45 (1972) 10.
144 O. Orama, G. Huttner, H. Lorenz, M. Mersili and A. Franz, Finn. Chem. Lett., (1976) 137.
145 R. Uggla, O. Orama, M. Sundberg, E. Tirronen and M. Klinga, Finn. Chem. Lett., (1974) 185.
146 O. Orama, Finn. Chem. Lett., (1976) 154.
147 O. Orama, Finn. Chem. Lett., (1976) 151.
148 R. Uggla, O. Orama and M. Klinga, Suom. Kemistilehti B, 46 (1973) 43.
149 O. Orama and G. Huttner, Finn. Chem. Lett., (1976) 140.
150 B. Ross, Acta Chem. Scand., 20 (1966) 1673.
151 M. Melník, R. Uggla and M. Sundberg, unpublished results.
152 L. Macášková and J. Gažo, Koord. Chim. (USSR), 4 (1978) 1314.
153 J. Gažo, I.B. Bersuker, J. Garaj, M. Kabešová, J. Kohout, H. Langfelderová, M. Melník, M. Serátor and F. Valach, Coord. Chem. Rev., 19 (1976) 253.
154 O. Orama and A. Pajunen, Finn. Chem. Lett., (1977) 193.
155 G. Ismailov, V.V. Zelentsov and Yu.V.Jablokov, J. Inorg. Chem. (USSR), 17 (1972) 2304.
156 F. Hanic and J. Michalov, Acta Crystallogr., 13 (1960) 299.
157 M. Inoue, M. Kishita and M. Kubo, Acta Crystallogr., 16 (1963) 699.
158 G.A. Popovič, A.V. Ablov and V.E. Suncov, J. Inorg. Chem. (USSR), 14 (1969) 2710.
159 M. Melník, M. Kabešová, F. Valach and J. Gažo, Finn. Chem. Lett., (1974) 8.
160 M. Melník and J. Mrozinski, Mater. Sci., in press.
161 J. Ploquin, Bull. Soc. Chim. Fr., (1951) 757.

162 M. Melník, J. Inorg. Nucl. Chem., 40 (1978) 463.
163 M. Melník and Z. Bačík, Proc. 7th Conf. Coord. Chem., Smolenice-Bratislava, Czechoslovakia, 1978, p. 159.
164 M. Melník, Z. Bačík and J. Mrozinski, Mater. Sci., 5 (1979) 135.
165 M. Melník, Z. Bačík and H. Sandström, Acta Chem. Scand. A, 33 (1979) 769.
166 D.W. Smith, J. Chem. Soc. A, (1970) 3108.
167 R.N. Bagchi and P. Sengupta, Indian J. Phys., 40 (1966) 675.