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FACTORS AFFECTING THE MAGNETIC PROPERTIES OF DIMERIC COPPER(II) COMPLEXES

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CONTENTS

A. INTRODUCTION

In the study of the magnetic interaction of polynuclear complexes of the first-row transition metals, copper(II) carboxylate dimers are important both

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from the historical and theoretical viewpoints. The study essentially began, except for the earlier work [1,2], with the measurement of ESR spectra by Bleaney and Bowers [3] and of the variable-temperature magnetic susceptibility by Figgis and Martin [4] of copper(II) acetate monohydrate. The structural determination of this compound by van Niekerk and Schoening [5,6] showed its very unusual cage-type dimeric structure with a Cu–Cu distance of 2.64 Å. This remarkable observation was the beginning of the subsequent explosively active research on the magnetism of polynuclear metal complexes. A second type of binuclear copper(II) complex on which magnetic studies have been done are the so-called "tri-coordinated" complexes.

Salicylal-*o*-hydroxyanilcopper(II), a compound of this second group, was first prepared by Pfeiffer et al. in 1937 [7]. Calvin and Barkelew noticed a low moment (1.58 BM) for this compound but ascribed it to possible impurities [8]. For the complexes of this group, magnetic studies were initiated by Kishita et al. in 1957 [9]. Subsequently in 1961, Barclay et al. determined the monoatom bridging structure of acetylacetone mono(*o*-hydroxyanil)copper(II), a compound of this group [10]. Among the monooxygen atom bridging copper(II) dimers with subnormal magnetic moments, copper(II) halides with pyridine *N*-oxides occupy an important area in magnetic studies of binuclear copper(II) complexes since the pyridine ring can be attached with a very wide range of substituents, giving rise to a wide range of magnetic moments, say, 1.0–0.2 BM. Thus they are a good group with which to study the substituent effects on magnetic interactions. In 1961, Quagliano et al. found that pyridine *N*-oxide copper(II) chloride has a very low magnetic moment [11] *. Then in 1965, Hatfield et al. [12] and later Muto et al. [13] began a magnetic study on this group of copper(II) dimers with extensive preparations. They also carried out a systematic study on copper(II) halide dimers with salicylaldimines. Finally, the present authors have concentrated their attention on copper(II) carboxylate dimers which may be a goal of magnetic studies of binuclear metal complexes. The magnetic susceptibility data for copper(II) dimers, systems with a pair of interacting ions of spin 1/2, are widely known to fit the modified Bleaney–Bowers equation (eqn. (1)) [14]:

$$\chi_{\mathrm{A}} = \frac{Ng^2\beta^2}{3kT}\left[1 + \left(\frac{1}{3}\right)\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1 - P) + \frac{Ng_{\mathrm{i}}^2\beta^2}{4kT}P + N\alpha \qquad (1)$$

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* Professor Fujita, Nagoya University, once told the authors an interesting story. One day he found a bottle labelled with pyridine *N*-oxide on a shelf in Quagliano's laboratory and tried without any particular expectation to mix the contents with copper(II) chloride in a solvent; however, the result was quite unique, as we now know [11].

where χ_A is the paramagnetic susceptibility per metal atom after the correction for diamagnetism, P the mole fraction of the monomeric copper(II) impurities, g_i the average g factor of the impurity (we assume it to be 2.2) and $-2J$ the singlet–triplet separation (a positive value means antiferromagnetic interaction or a singlet ground state). The value of $-2J$ lies in the range 100–1000 cm^{-1} and can be determined to an acceptable degree by susceptibility measurements by the Gouy or Faraday method in the range from liquid nitrogen temperature to room temperature; $N\alpha$, the temperature-independent paramagnetism, is usually assumed to be 60×10^{-6} c.g.s. e.m.u. for copper(II) compounds [3,15] but if possible, it should be parameterized, when a better fitting is obtained. The magnitude of the spin–spin coupling of the copper(II) dimers was given in our early studies in terms of magnetic moments standardized to the values at 25 °C, $\mu_{\text{eff}}^{25°\text{C}}$, by using the Bleaney–Bowers equation assuming $g = 2.2$. Such magnetic moments can be utilized to some extent for a discussion of the magnetic interaction, in place of $-2J$, since, when these magnetic moments have been carefully determined, the $-2J$ values derived from the room temperature moments agree fairly well with those obtained from temperature-variable magnetic susceptibility data [16,17].

The topics in the present review will be discussed in the following order: copper(II) halides with pyridine *N*-oxides, copper(II) halides with salicylaldimines, and copper(II) carboxylates.

B. DIMERIC COPPER(II) HALIDE COMPLEXES WITH PYRIDINE *N*-OXIDES

(i) Ortho *effect of substituents and magnetic exchange*

A study of the electronic effect of the substituents of dimeric metal compounds which modify the superexchange pathways on the bridging atom or atoms is of considerable interest. For this purpose the title compounds are very good examples, since copper(II) halide complexes of pyridine *N*-oxides with a variety of substituents attached at the 2-, 3- or 4-position of the pyridine ring can be prepared [12–13,18–31]. Hatfield and Paschal [24] discussed the electronic influence of substituent attached at the 4-position in the pyridine ring in R–PyO · CuX_2: $-2J$ (cm^{-1}) = 143, 616, 986, 1090 and 2150 for R(X) = NO_2(Br), H(Cl), CH_3(Cl), Cl(Cl) and OH(Cl). Kidd and Watson also studied a number of copper(II) chloride complexes with 4-substituted pyridine *N*-oxides [28]. They found two linear relationships between $-2J$ and the substituent parameter σ_R: one with CH_3O, CH_3, $(CH_3)_3C$, H, NO_2 and the other with Cl, Br, C_6H_5 and CN including 3-CH_3(Br). However, they did not give any reasonable explanation for the existence of two such linear relationships in these dimeric systems [27,28]. After several

TABLE 1

Magnetic and reflectance spectral data for 1:1 copper(II) halide complexes with substituted pyridine *N*-oxides, $CuX_2 \cdot R\text{–}PyO$[a]

Ligand[b]	$CuCl_2$ complex				$CuBr_2$ complex			
	T (K)	μ_{eff} (BM)	$\mu_{eff}^{25°C}$ (BM)	λ_{max} (nm)	T (K)	μ_{eff} (BM)	$\mu_{eff}^{25°C}$ (BM)	λ_{max} (nm)
PyO	292	0.73	0.75	940	292	0.53	0.55	900
3-Cl·PyO	297	0.46	0.46	820	291	0.25	0.27	775
4-Cl·PyO	296	0.49	0.50	800	294	0.45	0.46	800
3-Br·PyO					287	0.42	0.45	825
3-COOH·PyO	294	0.53	0.54	885				
$3\text{-}COOC_2H_5 \cdot PyO$	297	0.48	0.48	825	297	0.39	0.39	820
$4\text{-}COOC_2H_5 \cdot PyO$	297	0.50	0.50	830	296	0.28	0.29	790
$3\text{-}CH_3CO \cdot PyO$	303	0.58	0.57	900	304	0.52	0.50	840
$4\text{-}NO_2 \cdot PyO$	303	1.21	1.20	1100	298	0.45	0.45	830
4-CN·PyO	296	0.95	0.96	805	297	0.79	0.79	800
3-OH·PyO	286	0.33	0.37	795	287	0.34	0.37	780
4-OH·PyO	291	0.31	0.33		294	0.22	0.23	
$3\text{-}CH_3 \cdot PyO$	297	0.55	0.55	850	291	0.48	0.50	840
$4\text{-}CH_3 \cdot PyO$	298	0.52	0.52	835	291	0.47	0.49	830
$2\text{-}C_2H_5 \cdot PyO$	286	0.29	0.32	763	286	0.28	0.31	765
$3\text{-}C_2H_5 \cdot PyO$	286	0.42	0.46	810	288	0.34	0.37	812
$4\text{-}C_2H_5 \cdot PyO$	285	0.55	0.59	820	286	0.38	0.41	820
$2,4\text{-}(CH_3)_2 \cdot PyO$	289	0.34	0.37	765	289	0.32	0.35	760
$2,6\text{-}(CH_3)_2 \cdot PyO$	297	0.22	0.22	760	298	0.30	0.30	745
$2,4,6\text{-}(CH_3)_3 \cdot PyO$	294	0.27	0.28	750	289	0.42	0.45	735
$2\text{-}CH_2OH \cdot PyO$[c]	292	0.37	0.39	800	286	0.36	0.40	812
$3\text{-}CH_2OH \cdot PyO$	292	0.48	0.50	813	283	0.38	0.42	817
$4\text{-}CH_2OH \cdot PyO$	281	0.47	0.53	818	285	0.40	0.44	823
QNO	286	0.30	0.33	733	284	0.29	0.33	735
$4\text{-}CH_3 \cdot QNO$	283	0.36	0.40	750	285	0.30	0.33	745
iso·QNO	280	0.45	0.51	810	284	0.39	0.43	807

[a] The quality of the early magnetic data is often unacceptable for a comparative study such as the present case. The data in the table are taken from refs. 18, 21 and 22. Readers should also refer to the tables in refs. 27 and 29–31. [b] PyO, pyridine *N*-oxide; QNO, quinoline *N*-oxide. [c] For this ligand, many other modifications are produced under different reaction conditions [22].

years of work, we finally concluded that no apparent correlation exists between Hammett σ constants and the magnetic moments or the *d–d* band energies, but a linear relationship does exist between the *d–d* band energies and the magnetic moments: "the higher the *d–d* band energies, the lower the magnetic moments", irrespective of the polar nature of the substituents and the substituent positions on the aromatic ring (Table 1 and Fig. 1) [19,21]. Kidd and Watson also found the same type of linear relationship

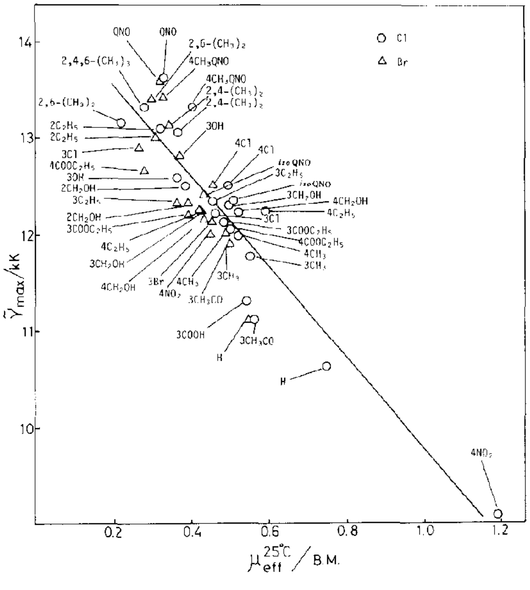


Fig. 1. A plot of the d–d band wavenumbers ($\tilde{\nu}_{\text{max}}$ in kilokaisers) of copper(II) halide complexes with substituted pyridine N-oxides against the corrected magnetic moments ($\mu_{\text{eff}}^{25°\text{C}}$ in Bohr magnetons): ○, chloro complexes; △, bromo complexes.

