

Antiferromagnetism in Transition-metal Complexes. Part IV.¹ Low-lying Excited States of Binuclear Copper(II) Carboxylate Complexes

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The singlet-triplet-singlet model describing the anomalous magnetic properties of binuclear copper(II) carboxylates is applied to the available experimental data on some 140 compounds. About one-sixth of the data was eventually rejected because of the poor fit with both this and the Bleaney-Bowers model. The trend in $|J|$, the singlet-triplet separation, parallels the trend in Δ , the singlet-singlet separation, when the terminal ligand is varied. This indicates that the trends in the σ - and δ -exchange integrals are of the opposite sense. All the exchange integrals are increased nephelauxetically by better bonding of terminal or bridging groups, but, because of the unique geometry of the system, the small component of σ -bonding is decreased overall by radial dispersal of d_{z^2} 'holes' onto the terminal ligands. This component of σ -bonding is of a direct nature, but no firm conclusions as to the nature of the δ -interaction may be drawn.

MANY binuclear copper(II) complexes with subnormal magnetic moments are known.² Crystallographic evidence exists for the binuclear structure of many of these compounds,³⁻²⁹ which often persist in solution.³⁰⁻³² However, cases of association between dimeric units^{17,33} and analogous polynuclear copper(II) complexes are known,^{1,33-42} as are similar bi- and poly-nuclear derivatives of many other metals.⁴³⁻⁴⁹ Many copper(II) compounds have extensive antiferromagnetic coupling

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²⁴ We have also found X-ray evidence for the binuclear structure of an arylcarboxylate, namely copper α -naphthoate. γ -picoline, with a Cu-Cu distance of 2.66 ± 0.02 Å.

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in one, two, or three dimensions, as exemplified by KCuCl_3 , $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$, and KCuF_3 respectively.⁵⁰⁻⁵² Recently, two binuclear Cu^{II} compounds have been reported to show a ferromagnetic interaction.^{21,53,54}

No compound has been reported in which a direct copper-copper bond can be adduced from either the absence of bridging ligands or from exceptionally short Cu-Cu distances, although such features have been used to characterise many other polynuclear systems.⁵⁵

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Thus it is commonly accepted that the special properties of these copper(II) compounds are intimately related to the electronic nature of the bridge systems, unless (as in the case of the carboxylates) the Cu-Cu distance is sufficiently short to admit, additionally, a discussion of the role of metal-metal bonding. Apart from the examples given above, all binuclear complexes which have been studied have a low magnetic moment at room temperature which itself falls rapidly with decreasing temperature.² They are therefore described as antiferromagnetic, although it may be held that this term is being used imprecisely, because none of these compounds has yet been observed to form a fully ordered magnetic system.

Of all the binuclear copper(II) complexes, cupric acetate monohydrate has been the most intensively studied (see Part III of this series for an extensive bibliography¹). Bleaney and Bowers first recognised that the magnetic properties of this compound could be explained by including an additional spin-coupling term, $-JS_1 \cdot S_2$, in the Hamiltonian used to describe the system.^{56,57} Perhaps the triumph of Bleaney and Bowers' paper⁵⁶ was the prediction of the dimeric unit, which was confirmed crystallographically in the following year,³ although it should be noted that the model cannot account for the band at 28,000 cm^{-1} observed in these compounds.^{58,59}

The effective spin-exchange model is easily applied to the interpretation of the magnetic properties of a wide range of polynuclear molecules.^{60,61} For the case of binuclear Cu^{II} complexes the bulk susceptibility of the dimer is described by equation (1) in which all symbols have their conventional meaning.⁶²

$$\chi'_M = \frac{Ng^2\beta^2}{3kT} \cdot \frac{6 \exp(J/kT)}{1 + 3 \exp(J/kT)} + N\alpha \quad (1)$$

Figgis and Martin, in their well-known discussion of the electronic structure of dimeric cupric acetate monohydrate, discussed two models.⁶³ The first was an extension of the treatment of Bleaney and Bowers in which the two copper ions are regarded as weakly coupled.⁵⁶ This model has been studied in detail by many workers and has, for example, led to the weakly coupled chromophore treatment of Hansen and Ballhausen.^{64,65} Figgis and Martin's particular contribution to the discussion of this model was the recognition that there exists a direct proportionality between the observed

Néel temperature and the exchange-integral parameter, J , which relationship is obtained by differentiating equation (1).