between d–d band energies and $-2J$ values for some 4-substituted pyridine N-oxide copper(II) halide complexes [28]. It is apparent that in these dimeric systems, structural or steric conditions which may be caused by substituents are more important than their electronic influence, and thus Hammett's rule is not applicable [21]. The steric effect operates in such a way that a greater magnetic interaction or a higher d–d band energy is produced when a substituent is attached at a position closer to the central metal atom. A typical example can be seen in the magnetic moments and the d–d band positions of complexes of copper(II) chloride with ethylpyridine N-oxides (Fig. 2). Thus, when a substituent is attached at position 2 of the pyridine ring, the greatest spin coupling tends to occur. Such a steric effect of substituent groups may operate because a substituent attached at the *ortho* position of the aromatic ring shields the fifth or sixth axial site of the central metal ion from the influence of other ions or molecules more effectively than *m* or *p* substituents. Such a substituent effect, which is called the *ortho* effect, should increase the strength of the four metal coordinate bonds and result in greater demagnetization and higher d–d band energies. In addition, such an *ortho* effect may decrease the partial tetrahedral stereochemistry more or less present in such systems, a factor

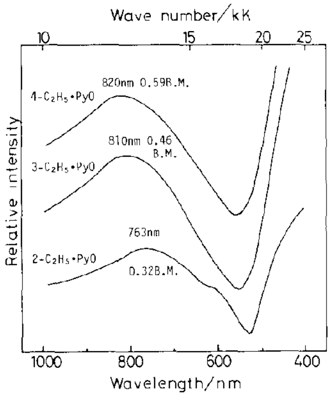


Fig. 2. Reflectance spectra of various ethylpyridine *N*-oxide copper(II) chloride complexes.

which favours a larger metal–ligand orbital overlap producing smaller magnetic moments and higher *d–d* band energies [21].

(ii) Magnetic and structural comparison of copper(II) chloride and bromide with pyridine N*-oxide*

It is important to compare the magnetic and structural data for 1 : 1 copper(II) chloride and bromide complexes with non-substituted pyridine *N*-oxide, the simplest system in the present study (Fig. 3 and Table 2). The degree of magnetic interaction is determined by several factors: the length of the metal–oxygen bridging bond, Cu–O; the bridging angle ϕ; the metal coordination geometry. The greater demagnetization (greater $-2J$ value) of the bromide is reflected in the shorter bridging metal–oxygen bond length, larger bridging angle and less strain from planar coordination geometry. All

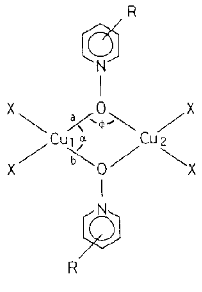


Fig. 3. A schematic view of the molecular structure of copper(II) halides with pyridine *N*-oxide.

TABLE 2

Magnetic and structural data for copper(II) halides with pyridine *N*-oxide

X	$(a+b)/2$ (Å)	c (Å)	ϕ (deg)	α (deg)	γ [a] (deg)	$-2J$ (cm^{-1})	$\mu_{\mathrm{eff}}^{25°\mathrm{C}}$ (BM)	d–d band (nm)	Reference
Cl	2.14	1.34	108	72	70	716	0.75	940	26, 28, 32–34
Br	1.98	1.38	110	70	83	935	0.55	900	26, 35

[a] Dihedral angle between the CuOCuO bridging plane and the pyridine ring.

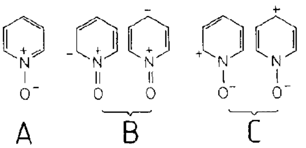


Fig. 4. Resonance structures of pyridine *N*-oxide.

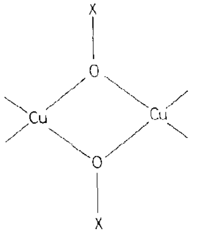
these characteristics favour a greater magnetic orbital overlap between the metal and bridging oxygen atoms, leading to a greater exchange interaction in the bromide. The greater magnetic interaction in the bromide is also reflected in the longer N–O bond of the pyridine *N*-oxide molecule in the complex. A stronger metal–oxygen bond is favoured by the resonance structures A or C (Fig. 4) which will lead to a longer N–O bond as observed in the bromide. In general, copper(II) bromides with pyridine *N*-oxides show smaller magnetic moments and higher *d–d* band energies than the corresponding chlorides (Table 1). This tendency was interpreted by a greater nephelauxetic effect of the bromide ion than of the chloride ion [21,29]. On the basis of the above comparative structural study, Whinnery and Watson considered that the nephelauxetic effect should not be introduced to rationalize the differences in magnetic behaviour between the bromide and chloride [35]. However, such a tendency is widely observed even in other bimetallic systems [31,36–40]. It is a problem worth studying further from wider viewpoints.

(iii) Characteristics of the magnetic exchange in dimeric copper(II) halides with pyridine N-oxides

In studies of the magnetic characteristics of dimeric copper(II) complexes, it is important to examine them with reference to the magneto–structural criteria which have been established on similar copper(II) dimers. The linear relationship between $-2J$ and the Cu–O–Cu bridging angle ϕ (eqn. (2)), which has been established in a series of symmetrically bridged copper(II) hydroxide complexes by Hatfield, Hodgson and coworkers [30,41,42], seems the best criterion for studying the characteristics of the magnetic exchange in copper(II) halides with pyridine *N*-oxides:

$$2J(\mathrm{cm}^{-1}) = -74.53\phi + 7270 \qquad (2)$$

The $-2J$ values for the halides calculated from eqn. (2) are 764 cm^{-1} for the chloride and 936 cm^{-1} for the bromide. These values are in good agreement with the experimental values of 716 cm^{-1} and 935 cm^{-1} for the respective halides. In the light of such a comparison, the exchange mechanism in these two bimetallic systems seems quite similar at a glance. However, there are important differences between them in the bridging properties. One is the large difference between these two systems in electron density on the bridging oxygen atoms. The electron density on the bridging oxygen atoms in the OH series is quite large compared with that in the PyO series. In general, the proton affinity of pyridine *N*-oxides is quite small: for instance, the pK_{BH^+} value of the parent compound PyO is only 0.79 [18,43]. Moreover, the Cu–O bridging distance which should be important in determining the magnetic orbital overlaps leading to the magnitude of the singlet–triplet separation, $-2J$, markedly differs in these two systems: the Cu–O distance equals 1.919 Å in the OH series and 1.994 Å in the PyO series; the difference of 0.075 Å is quite large. These facts indicate that the magnetic exchange mechanism works more effectively through PyO bridges than through OH bridges in these dimeric copper(II) systems. In other words, though the Cu–O(PyO)–Cu bridges in many ways appear not to be suitable for the pathway of magnetic exchange either in the bond length or in the electron density at the bridging oxygen atom, they can be as effective for the magnetic pathway as the Cu–O(OH)–Cu bridges. Among double-bridge copper(II) dimers, copper(II) halides with pyridine *N*-oxide have the largest bridging angle ϕ, a fact which may be correlated with their long or weak bridging bonds. Why can the copper(II) halides with pyridine *N*-oxides produce such large magnetic exchange regardless of their fragile bridging structure? It is an interesting puzzle. An answer to this question may be found in Bencini and Gatteschi's π-bonding effect on the singlet–triplet separation, $-2J$ [44]: a longer bridging bond will produce a decrease in the π-bonding effect which leads to an increase in the $-2J$ value. Another explanation for the superiority of the magnetic exchange through the Cu–O(PyO)–Cu bridges may be in terms of the mechanism proposed by Galy et al. [45] to explain the much greater observed $-2J$ value (650 cm^{-1}) for a phenolic-oxygen bridged dimer, $Cu_2(fsa)_2en \cdot CH_3OH$ ($H_4(fsa)_2en$ = *N*,*N*′-bis(2-hydroxy-3-carboxybenzilidene)-1,2-diaminoethane) (bridging angle, $\phi = 100.1°$) than the value expected from Hatfield's rule (eqn. (2)) for



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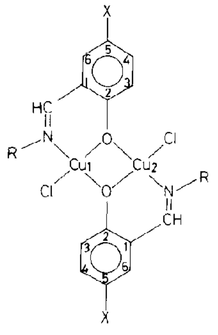
the OH-bridging series (190 cm^{-1}). In **1** the electronegativity of X, which is a single atom or an atom of a group directly σ-bonded to the bridging oxygen atom, is the important factor which determines the extent of the magnetic exchange between copper atoms in a pair. When the electronegativity of X increases from that of hydrogen, the energy of the highest symmetric molecular orbital ϕ_S decreases more rapidly than that of the antisymmetric molecular orbital ϕ_A in Hoffmann's mechanism [46], resulting in a larger gap between the energies of the two molecular orbitals, and thus a larger $-2J$ in the dimeric system **1**, a result opposite to Hoffmann's conclusion. Thus when the bridging angle Cu–O–Cu is kept the same in **1**, the $-2J$ value increases with the increase in the electronegativity of X: H < C < N, i.e. OH series < O–C$<$ series < O–N$<$ series. In this connection, it is noteworthy that Lintvedt et al. have claimed the importance of the nature of the bridging atom in such dimeric systems [47]. They have shown that some ketonic-oxygen bridged copper(II) dimers produce much larger $-2J$ values than the corresponding OH-bridged systems with nearly the same bridging angles, regardless of the distinctly longer bridging bond lengths in the keto systems. Further, what meaning does the linear relationship between the magnetic moments and the *d–d* band energies have in these systems? At present, structural data for 1 : 1 copper(II) halides with pyridine *N*-oxides are too few. The structural examination of the *ortho* effect of substituents in these systems is an interesting area for further study.

C. DIMERIC COPPER(II) COMPLEXES WITH *N*-SUBSTITUTED (R) SALICYLIDENEIMINES

(i) Copper(II) chloride complexes with bidentate Schiff's bases

(a) R = alkyl or some related group

The aim of our magnetic and spectral study on the system **2** is to see the effect of substituent R combined with the aldimine N atom which coordinates to the central Cu atom in the CuOCuO bridging framework. Then, in contrast with the copper(II) halides with pyridine *N*-oxides, where the electronic effect of the substituents attached to the pyridine ring should be transmitted directly to the bridging oxygen atom (Section B), in the present dimeric system the electronic effect, if any, of the substituent R should be indirect. It may work in such a way that the change in the nature of the Cu–N bond caused by the R group combined with the aldimine N atom affects the bridging Cu–O bond in the superexchange pathway by changing the copper(II) environment. In fact, in the pyridine *N*-oxide systems, the nature of the halide ion which is not included in the bridging framework consistently causes an effect on the magnetic exchange of the systems



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(Section B). The results are shown in Table 3 and Fig. 5. These complexes are roughly classified into three groups: B type (brown; pseudotetrahedral, four-coordinate), YG type (yellow–green; dimethylformamide (DMF) or dimethyl sulphoxide (DMSO) adducts; distorted square pyramidal, five-coordinate) and Y type (yellow–orange; distorted trigonal bipyramidal, five-coordinate) on the basis of their colour and spectral criteria (Fig. 6) [53–55]. The data are plotted on a two-dimensional diagram with magnetic moments ($\mu_{\text{eff}}^{25^\circ\text{C}}$) on the abscissa and *d–d* band positions ($\tilde{\nu}_{\text{max}}$) on the ordinate (Fig. 5). On the diagram the complexes are further divided into several subgroups: the B-type complexes into subgroup (a) with the chemical formula Cu(Sal · N–R)Cl and subgroup (b) with Cu(5X–Sal · N–R)Cl. The spectral and magnetic behaviour of the complexes of subgroup (a) fit the linear relationship between $\tilde{\nu}_{\text{max}}$ and $\mu_{\text{eff}}^{25^\circ\text{C}}$ which is well established for copper(II) halide complexes with pyridine *N*-oxides (Section B). The effect of steric hindrance due to the bulkiness of *N*-alkyl groups was clearly observed. The effect of the bulkiness increased in the following order: R = *n*-C_3H_7 < R = *i*-C_3H_7, *n*-C_4H_9 < R = *sec*-C_4H_9, *t*-C_4H_9. The observed linear relationship was interpreted in terms of the mechanism of the shift of the stereochemistry between the tetrahedral and planar configuration (tetrahedral $\rightleftharpoons$ planar). An increase toward tetrahedral symmetry in the stereochemistry leads to an increase in the magnetic moments (a weakening in magnetic exchange) and a decrease in the *d–d* band energy or vice versa. The complexes of subgroup (b) are concentrated in a relatively small area on the $\tilde{\nu}_{\text{max}}$ vs. $\mu_{\text{eff}}^{25^\circ\text{C}}$ diagram, indicating that their spectral and magnetic characteristics are somewhat different from those of the subgroup (a). The Y-type and YG-type complexes are not markedly different in their spectral pattern. However, on the basis of the distorted trigonal bipyramidal structure of

TABLE 3

Magnetic and reflectance spectral data for Cu(5X–Sal·N–R)Cl [a]

Complex	T (K)	μ_{eff} (BM)	$\mu_{\text{eff}}^{25\,°\text{C}}$ (BM)	$-2J$ (cm^{-1})	$\lambda_{\max}$ (nm)
X = H					
R = CH_3 (brown form)	285	1.44	1.46	242 292 [b], 298 [b]	790
CH_3 (yellow–orange form)	290.8	0.84	0.87	580	1055
C_2H_5	301	1.08	1.07	480 [b]	775
n-C_3H_7	303	1.06	1.04	510 [b]	780
i-C_3H_7	303	1.35	1.34	290 [b]	880
n-C_4H_9	296	1.10	1.11	410 [b]	760
i-C_4H_9·0.5C_2H_5OH	289	0.77	0.80		660
i-C_4H_9				490 [b]	
sec-C_4H_9	292.8	1.36	1.37	300, 310 [b]	900
t-C_4H_9	289.5	1.38	1.40		900
n-C_6H_{13}				376 [b]	
n-C_8H_{17}				360 [b]	
$(CH_2)_2OH$	289.7	1.65	1.66	124	710
$(CH_2)_3OH$	300	1.01	1.01	504	950
$(CH_2)_3OCH_3$	287.7	1.00	1.03	491	900
$(CH_2)_3N(CH_3)_2$ (green form)	298	1.44	1.44	248	893
$(CH_2)_3N(CH_3)_2$ (red–violet form)	293	1.80			526
X = CH_3					
R = CH_3	290.6	1.45	1.46		820
C_2H_5	295	1.53	1.53		860
n-C_3H_7	293.5	1.36	1.37		780
i-C_3H_7	295.5	1.39	1.39		850
$(CH_2)_2OH$	286.1	1.64		110	
X = Cl					
R = CH_3	289.1	0.87	0.90	560 [b]	1065
C_2H_5	294	1.40	1.41	280 [b]	810
n-C_3H_7	296.5	1.31	1.32	376 [b]	780
i-C_3H_7	296	1.40	1.41	272 [b]	855
X = NO_2					
R = CH_3	300	0.99	0.98		965
C_2H_5	297.1	0.91	0.91		930
n-C_3H_7	294.5	1.83			
i-C_3H_7	292.5	1.88			
Cu(5X–Sal·N–R)Cl·L					
X = H, R = CH_3, L = DMF	295.1	1.13	1.14		915
X = H, R = CH_3, L = DMSO	291.2	1.02	1.04		925
X = H, R = $(CH_2)_3OH$, L = DMF	302.1	0.99	0.97		905
X = CH_3, R = CH_3, L = DMSO	287.0	0.93	0.95		860

[a] See formula **2**; Cu(5X–Sal·N–R)Cl = $\text{Cu}(\overset{2}{\text{O}}\cdot\text{C}_6\text{H}_4\cdot(\overset{5}{\text{X}})\cdot\overset{1}{\text{C}}\text{H}{=}\text{N}{-}\text{R})\text{Cl}$. Data from refs. 38, 39 and 48–51. [b] Data from ref. 52.

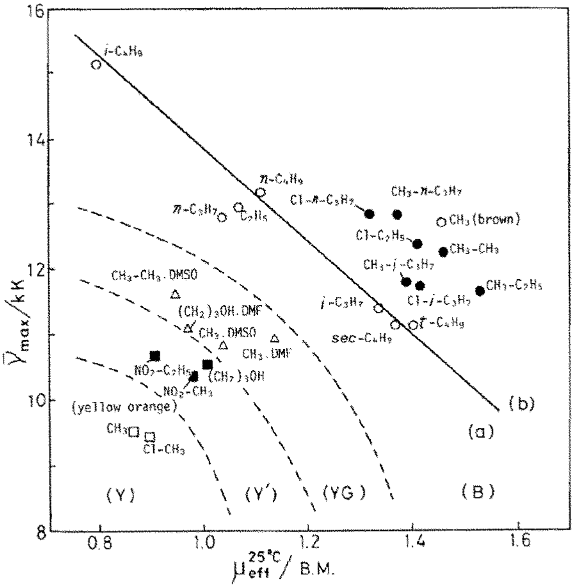


Fig. 5. Diagram of the plots of *d–d* band positions ($\tilde{\nu}_{max}$) and magnetic moments ($\mu_{eff}^{25°C}$). In the diagram, the complexes are designated by X–R for Cu(5X–Sal·N–R)Cl and by R for Cu(Sal·N–R)Cl. For adducts, the combined molecule is indicated at the end of each designation of complexes (see (b)). The complex types are indicated in parentheses above the abscissa.

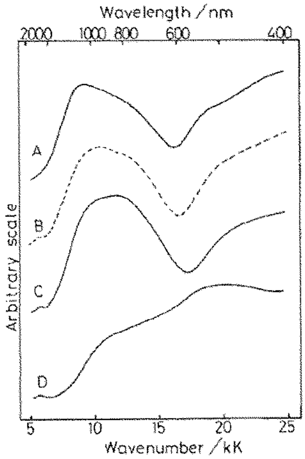
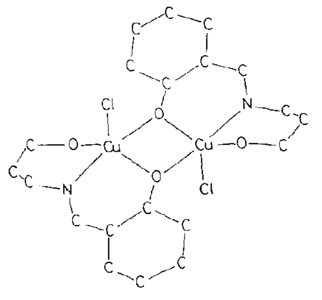


Fig. 6. Reflectance spectra of Y (or Y′)-, YG- and B-type complexes: A, Cu(5Cl–Sal·N–CH_3)Cl (Y type); B, Cu(Sal·N–$(CH_2)_3OH$)Cl (Y′ type); C, Cu(Sal·N–CH_3)Cl·DMF (YG type); and D, Cu(5CH_3–Sal·N–CH_3)Cl (B type).



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Cu(Sal · N–$(CH_2)_3OH$)Cl, **3**, determined by Bertrand et al. [56], an area of subgroup Y′ complexes is provided in between the areas of Y and YG complexes. The Y′-type complexes tend to contain very negative substituents (NO_2 and $CO_2C_2H_5$). The shift between the stereochemistries of each group may be given as follows:

TABLE 4

Magnetic and reflectance spectral data for Cu(Sal·N–Ph–X)Cl [a]

Substituent X	T (K)	μ_{eff} (BM)	$\mu_{eff}^{25°C}$ (BM)	$-2J$ (cm^{-1})	λ_{max} (nm)
H	295	1.38	1.39		890
2-CH_3	303	1.26	1.24		830
3-CH_3	302	1.56	1.56		920
4-CH_3	287	1.33	1.35		870
2-Cl	295	1.14	1.15		825
3-Cl	299	1.28	1.27		830
4-Cl	302.5	1.32	1.31		880
2-NO_2 [b]	296	1.06	1.06		880
3-NO_2	296	1.54	1.54	241	915
4-NO_2 [b]	300	0.98	0.97	563	900
2,6-$(CH_3)_2$	290	1.30	1.32		871
2,4-$(CH_3)_2$ (1/4C_2H_5OH)	290	1.26	1.28		855
2,6-Cl_2	285	1.17	1.21		857
2,3-Cl_2 (1/4C_2H_5OH)	286	1.24	1.27		975
2,5-Cl_2 (1/4C_2H_5OH) [b]	286	1.15	1.18		885
3,4-Cl_2 (1/2C_2H_5OH)	286	1.27	1.30		868
2-$CO_2C_2H_5$ [b]	296	0.95	0.96		903
4-$CO_2C_2H_5$ [b]	300	0.83	0.83		905

[a] See formula **4**. Data from refs. 51 and 57. [b] These complexes fall off the linear relationship between $\tilde{\nu}_{max}$ and μ_{eff}; they are to be placed in the Y′ or YG region of Fig. 5.

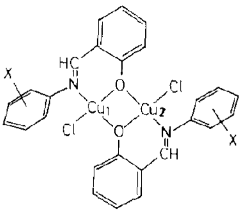
pseudotetrahedral ↔ square pyramidal ⇌ trigonal bipyramidal

B type	YG type	Y type	
		Y′	Y
	small distortion toward trigonal bipyramidal	large distortion toward square pyramidal	small distortion toward square pyramidal

The two modifications of $\mathrm{Cu(Sal \cdot N\text{-}CH_3)Cl}$, brown and yellow-orange in colour, are assigned to the two bilateral extreme areas on the stereochemistry shift diagram. On the whole, in dimeric copper(II) chloride complexes with *N*-alkyl salicylideneimines, the steric effect plays a more effective role than the electronic effect of the substituents as observed in the dimeric copper(II) halide complexes with pyridine *N*-oxides (Section B).