The second model considered by Figgis and Martin was one in which there exists a δ -bond between the $d_{x^2-y^2}$ orbitals (or antibonding $|x^2 - y^2\rangle$ orbitals in a ligand-field description) of the two copper ions. This model has also been studied with particular attention to the relative merits of σ - and δ -bonded structures.⁶⁶⁻⁷⁰

We have recently examined both of the Figgis and Martin models,^{1,71,72} in the light of our recognition that there exists a *prima facie* case for the existence of an additional thermally-accessible singlet level in addition to the spin singlet and triplet proposed by Bleaney and Bowers. Although both models can lead to the prediction of such an additional singlet, the symmetry of the level predicted differs in the two cases. Of the two models, that involving metal-metal bonding is undoubtedly the inferior because of the neglect of the magnitude of some of the electron-electron repulsion terms which are essential to its use. This point has also been recognised by other workers.⁵⁹

As a consequence of our application of the weakly coupled ion model to cupric acetate monohydrate,¹ it was concluded that the appropriate state-energy level diagram is given in the Figure. On the basis of our treatment, however, it is not possible to make a general statement about the magnitude of the ${}^1A_{1g}(1) - {}^1A_{1g}(2)$ state separation. If this separation is large, our model reduces to that of Bleaney and Bowers. In view of this it seems desirable to submit the considerable body of available experimental magnetic susceptibility data on dimeric copper carboxylates to a detailed examination in order to assess the general applicability of equation (2). This is a modified form of equation (1) which includes the singlet-singlet separation, Δ , (J , regarded as an exchange parameter rather than an exchange integral, is intrinsically negative in these systems).

$$\chi'_M = \frac{Ng^2\beta^2}{3kT} \cdot \frac{6 \exp(J/kT)}{1 + 3 \exp(J/kT) + \exp(-\Delta/kT)} + N\alpha \quad (2)$$

At the outset it was recognised that the available data is of variable reliability. In particular, it is well known that only cupric acetate recrystallised from media containing an excess of acetic acid is free from paramagnetic impurities. A similar situation exists for all complexes of this type and it is not always clear from

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TABLE 1
E.s.r. values of g for binuclear copper(II) complexes

Compound ^a	Ref.	g_x	g_y	g_z	g_{\perp}	\bar{g}^b
[Cu(CH ₃ COO) ₂ ,H ₂ O] ₂	56				2.08	2.20
	75	2.053	2.093			2.17
	78				2.08	2.17
[(Cu,Zn)(CH ₃ COO) ₂ ,H ₂ O] ₂	64	2.052	2.082			2.16
[Cu(CH ₃ COO) ₂ ,H ₂ O] ₂ ^{-c}	101	2.068	2.085			2.19
[Cu(CH ₃ COO) ₂] ₂	92				2.084	2.19
[Cu(CH ₂ ClCOO) ₂ ,2.5H ₂ O] ₂	89				2.07	2.18
[Cu(CH ₂ ClCOO) ₂ ,H ₂ O] ₂	88				2.13	2.22
[Cu(CH ₂ ClCOO) ₂] ₂	92				2.088	2.19
[Cu(CH ₂ (CN)COO) ₂] ₂	93				2.08	2.19
[Cu(C ₂ H ₅ COO) ₂ ,H ₂ O] ₂	87	2.095	2.093			2.18
	76	2.10	2.09			2.18
	77				2.060	2.16
[Cu,Zn(C ₂ H ₅ COO) ₂ ,H ₂ O] ₂	77				2.064	2.16
[Cu(C ₃ H ₇ COO) ₂ ,H ₂ O] ₂	88				2.04—2.10	2.16—2.20
[Cu(PhCH ₂ COO) ₂] ₂	78				2.05	2.16
	92				2.085	2.19
[Cu(<i>o</i> -NO ₂ -C ₆ H ₄ CH ₂ COO) ₂] ₂	78				2.03	2.14
[Cu(CH ₃ COO) ₂ (quin)] ₂	92				2.086	2.18
[Cu(CH ₃ COO) ₂ (py)] ₂	94	2.065	2.070			2.17
[Cu(CH ₃ COO) ₂ (β -nquin)] ₂	84				2.066	2.17
[Cu(C ₂ H ₅ COO) ₂ (β -nquin)] ₂	84				2.070	2.17
[Cu(CH ₂ F ₂ COO) ₂ (Clpy)] ₂	85				2.062	2.17
[Cu(CH ₂ F ₂ COO) ₂ (quin)] ₂	92				2.095	2.20
[Cu(CH ₂ ClCOO) ₂ (quin)] ₂	92				2.087	2.20
[Cu(CH ₂ ClCOO) ₂ (β -nquin)] ₂	84				2.072	2.18
[Cu(CH ₂ ClCOO) ₂ (Clpy)] ₂	85				2.059	2.17
[Cu(CHCl ₂ COO) ₂ (quin)] ₂	92				2.094	2.19
[Cu(CHCl ₂ COO) ₂ (Clpy)] ₂	85				2.066	2.18
[Cu(CCl ₃ COO) ₂ (β -nquin)] ₂	84				2.080	2.19
[Cu(CCl ₃ COO) ₂ (Clpy)] ₂	85				2.070	2.18
[Cu(PhCH ₂ COO) ₂ (quin)] ₂	84				2.066	2.17
	92				2.077	2.18
[Cu(PhCH ₂ COO) ₂ (α -pic)] ₂	84				2.072	2.17
[Cu(PhCH ₂ COO) ₂ (β -nquin)] ₂	84				2.060	2.17
[Cu(PhCH ₂ COO) ₂ (Clpy)] ₂	84				2.070	2.17
	85				2.066	2.16
[Cu(PhCH ₂ COO) ₂ (urea)] ₂	84				2.080	2.18
[Cu(PhCH ₂ COO) ₂ (Ph ₃ P)] ₂	84				2.066	2.17
[Cu-DL-(OOCCH(OH)CH(OH)COO)] ₂	90				2.08	2.13
[Cu(PhCOO) ₂ ,PhCOOH] ₂	95	2.048	2.074			2.16
[Cu(<i>o</i> -Me-C ₆ H ₄ COO) ₂] ₂	78				2.07	2.16
[Cu(<i>o</i> -MeO-C ₆ H ₄ COO) ₂ ,2H ₂ O] ₂	78				2.03	2.13
[Cu(<i>o</i> -FC ₆ H ₄ COO) ₂ ,H ₂ O] ₂	78				2.07	2.18
[Cu(<i>p</i> -ClC ₆ H ₄ COO) ₂] ₂	78				2.06	2.16
[Cu(2,4-Cl ₂ C ₆ H ₃ COO) ₂] ₂	78				2.07	2.16
[Cu(<i>o</i> -BrC ₆ H ₄ COO) ₂ ,H ₂ O] ₂	78				2.06	2.16
[Cu(<i>p</i> -BrC ₆ H ₄ COO) ₂] ₂	78				2.05	2.16
[Cu(<i>o</i> -IC ₆ H ₄ COO) ₂] ₂	78				2.06	2.16
[Cu(<i>o</i> -NO ₂ C ₆ H ₄ COO) ₂ ,H ₂ O] ₂	78				2.05	2.15
[Cu(PhCOO) ₂ (quin)] ₂	78				2.07	2.16
[Cu(PhCOO) ₂ (quinoxaline)] ₂	78				2.06	2.15
[Cu(α -naphthoate) ₂ ,H ₂ O] ₂	78				2.07	2.17
[Cu(α -naphthoate) ₂ (py)] ₂	78				2.07	2.18
[Cu(α -naphthoate)(α -picoline)] ₂	78				2.08	2.18
[Cu(salicylate) ₂] ₂	96				2.062	2.15
[Cu(acetylsalicylate) ₂] ₂	78				2.09	2.17
[Cu(C ₅ H ₅ N ₃) ₂ ,2H ₂ O] ₂	86				2.05	2.10
[Cu(C ₅ H ₅ N ₃) ₂ ,ClO ₄] ₂ , <i>n</i> H ₂ O	86				2.05	2.11
[CuCl ₂ (bipy)] ₂	97				2.06	2.13
[CuCl ₂ (pno)] ₂	98	2.06	2.08			2.15
[Cu,ZnCl ₂ (pno)] ₂	99	2.056	2.08			2.15
[Copper diethylthiocarbonate] ₂	79				2.06	2.13
[Cu(<i>o</i> -hydroxyanil)] ₂	100				2.07	2.13