(b) R = substituted phenyl groups; ortho *effect of substituents*

The purpose of the magnetic and spectral study on the title dimeric copper(II) complexes **4** is to see if the *ortho* effect of the substituents observed for dimeric copper(II) halide complexes with pyridine *N*-oxides is really present in any other dimeric copper(II) systems and to see the electronic effect of the substituents on the magnetic exchange. The data are given in Table 4. A plot of the *d–d* band energies against the magnetic moments is shown in Fig. 7. For these dimeric chloro copper(II) complexes, as for the copper(II) chloride complexes with pyridine *N*-oxides (Section B), no correlation was observed to exist between the Hammett σ substituent constants and the *d–d* band positions or the magnetic moments. However, the *ortho*-substituent effect was again observed for the magnetic moments or the *d–d* band positions of these complexes:



4

$$\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}(o\text{-}) < \mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}(m\text{-}) \approx \mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}(p\text{-})$$

$$\tilde{\nu}_{\max}(o\text{-}) > \tilde{\nu}_{\max}(m\text{-}) \approx \tilde{\nu}_{\max}(p\text{-})$$

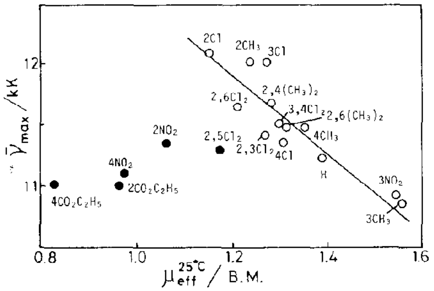


Fig. 7. A plot of the *d–d* band wavenumber ($\tilde{\nu}_{max}$ in kilokaisers) of Cu(Sal·N–Ph–X)Cl against the corrected magnetic moments ($\mu_{eff}^{25°C}$ in Bohr magnetons).

Further, for the complexes which are brown in colour, a linear relationship is observed to exist between $\tilde{\nu}_{max}$ and $\mu_{eff}^{25°C}$, irrespective of the polar nature of substituents and their attachment positions on the aromatic ring (**4**) just as observed for the copper(II) halide complexes with pyridine *N*-oxides (Section B). The complexes with 2-NO_2, 4-NO_2, 2-$CO_2C_2H_5$ and 4-$CO_2C_2H_5$ substituents fall off the linear relationship on the $\tilde{\nu}_{max}$ vs. $\mu_{eff}^{25°C}$ diagram (Fig. 7). These complexes are greenish orange in colour. Their spectral pattern is quite different from that of the brown complexes and resembles that of the Y′ or YG type of complex with *N*-alkyl substituents (Fig. 6). Their low magnetic moments, about 1 BM, are also in the range of the moment values for the complexes in the Y′ or YG region. The stereochemistry of those complexes, brown in colour, is assigned as pseudotetrahedral on the basis of the spectral criterion, similar to that for the *N*-alkyl aldimine complexes discussed in Section C(i)(a). The relationship "the higher the *d–d* band energies, the lower the magnetic moments" for these complexes can be interpreted in terms of the same shift mechanism of the stereochemistry

TABLE 5

Magnetic, spectral and structural data for Cu(Sal·N–R)Cl [a]

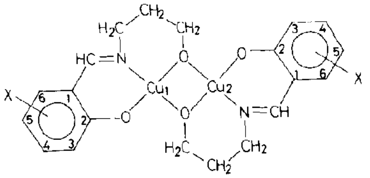
Substituent R	$\mu_{eff}^{25°C}$ (BM)	$-2J$ (cm^{-1})	λ_{max} (nm)	Cu–O (Å)	τ [b] (°)	ϕ [b] (°)
1 CH_3 (brown form)	1.46	292, 298	790	1.919	39.3	102.2
2 C_2H_5	1.07	480	775	1.945	33.1	103.3
3 *i*-C_3H_7	1.34	290	880	1.952	40.1	103.5
4 C_6H_5	1.39	360	890	1.943	37.3	103.3

[a] See formulae **2** and **4**. See Tables 3 and 4 for magnetic and spectral data. Structural data for 1–3 are from refs. 40, 58 and 59 and for 4 from ref. 60. [b] See Section C(iii).

between tetrahedral and planar configurations, tetrahedral $\rightleftharpoons$ planar, as observed for the complexes with *N*-alkyl salicylaldimines (Section C(i)(a)) (Table 5).

(ii) Copper (II) complexes with tridentate Schiff's base, R = n*-propanoate ion*

The aim of the magnetic and spectral study of the title copper(II) complexes is to see the effect of the substituents attached to the aromatic ring on the magnetic exchange of the dimeric systems **5** [16]. The subnormal magnetic moment of the parent compound (X = 5-H in **5**) was first reported by Yamada et al. [61]. These di-alkoxo-bridged binuclear copper(II) complexes are extraordinarily stable [62], as reflected in the short Cu–O bridging bond lengths of these complexes (Table 6). They have the shortest Cu–O bonds of the doubly oxygen-bridged dimeric copper(II) complexes. In the early stages of the work, the complexes of this group seemed to be one of the most appropriate dimeric systems to show the substituent effect because of their rigid dimeric framework. However, again, in these systems, no substituent effect was found to exist between the polar nature of the substituents in terms of the Hammett σ constants and the magnetic moments, $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$. The linear relationship between $\tilde{\nu}_{\mathrm{max}}$ and $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$, which had been widely observed in copper(II) halide complexes with pyridine *N*-oxides (Section B) and in a large number of copper(II) chloride complexes with *N*-substituted salicylideneimines (Sections C(i)(a) and C(i)(b)), was not found in these di-alkoxo-bridged systems. The reason for this is to be found in the relatively small number of complexes studied and in the very narrow range of *d*–*d* band energies of the systems.



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(iii) Characteristics of magnetic exchange in dimeric copper(II) complexes with N*-substituted salicylideneimines*

On the basis of structural and magnetic studies of a number of dimeric copper(II) complexes with the bidentate Schiff's base **2** [40,58,59], Sinn and coworkers concluded that the leading factor for determining the magnitude

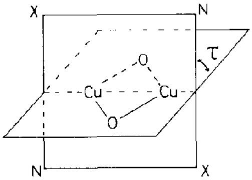
TABLE 6

Magnetic, reflectance spectral and structural data for Cu(X–Sal·N–$(CH_2)_3O$) [a]

Substituent X	T (K)	μ_{eff} (BM)	$\mu_{eff}^{25°C}$ (BM)	$-2J$ (cm^{-1})	λ_{max} (nm)	Cu–O (Å)	τ [b] (°)	ϕ [b] (°)
5-H	288	0.45(7)	0.49(0)	884	570			
5-CH_3	290	0.53(0)	0.56(2)		567			
5-Cl	288	0.49(7)	0.52(8)		566	1.925	13.7	103.7
5,6-benzo	302	0.58(8)	0.57(6)		565	1.899	10.4	104.0
5-NO_2	303	0.46(3)	0.44(7)		566	1.90	4.0	106.0

[a] See formula **5**. Magnetic and spectral data from refs. 16 and 50. Structural data from refs. 62–64. [b] See Section C(iii).

of the spin pairing in these systems is the dihedral angle τ, the angle between the CuOCuO bridging plane and the remaining coordinating plane,



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CuNXCuNX (X = Cl) (**6**). The $-2J$ values decrease steadily with increasing τ values. Thus changes in the CuOCuO bridging angle ϕ are relatively unimportant. In this connection, it is interesting to note the observation of Kida and coworkers that the plot of CuOCuO bridging angles vs. $-2J$ values for a series of alkoxo-bridged dimers does not obey the linear relationship of eqn. (2); the $-2J$ values for these complexes increase more rapidly than the values predicted by eqn. (2) with increasing CuOCuO bridging angle [17]. The conclusions of Sinn and coworkers are in conformity with our earlier proposal that the linear relationship between $\bar{\nu}_{max}$ and $\mu_{eff}^{25°C}$, which was observed with the brown complexes of Cu(5X—Sal·*N*–R)Cl (Table 3) and of Cu(Sal·*N*–Ph–X)Cl (Table 4), can be accounted for by the mechanism of the shift of the stereochemistry between tetrahedral and planar configurations, tetrahedral $\rightleftharpoons$ planar (Table 5). Actually, on the basis of the spectral criterion, pseudotetrahedral geometries have been assigned to those complexes which are brown in colour [51,57]. Very recently, Chiari et al. have shown that there exists a good linear relationship between τ and $2J$ for binuclear copper(II) halide complexes with bidentate

Schiff's bases (eqn. (3)) [60]:

$$2J\ (\mathrm{cm}^{-1}) = 29.7\tau - 1473.4 \tag{3}$$

In addition, by means of semiempirical MO calculations, they have shown that there is a small area of τ, less than about 10°–20°, where ϕ is a leading factor in determining $-2J$, and there is an adjoining fairly large area of τ in between about 20°–50° where τ plays a key role in determining $-2J$. Equation (2) is valid in the former area and eqn. (3) is applicable in the latter region to which the brown complexes of Cu(Sal · *N*–R)Cl and Cu(Sal · *N*–Ph–X)Cl should belong (Tables 3 and 4). The spin pairing of the complexes of Cu(X–Sal · *N*–$(CH_2)_3O$) seems to operate in a way somewhat different from that of hydroxo-bridged complexes where the ϕ mechanism works or from that of Cu(5X—Sal · *N*–R)Cl and Cu(Sal · *N*–Ph–X)Cl with pseudotetrahedral geometry where the τ mechanism operates. The $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$ values for the three complexes in Table 6 (X = 5-Cl, 5,6-benzo and 5-NO_2) are expected to decrease in the same order by either the τ mechanism or the ϕ mechanism since τ decreases and ϕ increases in the same order in these complexes. However, the order of magnetic moments is $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$(5-Cl) < $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$(5,6-benzo) > $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$(5-$NO_2$). These three complexes can be said to belong roughly to the area of the ϕ mechanism on Chiari's diagram. Then, if we take into account the small differences in both τ and ϕ between 5-Cl and 5,6-benzo complexes, $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$ decreases in the order (5-Cl, 5,6-benzo) > 5-NO_2, as predicted by either mechanism, τ or ϕ. Here we have a puzzle which may as yet be unsolved; the relationship between the magnitude of the spin exchange and the electron density at the bridging oxygen atoms or the bridging Cu–O bond lengths (cf. Section B). The $-2J$ values calculated from the $\mu_{\mathrm{eff}}^{25^\circ\mathrm{C}}$ values [16] for the three alkoxo-bridged complexes in Table 6, where the ϕ mechanism on Chiari's diagram [60] may operate, are greater by 250–350 cm^{-1} than those predicted from eqn. (2). This fact might be attributed to the greater electron density at the bridging oxygen atoms in the alkoxo-bridged complexes than that in the hydroxo-bridged complexes [60,62]. Somewhat shorter Cu–O bridging bonds in the alkoxo-bridged complexes, about 0.01 Å, may reflect the higher electron density at the bridging oxygen atoms in these complexes than in the hydroxo-bridged complexes [42,60]. How do these facts correlate with the π mechanism of Bencini and Gatteschi [44] or the electronegative mechanism of X in **1** according to Kahn and coworkers [45] to which we referred to explain the prominent antiferromagnetic exchange in copper(II) halides with pyridine *N*-oxides (Section B(iii))? It seems of interest to examine further the relationship between $-2J$ and the electron density at the bridging oxygen or the bridging Cu–O bond length in these binuclear copper(II) complexes [30,31,37,60,65–67].

D. DIMERIC COPPER(II) CARBOXYLATE COMPLEXES

(i) Influence of axial ligand L on the magnetic properties of dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2 \cdot L]_2$

Dimeric copper(II) carboxylate adducts have the structure shown in Fig. 8 and are antiferromagnetic with a singlet ground state and a thermally populated triplet excited state. It has already been pointed out that the antiferromagnetic interaction in $[Cu(RCOO)_2 \cdot L]_2$ tends to increase as either the axial ligand L or the carboxylate substituent R becomes a stronger electron donor [68]. Therefore the singlet–triplet separation ($-2J$, a measure of the magnitude of the magnetic interaction) is expected to increase as the pK_a of L becomes higher [69]. In the previous study of dimeric copper(II) acetate adducts with thiazoles [70], however, we found that, while the pK_a of thiazole (2.44) is lower than that of pyridine (5.32), the $-2J$ value of the thiazole adduct (344 cm^{-1}) is higher than that of the pyridine adduct (325 cm^{-1}) [71]. Thus in order to obtain accurate information on the effect of L on the magnetic interaction, we have studied the magnetic and spectral properties of copper(II) acetate, chloroacetate and dichloroacetate complexes with 3,5-dichloropyridine (3,5-Cl_2py), which is a much weaker base ($pK_a = 0.67$) than pyridine (py), and compared the properties with those of the corresponding pyridine adducts. For the sake of discussion, the magnetic susceptibility of the dimeric copper(II) acetate complex with 4-cyanopyridine (4-CNpy) was also re-examined [72]. Table 7 shows that the antiferromagnetic interactions in the respective 3,5-dichloropyridine adducts are stronger than those in the corresponding pyridine adducts. The reflectance spectra of the complexes resemble each other in shape and are quite similar to those of $[Cu(CH_3COO)_2(py)]_2$ (Fig. 9). The spectra show two

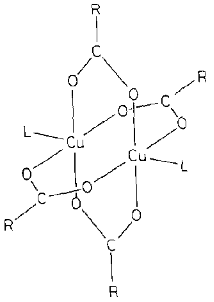


Fig. 8. Molecular structure of $[Cu(RCOO)_2 \cdot L]_2$.

TABLE 7

$-2J$ values for dimeric copper(II) carboxylate complexes

Complex	$-2J$ (cm^{-1})	Complex [a]	$-2J$ (cm^{-1})
$Cu(CH_3COO)_2(3,5\text{-}Cl_2py)$	349	$Cu(Me_3CCOO)_2$	403
$Cu(CH_3COO)_2(py)$	333	$Cu(Me_3CCOO)_2(py)$	366
$Cu(CH_3COO)_2(4\text{-}CH_3py)$	333	$Cu(Me_3CCOO)_2(ac)$	397
$Cu(CH_3COO)_2(4\text{-}CNpy)$	345	$Cu(Me_3CCOO)_2(qu)$	393
$Cu(CH_3COO)_2(caf)$	353	$Cu(Me_3CCOO)_2(2\text{-}pic)$	371
$Cu(ClCH_2COO)_2(3,5\text{-}Cl_2py)$	340	$Cu(Me_3CCOO)_2(4\text{-}pic)$	319
$Cu(ClCH_2COO)_2(py)$	333	$Cu(Me_3CCOO)_2(2,6\text{-}lu)$	379
$Cu(Cl_2CHCOO)_2(3,5\text{-}Cl_2py)$	312		
$Cu(Cl_2CHCOO)_2(py)$	288		
$Cu(ClCH_2COO)_2(PhCN)$	352		
$Cu(ClCH_2COO)_2(4\text{-}CH_3C_6H_4CN)$	339		
$Cu(Cl_2CHCOO)_2(4\text{-}CH_3C_6H_4CN)$	314		
$Cu(Cl_3CCOO)_2(PhCN)$	224		
$Cu(Cl_3CCOO)_2(4\text{-}CH_3C_6H_4CN)\cdot 1/2bz$	216		

[a] qu = quinaldine; 2-pic = 2-picoline; 4-pic = 4-picoline; 2,6-lu = 2,6-lutidine.

bands having maxima at about 26000 cm^{-1} (band II) and about 14000 cm^{-1} (band I) with a shoulder at about 8000 cm^{-1}. It is now generally recognized that band I and band II can be assigned respectively to a

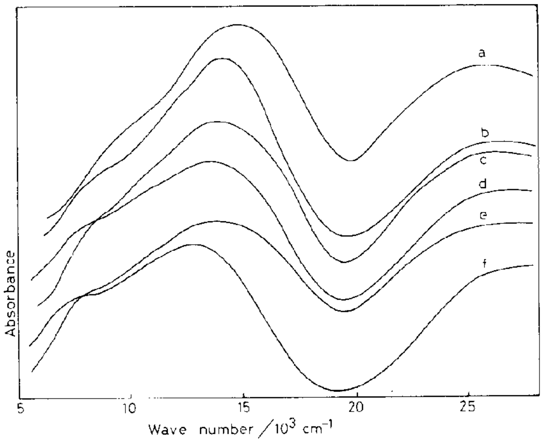


Fig. 9. Reflectance spectra of $Cu(CH_3COO)_2(3,5\text{-}Cl_2py)$ (curve a), $Cu(CH_3COO)_2(py)$ (curve b), $Cu(ClCH_2COO)_2(3,5\text{-}Cl_2py)$ (curve c), $Cu(ClCH_2COO)_2(py)$ (curve d), $Cu(Cl_2CHCOO)_2(3,5\text{-}Cl_2Py)$ (curve e), $Cu(Cl_2CHCOO)_2(py)$ (curve f).

TABLE 8

Reflectance spectral data for dimeric copper(II) carboxylate adducts with 3,5-dichloropyridine and pyridine

Complex	Band I		Band II
	$\tilde{\nu}_{max}/10^3$ (cm^{-1})		$\tilde{\nu}_{max}/10^3$ (cm^{-1})
$Cu(CH_3COO)_2(3,5\text{-}Cl_2py)$	14.7	9.5 [a]	25.7
$Cu(CH_3COO)_2(py)$	14.1	9.1 [a]	26.4
$Cu(ClCH_2COO)_2(3,5\text{-}Cl_2py)$	14.0	8.0 [a]	26.2
$Cu(ClCH_2COO)_2(py)$	13.6	7.5 [a]	26.5
$Cu(Cl_2CHCOO)_2(3,5\text{-}Cl_2py)$	13.6	7.7 [a]	Broad
$Cu(Cl_2CHCOO)_2(py)$	12.8	7.4 [a]	Broad

[a] Shoulder.

ligand-field transition involving the positive hole promotion $d_{x^2-y^2} \rightarrow d_{xz}$, d_{yz} [73,74] and to a charge transfer from the carboxylato-oxygen atoms to the metal ion [75,76]. Accordingly, band I is expected to be sensitive to the nature of both the ligands $RCOO^-$ and L. As can be seen in Table 8 and Fig. 9, the $\tilde{\nu}_{max}$ values of band I for the 3,5-dichloropyridine adducts are higher than those for the corresponding pyridine adducts. The order of the increase in the $\tilde{\nu}_{max}$ values is the same as that in the $-2J$ values, giving a parallel relationship between the $\tilde{\nu}_{max}$ and $-2J$ values (the higher the $\tilde{\nu}_{max}$ value, the higher the value $-2J$). This parallelism may be explained in terms of the electroneutrality principle [77] as follows. In dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2 \cdot L]_2$, when the L → Cu donation becomes weaker, the covalent Cu–O bonds in the CuO_4 basal plane will become stronger to maintain the electroneutrality over the whole molecule, i.e. a weaker L → Cu donation will cause a stronger ligand field of the four carboxylato-oxygen atoms around the metal ion. This leads to a larger splitting of the *d–d* energy levels, resulting in a blue shift of band I. This assumption is consistent with the observation by Dubicki and Martin [78] that, in a series of dimeric copper(II) acetate adducts with pyridine analogues, band I shifts to a higher energy as the pK_a of the axial ligand decreases. For the mechanism of the magnetic interaction in dimeric copper(II) carboxylates, experimental evidence [1,79–81] shows that the spin coupling between the unpaired electrons of copper(II) ions operates predominantly by a superexchange interaction through the bridging carboxylato ligands rather than by direct Cu–Cu interaction (see Section D(iv)). Accordingly, the magnetic interaction will become stronger as the Cu–O bonds become stronger. From the above experimental results and discussion, we can conclude that, contrary to the claim by Jotham et al. [68], the antiferromagnetic interaction in dimeric copper(II) carboxylate adducts should become stronger as the basicity of the axial ligands becomes weaker. Therefore a larger $-2J$ is attributed to a weaker σ donation of the axial ligand. The $-2J$ values for dimeric copper(II) acetate adducts with some pyridine analogues were previously reported to decrease as the pK_a values of the axial ligands decrease: 4-CH_3py (325 cm^{-1}) > 4-CH_3COpy (311 cm^{-1}) > 4-CNpy (300 cm^{-1}) [78]. However, we have found the reverse order: 4-CH_3py (333 cm^{-1}) < 4-CNpy (345 cm^{-1}) (Table 7). We have further found that the $-2J$ value for the 4-cyanopyridine adduct of dimeric copper(II) trichloroacetate (229 cm^{-1}) is higher than that for the corresponding pyridine adduct (188 cm^{-1}) (Tables 11 and 14). The present result can explain the anomalously large $-2J$ values for dioxane adducts. Dioxane has no appreciable π-acceptor ability, and it usually appears to be the weakest base ($pK_a = -2.92$) in a series of adducts for a given copper(II) carboxylate dimer. Thus dioxane adducts usually give the highest values for both $-2J$ and $\tilde{\nu}_{max}$ (band I) for dimeric copper(II) carboxylate adducts [82].

On the basis of the axial ligand effect described above, the magnetic properties of dimeric copper(II) 2,2-dimethylpropanoate adducts listed in Table 7 can be interpreted [83]. The X-ray structural determination by Kirillova et al. [84] on the dimeric copper(II) 2,2-dimethylpropanoate adduct with acridine (ac), $[Cu(Me_3CCOO)_2(ac)]_2$, shows that the Cu–N(ac) distance of 2.371 Å is considerably longer than those found for other copper(II) carboxylate adducts with pyridine analogues (2.10–2.20 Å) [1,31]. The longer distance, indicating a weak σ donation of the axial ligand, is reflected in the $-2J$ value of 397 cm^{-1} which is the largest among the values for the adducts studied so far. Table 7 also shows that the $-2J$ values for the adducts with quinaldine and 2,6-lutidine, both of which have substituents at 2- and 6-positions of the pyridine ring, are larger than those for other adducts with apical ligands which have no substituent or only one substituent at the *ortho* position of the pyridine ring. Then the apical ligation is more or less hindered by the *ortho* substituents as in the case of acridine in $[Cu(Me_3CCOO)_2(ac)]_2$ and, consequently, the N–Cu bonds in both the adducts must be weak. However, the $-2J$ value for the 4-picoline adduct is much smaller than those for other adducts. Since 4-picoline has no substituent at the *ortho* position of the donor site and the basicity is higher than that of other pyridine bases examined, except 2,6-lutidine, the N–Cu bond in the 4-picoline adduct is considered to be much stronger than in other adducts. Thus in contrast with the acridine adduct, the smallest $-2J$ value of 319 cm^{-1} found for the 4-picoline adduct can be ascribed to the strong Cu–N bond.

In contrast with our conclusion on the axial ligand effect, Hibdon and Nelson have reported that the antiferromagnetic interaction in a series of

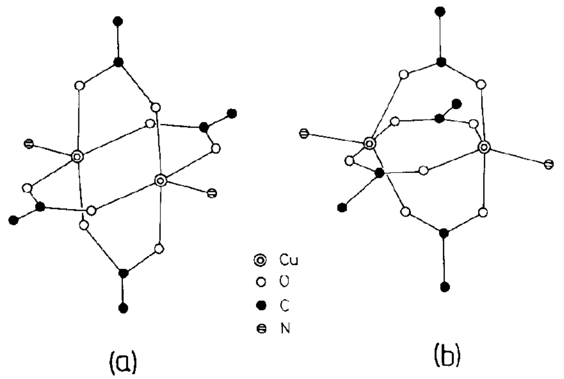


Fig. 10. Cage structures of [Cu(Cl$_3$CCOO)$_2$(PhCN)]$_2$ (a) and [Cu(ph$_3$CCOO)$_2$(py)]$_2$ benzene (b).

dimeric copper(II) acetate adducts with 4-substituted pyridine *N*-oxides becomes stronger as the π back-donation from the metal ion to the axial ligand increases [85]. In order to elucidate this discrepancy, we have studied several dimeric copper(II) chloroacetate adducts with benzonitrile (PhCN) and 4-methylbenzonitrile (4-$CH_3C_6H_4CN$) [86]. The structure of the benzonitrile adduct of copper(II) trichloroacetate has been determined by a single-crystal X-ray analysis to obtain accurate information about the coordination mode of the axial ligand. In particular, the relationship between the stretching frequency of the C≡N group and its bond length has been studied. The crystal structure of the copper(II) trichloroacetate adduct with benzonitrile contains two independent molecules; they are abbreviated as A and B. The two independent molecules are quite similar to each other in shape, although there are small differences in their interatomic distances and bond angles. As shown in Fig. 10(a), each molecule has the well-known dimeric copper(II) acetate monohydrate structure. A noteworthy feature of the coordinated benzonitrile is the C–N distances of 1.113 Å (A) and 1.122 Å (B), which are significantly shorter than that in the free molecule (1.159 Å) [87]. This apparent shortening indicates that the C–N bond strength increased upon formation of the CN → metal coordination bond [88,89]. The $-2J$ values found for the respective benzonitrile adducts are larger than those found for the corresponding 4-methylbenzonitrile adducts (Table 7). This is in accord with the conclusion that the antiferromagnetic interaction in dimeric copper(II) carboxylate adducts becomes stronger as the basicity of the axial ligands becomes weaker, because benzonitrile must be less basic than 4-methylbenzonitrile. A remarkable feature of the IR spectra of the nitrile adducts is that, in each case, the C≡N stretching absorption appears

TABLE 9

C≡N stretching vibrations (cm^{-1}) for nitrile adducts of copper(II) chloroacetates

Complex	Coordinated	Free [a]	$\Delta\tilde{\nu}$(C≡N) [b]
$Cu(ClCH_2COO)_2(PhCN)$	2257	2231	26
$Cu(ClCH_2COO)_2(4\text{-}CH_3C_6H_4CN)$	2264	2230	34
$Cu(Cl_2CHCOO)_2(4\text{-}CH_3C_6H_4CN)$	2262	2230	32
$Cu(Cl_3CCOO)_2(PhCN)$	2262	2231	31
$Cu(Cl_3CCOO)_2(4\text{-}CH_3C_6H_4CN)\cdot 1/2bz$	2264	2230	34

[a] Ref. 90. [b] Change in $\tilde{\nu}$(C≡N) on coordination.

at a wavenumber higher by 30–40 cm^{-1} than that of the free nitrile (Table 9). Such an increase in $\tilde{\nu}$(C≡N) has been attributed either to an increase in the C≡N bond strength resulting from a hybridization change in the coordinated CN group or to a greater contribution of the donor atom N_{2s} orbital to the CN σ-bonding system upon σ donation of the lone pair of electrons on the nitrile N atom [91,92]. Thus both the shortening of the CN bond and the increase in the $\tilde{\nu}$(C≡N) observed for $[Cu(Cl_3CCOO)_2(PhCN)]_2$ can be ascribed to the formation of a CN → metal σ-donating bond. However, if the metal–axial ligand bond is, on the whole, of the C≡N ← metal π back-bonding type, the CN bond order should decrease; consequently, $\tilde{\nu}$(C≡N) is expected to decrease [89,93,94]. Thus the X-ray crystallographic, magnetic and IR spectroscopic results indicate that the nitriles in the complexes act as σ-donor ligands. This conclusion is in accord with the recent claim by Rao et al. that the pyridine in the $[Cu(CH_3COO)_2(py)]_2$ complex functions as a σ-donor base [95].

(ii) Magnetic interaction in non-adduct complexes of copper(II) carboxylates

In many dimeric copper(II) carboxylates, the $-2J$ values for the non-adduct complexes are often lower than those for the corresponding adduct complexes [68,96], as seen in the following case: $Cu(C_2H_5COO)_2$ (300 cm^{-1}) [97] < $Cu(C_2H_5COO)_2(py)$ (350 cm^{-1}) [98]. The crystal structure of $Cu(C_2H_5COO)_2$ is composed of carboxylato-bridged dimers which are linked into one-dimensional polymeric chains by apical Cu–O interactions (Fig. 11) [99]. Such an apical Cu–O interaction will disturb the superexchange interaction through the carboxylato bridges [100], leading to a lower $-2J$ value. In accord with the general tendency described above, we have found in the study of dimeric copper(II) phenylpropynoate complexes [101] that the $-2J$ value of 213 cm^{-1} found for the non-adduct complex, $Cu(Ph\text{–}C{\equiv}C\text{–}COO)_2$, is much smaller than those found for the adduct complexes listed in Table 10. Further, only the non-adduct compound shows

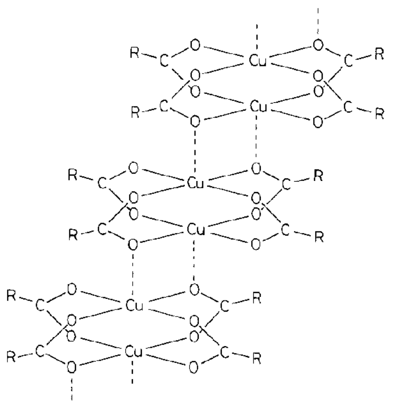


Fig. 11. Schematic representation of the polymeric chain structure of $[Cu_2(C_2H_5COO)_4]_n$.

an appreciably large positive θ value ($+6.86$ K) which was introduced in the Bleaney–Bowers equation as the Weiss constant for an intercluster interaction (Table 10). The positive value for θ is considered to arise from the presence of a ferromagnetic spin–spin interaction through the apical-to-basal Cu–O–Cu bonds shown in Fig. 11. However, the $-2J$ value of 403 cm^{-1} found for the non-adduct compound of copper(II) 2,2-dimethylpropionate, $Cu(Me_3CCOO)_2$, is larger than those for any other adduct examined (319–397 cm^{-1}; Table 7). This fact differs from the general tendency described above. In addition, the *X*-band ESR spectral pattern of $Cu(Me_3CCOO)_2$ is quite different from that of many non-adduct copper(II) carboxylates. In many cases, the ESR spectra of non-adduct copper(II) carboxylates show a single broad line in the 0.2–0.4 T region, and this fact has been regarded as a sign of the existence of a polymeric chain structure consisting of dimeric molecules [102–104]. The ESR spectral feature of $Cu(Me_3CCOO)_2$ shown in Fig. 12 is fundamentally the same as that usually

TABLE 10

Magnetic data for dimeric copper(II) phenylpropynoate complexes

Complex	$-2J$ (cm^{-1})	θ (K)
$Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2(PhCN)$	318	0
$Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2(3,5\text{-}Cl_2py)$	300	0
$Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2(DMSO)$	287	0
$Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2(Ph_3PO)$	283	0
$Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2$	213	+6.86

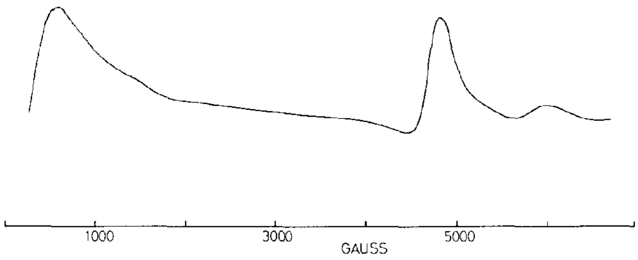


Fig. 12. Room temperature polycrystalline powder ESR spectrum of $[Cu(Me_3CCOO)_2]_2$ at *X*-band frequency.

observed for dimeric copper(II) carboxylates with axial ligands [105]. The ESR parameters obtained are $g_\perp = 2.139$, $g_\parallel = 2.415$, $g_{av} = 2.235$ and $D = 0.340\ cm^{-1}$. The relationship commonly observed for dimeric copper(II) carboxylates holds, i.e. D ($0.340\ cm^{-1}$) > H_0 ($0.316\ cm^{-1}$) [105,106]. These facts suggest that the strong antiferromagnetic interaction in $Cu(Me_3CCOO)_2$ is due to the absence of (or very weak) coordination at the apical positions.

(iii) Magnetic properties of dimeric copper(II) trichloroacetate adducts with 3-substituted pyridines

The recent structural studies on dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2 \cdot L]_2$, have demonstrated that the metal–metal distance becomes longer as either the acidity of the parent carboxylic acid RCOOH [107] or the basicity of the axial ligand L [95] becomes stronger. Therefore a larger Cu–Cu distance is usually associated with a greater displacement of the metal ion from the equatorial plane composed of four oxygen atoms. Consequently, the variations in both the group R and ligand L affect the strength of the Cu–O bonds in the CuO_4 basal plane, with an accompanying deformation of the bridging framework. Of 13 dimeric copper(II) acetate adducts reported to date, the Cu–Cu distances span a range of 2.581 2.671 Å with a variation of 0.09 Å [95]. However, the Cu–Cu distances found for dimeric copper(II) trichloroacetate adducts, $[Cu(Cl_3CCOO)_2 \cdot L]_2$, span a considerable range; 2.731 Å for L = benzonitrile [86], 2.776 Å for L = 2-chloropyridine (2-Clpy) [107], 2.852 Å for L = caffeine [108], 3.197 Å for L = 2,2,5,5-tetramethylpyrrolinyl-1-oxy [109] and 3.256 Å for L = 2,2,6,6-tetramethylpiperidinyl-1-oxy [109]. The coordination environment around each copper(II) ion in the first three adducts is square pyramidal, whereas that in the last two adducts is trigonal bipyramidal. These structural data indicate that, for a variation in L, the bridging trichloroacetato ligand coordinates more flexibly than the bridging acetato ligand does. Dimeric

TABLE 11

$-2J$ values for $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$

X	Cl	Br	H	CN	CH_3
$-2J$ (cm^{-1})	193	191	188	138	83

copper(II) trichloroacetate adducts may therefore be a suitable choice for the study of structural factors which affect the magnetic properties of copper(II) carboxylate dimers with distorted trigonal-bipyramidal metal geometry. In a study of copper(II) trichloroacetate adducts with 3-substituted pyridines, $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$, we found that the antiferromagnetic interaction in the adducts with X = Cl, Br and H is much stronger than that in the adducts with X = CN and CH_3 [110]. As shown in Table 11, the $-2J$ values for the first three adducts are comparable to those for $[Cu(Cl_3CCOO)_2]_2(2\text{-}Clpy)$ (217 cm^{-1}) [107] and $[Cu(Cl_3CCOO)_2(PhCN)]_2$ (224 cm^{-1}) [86], whereas those for the last two adducts are considerably smaller. In order to elucidate the structural factors which cause such different magnetic properties between the first three adducts and the last two adducts, we then studied their reflectance and ESR spectral properties.

The electronic spectra of the adducts with X = Cl, Br and H are similar to one another and closely resemble that of $[Cu(Cl_3CCOO)_2(2\text{-}Clpy)]_2$ (Fig. 13), giving a band maximum at about 12500 cm^{-1} and a low energy shoulder at about 8000 cm^{-1}. The separation between these two peaks, $\Delta\tilde{\nu}_{max}$ = 3890–4930 cm^{-1}, is comparable with those observed for $[Cu(CH_3COO)_2(py)]_2$ (5000 cm^{-1}) [111] and $[Cu(Cl_3CCOO)_2(2\text{-}Clpy)]_2$

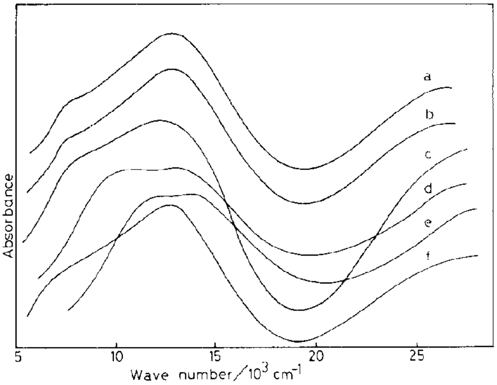


Fig. 13. Reflectance spectra of $[Cu(Cl_3CCOO)_2 \cdot L]_2$: curve a, L = 3-Clpy; curve b, L = 3-Brpy; curve c, L = py; curve d, L = 3-CNpy; curve e, L = $3\text{-}CH_3py$; curve f, L = 2-Clpy.

TABLE 12

Reflectance spectral data for $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$

X	$\tilde{\nu}_{max}/10^3$ (cm^{-1})		$\Delta\tilde{\nu}/10^3$ (cm^{-1})
Cl	12.50	7.57	4.93
Br	12.50	7.57	4.93
H	12.27	8.40	3.89
CN	12.82	10.86	1.96
CH_3	14.28	12.50	1.78

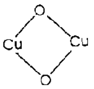
(4900 cm^{-1}). These facts indicate that these three adducts have a distorted square-pyramidal copper(II) geometry similar to that in $[Cu(Cl_3CCOO)_2(2\text{-}Clpy)]_2$ [107]. However, the spectral feature of the adducts with X = CN and CH_3 is quite similar to those of distorted trigonal-bipyramidal copper(II) complexes such as $Cu_4OCl_6(Ph_3PO)_4$ ($\Delta\tilde{\nu}_{max} = 1300$ cm^{-1}) [112], $[Cu(bipy)_2Cl]NO_3 \cdot 3H_2O$ ($\Delta\tilde{\nu}_{max} = 2000$ cm^{-1}) [113], $[Cu(bipy)_2CN]NO_3 \cdot 2H_2O$ ($\Delta\tilde{\nu}_{max} = 2100$ cm^{-1}) [114] and $[Cu(Ph_3CCOO)_2(py)]_2 \cdot$ benzene ($\Delta\tilde{\nu}_{max} = 2510$ cm^{-1}) whose structure is shown in Fig. 10(b) [115]. The spectra of the latter two trichloroacetate adducts show two peaks of about equal intensity with a separation of about 1800–1900 cm^{-1} in the range 10000–15000 cm^{-1} (Fig. 13 and Table 12). These $\Delta\tilde{\nu}_{max}$ values are comparable to those for the distorted trigonal-bipyramidal copper(II) complexes described above. The spectral similarity suggests that these two adducts have a distorted trigonal-bipyramidal copper(II) geometry which may be produced rather by steric effects of the CN and CH_3 substituents than by their electronic effects. A large substituent size probably hinders smooth packing of molecules in crystal lattices, resulting in steric strain in the environment around the metal ion. Hathaway et al. [113] demonstrated in their study of $[Cu(bipy)_2Cl]X$, where X = ClO_4, $NO_3 \cdot 3H_2O$, $1/2[(S_5O_6) \cdot 6H_2O]$, Cu^ICl_2 and $Cl \cdot 6H_2O$, that copper(II) complexes with the metal geometry close to a regular trigonal bipyramid show a single broad peak in their electronic spectra at 12500 cm^{-1} ($^2E' \leftarrow {}^2A_1'$ transition in D_{3h} symmetry) while those with a square pyramidal distorted trigonal-bipyramidal CuN_4Cl chromophore show a twin-peaked band in the region of 10000–14500 cm^{-1}, with the maximum splitting of 4060 cm^{-1} for the complex whose metal geometry is closest to a regular square pyramid. This fact suggests that for five-coordinate copper(II) complexes the $\Delta\tilde{\nu}_{max}$ value can be taken as a measure of the degree of distortion in metal geometry from square pyramidal to trigonal bipyramidal. As can be seen from Table 12, the $\Delta\tilde{\nu}_{max}$ value observed for the present complexes decreases in the following order: 3-Clpy and 3-Brpy adducts > py adduct > 3-CNpy adduct > 3-CH_3py adduct. This order is just the same as that of the decrease in the $-2J$ values for these complexes

TABLE 13

ESR parameters for $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$

X	D (cm^{-1})	$g_\parallel$	$g_\perp$	g_{av}
Cl	0.397	2.536	2.143	2.282
Br	0.399	2.575	2.154	2.304
H	0.385	2.562	2.159	2.301
CN	0.216	2.425	2.155	2.248
CH_3	0.182	2.396	2.183	2.256

(Table 11); there exists a parallel relationship between the $-2J$ and $\Delta\tilde{\nu}_{max}$ values (the smaller the $-2J$ value, the smaller the $\Delta\tilde{\nu}_{max}$ value). This parallelism indicates that the strength of antiferromagnetic interaction in $[Cu(Cl_3CCOO)_2(3\text{-}Xpy)]_2$ complexes decreases as the distortion of copper(II) geometry increases from square pyramidal toward trigonal bipyramidal. This conclusion is the same as that previously proposed for five-coordinate copper(II) dimers containing the following bridging system [39,116]:



The ESR spectral features of the adducts with X = Cl, Br and H are the same as those usually observed for dimeric copper(II) carboxylate adducts which have a square-pyramidal metal geometry [105]. For these three

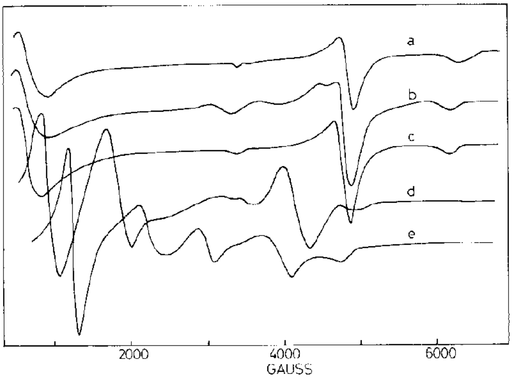


Fig. 14. Room temperature polycrystalline powder ESR spectra of $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$ at X-band frequency: curve a, X = Cl; curve b, X = Br; curve c, X = H; curve d, X = CN; curve e, X = CH_3.

TABLE 14

Magnetic data for $[Cu(Cl_3CCOO)_2 \cdot L]_2$

L	Type [a]	Solvent	$-2J$ (cm^{-1})	L	Type	Solvent	$-2J$ (cm^{-1})	D (cm^{-1})
2-Fpy	SP	C_6H_6	225	2,3-luti [d]	SP	$CHCl_3$	215	0.290
2-Clpy	SP	C_6H_6	220	2,3-luti·1/2S	TB	$C_6H_5CH_3$	95	0.183
2-Brpy	SP	C_6H_6	217	2,4-luti	SP	$CHCl_3$	223	0.386
2-pic	SP	C_6H_6	234	2,4-luti·1/2S	TB	C_6H_6	99	0.186
2-Etpy	TB	C_6H_6	79	2,5-luti	TB	$CHCl_3$	136	0.203
4-CNpy	SP	CCl_4	229	2,5-luti·1/2S	TB	$C_6H_5CH_3$	102	0.180
4-pic	SP	C_6H_{12}		3,4-luti	TB	C_6H_6	107	0.192
4-pic·1/2S [b]	TB	C_6H_6		3,5-luti	TB	C_6H_6	74	0.194
2,5-Cl_2py	SP	C_6H_{12}	191	2-Cl-5-NO_2py	TB	C_6H_6	131	
2,5-Cl_2py·1/2S	TB	C_6H_6	141	5-NO_2-2-OHpy	SP	C_6H_6	230	
3,5-Cl_2py	TB	$C_6H_5CH_3$	92	2-Brtz [e]	SP	C_6H_6	234	
caff [c]	TB	$CHCl_3$	136	2-Fbtz [f]	SP	C_6H_6	240	
caff	SP	$C_6H_5CH_3$	177	2-Clbtz	SP	C_6H_6	225	
caff·S	SP	C_6H_6	203	4,7-Cl_2quin [g]	SP	C_6H_6	237	

[a] SP, square pyramid; TB, trigonal bipyramid. [b] S, solvent molecule. [c] caff, caffeine. [d] luti, lutidine. [e] tz, thiazol. [f] btz, benzothiazol. [g] quin, quinoline.

adducts, the common relationship $D > H_0$ [105,106] (Table 13) was observed. The ESR spectra of the adducts with X = CN and CH_3, however, are quite different from those of the former adducts (Fig. 14) and fundamentally the same as that of $[Cu(Ph_3CCOO)_2(py)]_2 \cdot$ benzene ($D = 0.204$ cm^{-1}) [115]. For the latter two adducts, an uncommon relationship, $D < H_0$, was observed (Table 13): this relationship has recently been detected for $[Cu(Ph_3CCOO)_2(py)]_2 \cdot$ benzene whose $-2J$ value (184 cm^{-1}) is quite small compared with those for common dimeric copper(II) carboxylates [115]. The order of decrease in the D values for $[Cu(Cl_3CCOO)_2(3\text{-}Xpy)]_2$ is the same as that in the $-2J$ values. Thus it is concluded that the zero-field splitting of $[Cu(Cl_3CCOO)_2(3\text{-}Xpy)]_2$ decreases as the distortion of the metal geometry increases from square pyramidal toward trigonal bipyramidal, just as the singlet–triplet separation does.

The $-2J$ values of dimeric copper(II) trichloroacetate adducts with a variety of axial ligands are listed in Table 14 together with their structural types, the solvents used for synthesizing the adducts, and D values determined for a few of them [117].

(iv) Characteristics of magnetic exchange in dimeric copper(II) carboxylate complexes

The mechanism governing the magnetic exchange interaction in copper(II) carboxylate dimers has been subject to considerable controversy since the study of Figgis and Martin on copper(II) acetate monohydrate (δ-bond mechanism) [4]. A large number of studies have been made to see what structural and physico-chemical properties correlate with $-2J$ values: pK_a of the parent carboxylic acids and of the apical ligands; *d–d* band energy; Cu–Cu, Cu–O–C–O–Cu and (plane of O_4)–Cu distances; Cu–Cu–L and O–Cu–L angles; polarizability of R, and others [1,4,23,31,68,82,107, 118–124]. A reason for such controversies seems to be the admixture of magnetic and structural data of high and low quality in the literature. A distinct characteristic of the magnetic exchange in the dinuclear copper(II) carboxylates, which markedly differs from those of other dimeric copper(II) complexes (Sections B and C), is that the electronic effect of R or L in $[Cu(RCOO)_2 \cdot L]_2$ can be detected, though the conclusions deduced often differ among investigators as mentioned above. The reason for this fact may be found in the solidity of the cage-type binuclear framework. Actually the variation in the structural parameters is small among a large number of copper(II) carboxylates [31,82]. In this connection, it may be worth pointing out that the electronic substituent effects in other dimeric copper(II) systems, such as those in the previous sections, might be seen if the dimeric framework could be kept rigid. In fact, within a certain range of changes in the apical ligand L or in the chemical group R in copper(II) carboxylates, certain definite trends have been observed between the $-2J$ value and the electronic nature of L or R (cf. Sections D(i)–D(iii)). Under these conditions, in those copper(II) carboxylate dimers with the cage-type rigid structural framework, there still exists the linear relationship between *d–d* band energies and $-2J$ values, "the higher the value of $\tilde{\nu}_{max}$, the higher the value of $-2J$", which has been widely observed for a large number of dimeric copper(II) complexes with different types of structure (Sections B and C).

The most attractive puzzle in the magneto–structural correlations in dimeric copper(II) carboxylates is the question: Why do dimeric copper(II) formates with a stronger parent acid (p$K_a = 3.75$) show much larger $-2J$ values (about 500 cm^{-1}) than the corresponding copper(II) acetate dimers with a weaker parent acid (p$K_a = 4.75$) whose $-2J$ values are about 300 cm^{-1} [46]? On the basis of a comparative magnetic and structural study on $[(CH_3)_4N]_2[Cu(HCOO)_2(NCS)]_2$ (Cu–Cu = 2.716 Å; $-2J = 485$ cm^{-1}) and $[(CH_3)_4N]_2[Cu(CH_3COO)_2(NCS)]_2$ (Cu–Cu = 2.643 Å; $-2J = 305$ cm^{-1}), Goodgame et al. [79] first showed the superiority of the superexchange mechanism over the metal–metal direct exchange mechanism [4]. Why does formate produce a larger $-2J$ than acetate? Hoffmann and coworkers [46] tried to find the answer to this question in the shorter Cu–O bond length of the formate (1.983 Å) than of the acetate (2.03 Å) in Goodgame's complexes [79]. The same trend is observed between the urea adducts of formate and acetate: $[Cu(HCOO)_2(urea)]_2$ (Cu–O = 1.952 Å)

TABLE 15

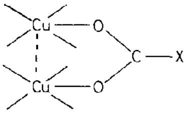
Comparative data for structures of copper(II) acetate and formate adducts (L = pyridine and urea)

	Cu–Cu (Å)	Cu–O (basal) (Å)	Cu–O–C–O–Cu (Å)	Cu–L (apical) (Å)	Cu–basal plane (Å)	*R* factor	Reference
$Cu(CH_3COO)_2 \cdot py$							
Orthorhombic	2.641(1)	1.974(3)	6.453(5)	2.191(2)	0.208	0.034	128, 130
Monoclinic	2.628(1)	1.972(3)	6.447(5)	2.163(4)	0.207	0.030	129, 130
$Cu(HCOO)_2 \cdot py$	2.641(1)	1.981(2)	6.451(5)	2.145(2)	0.207	0.036	127
$Cu(CH_3COO)_2 \cdot urea \cdot H_2O$	2.624(1)	1.970(2)	6.441(5)	2.135(2)	0.205	0.022	126, 130
$Cu(HCOO)_2 \cdot urea$	2.655(1)	1.977(2)	6.445(5)	2.120(2)	0.213	0.030	125, 130

[125] and $[Cu(CH_3COO)_2(urea)]_2 \cdot 2H_2O$ (Cu–O = 2.00 Å) [126]. The trend reported for pyridine adducts deviates somewhat from the above: $[Cu(HCOO)_2py]_2$ (Cu–O = 1.981 Å) [127] and $[Cu(CH_3COO)_2py]_2$ (orthorhombic form, Cu–O = 1.955 Å) [128] or $[Cu(CH_3COO)_2py]_2$ (monoclinic form, Cu–O = 1.981 Å) [129]. Saito, Ohba and coworkers have very recently redetermined the structures of these pyridine and urea adducts of copper(II) formate and acetate (Table 15) [130]. No significant differences in structure, within experimental limits, have been confirmed between the formates and acetates.

However, if the bridging Cu–O bonds are slightly longer in the formates than in the acetates, by about 0.007–0.008 Å (Table 15), it may be concluded that the slightly longer or weaker bridging Cu–O bonds in the formates are due to the stronger acidity of the parent formic acid, a quite reasonable result.

The Cu–O bridging bond in copper(II) carboxylate dimers is considered to be quite important in the superexchange mechanism in these systems; it is the very entrance of the superexchange pathway. However, the present results seem to indicate that the role of Cu–O in the superexchange pathway is not of primary importance. In 1973, Steward and Piskor [131] reported unusually low magnetic moments for copper(II) complexes of triphenylsilane carboxylates and triphenylgermane carboxylates, about 0.8 BM, lower than the moments for copper(II) formate dimers, about 1.0 BM. They have recently reported a structural and an ESR study on $[Cu(PhMe_2SiCOO)_2 \cdot H_2O]_2$ ($-2J \approx 1000$ cm^{-1}) [132]. The present authors and Steward and coworkers have confirmed large $-2J$ values (about 1000 cm^{-1}) for a number of copper(II) complexes of carboxysilane and carboxygermanes [120]. Now the structural key role of the superexchange mechanism in the copper(II) carboxylate dimers with the cage-type rigid structure seems to be in the C–X bond in **7** (X is the atom σ-bonded to carboxylato carbon). The magnitude of the antiferromagnetic exchange increases in the order, X = C < X = H < X = Si or Ge. The most representative theoretical treatments of the spin coupling in dinuclear copper(II) carboxylates were first made in 1975 by Hoffmann and coworkers [46], and then by de Loth et al. [133] and by Harcourt et al. [134]. However, their calculations do not answer the following question. Why do copper(II) formates show a larger antiferromagnetic interaction ($-2J \approx 500$ cm^{-1}) than do copper(II) acetate adducts or the homologues ($-2J \approx 300$ cm^{-1})? The magnetic exchange mechanism of the copper(II) carboxylate dimers should explain the variations in $-2J$ caused by changing X in the order as above.



7

E. CONCLUSION

The present authors have been engaged in the magnetochemical study of dinuclear copper(II) complexes for around 20 years. Copper(II) halide complexes with pyridine *N*-oxides were their earliest concerns and are now re-examined in view of wider magneto–structural correlations. Despite the long bridging Cu–O bond and low electron density at the bridging oxygen, the 1 : 1 copper(II) halide complexes with pyridine *N*-oxides show a very large magnetic interaction as $\mu_{\text{eff}}^{25°\text{C}} = 1\text{–}0.2$ BM. Theoretical studies are needed on these systems. The *ortho* effect in these systems also needs further extensive structural study.

The characteristics of the magneto–structural correlation for the copper(II) chloride complexes with bidentate Schiff's bases (**2** and **4**) seem to have been well established by the structural studies of Sinn and coworkers [40,58,59] and by the recent structural and theoretical studies of Chiari et al. [60] (Section C(i)). The mechanism of the linear relationship, "the higher the *d–d* band energies, the lower the magnetic moments," observed for those copper(II) chloride complexes brown in colour has now been fully understood in terms of the early proposal of the shift mechanism between the complexes with pseudo-tetrahedral coordination geometry [51]. However, *N*-*n*-propanolsalicylaldiminato copper(II) complexes (**5**) merit more magneto–structural and theoretical studies (Section C(ii)).

The unusual magnetic properties of $[Cu(Ph_3CCOO)_2(py)]_2 \cdot$ benzene observed by Steward, the present authors and coworkers are quite novel: the unusually low value for $-2J$; the uncommon ESR spectral pattern; the uncommon relationship $D < H_0$ [115]. Muto and coworkers have quite recently observed the same trend in the magnetic properties for a number of newly prepared copper(II) trichloroacetate adducts (Section D(iii)), an interesting new area of copper(II) carboxylate magnetochemistry.

The elucidation of the magneto-structural correlations for copper(II) carboxylate dimers should be an important goal of modern magnetochemistry. The superexchange mechanism in these dimeric copper(II) systems is an interesting puzzle. A redetermination of structure should be called for in a number of complexes in this area (Section D(iv)). The magnetic susceptibility should also be re-examined [111, 135] (Sections D(i) and D(ii)). Structural, magnetic and theoretical studies should be carried out in a comparative manner for complexes with a variety of X in **7**. Saito, Ohba, the present authors, Steward, and coworkers have now focused their attention onto this final goal. As regards the importance of the C–X bond in **7**, theoretical calculations are in progress by Benard on both the acetate and formate systems [136].

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