^a quin = quinoline; py = pyridine; bipy = 2,2'-bipyridyl; α -pic = α -picoline; pno = pyridine-*N*-oxide; *o*-hydroxyanil = acetylacetonate(mono-*o*-hydroxyanil); β -nquin = β -naphthoquinoline; Clpy = 2-chloropyridine. ^b $\bar{g} = (\frac{1}{3}(g_x^2 + g_y^2 + g_z^2))^{\frac{1}{2}}$. ^c By γ -irradiation of the parent compound.

the literature whether appropriate preparative precautions have been taken. Indeed, in fitting susceptibility data, some workers include a term in a least-squares analysis to allow for the presence of paramagnetic impurities. Further, and particularly for precipitated samples, there may be more than one crystal habit. If all contain dimeric units this should not affect the analysis too seriously, but should one containing, say, a chain structure, be present in appreciable concentration, then no agreement with either our theory or that of Bleaney and Bowers could be expected.

We anticipated, therefore, that the available data may be divided into two sets; those that gave reasonable agreement with our model (and, usually, acceptable agreement with that of Bleaney and Bowers also) and those which gave poor or bad agreement with either model. Although we report our analysis of both types in this paper we shall confine our detailed discussion to those cases where impurities or other species may, with confidence, be claimed to be almost absent.

As it is commonly used to fit the data, in the Bleaney and Bowers equation, (1), J is obtained from the Néel temperature using the relation

$$J = -1.6 kT_N \quad (3)$$

and g is obtained by a best-fit procedure. Alternatively, and whenever a Néel temperature is not reached in the experiment, both g and J are obtained by best-fit procedures. $N\alpha$ is commonly assumed to be 120×10^{-6} c.g.s.u. for the dimeric unit, although some workers obtain a value from their best-fit analysis. We prefer to set this quantity equal to 150×10^{-6} c.g.s.u., a value derived using a generally accepted interpretation of the relevant part of the visible spectra of cupric acetate.^{35,43,73,74} The spectra of all complexes of this type are so similar that it seems reasonable to use this value for their temperature independent paramagnetism term also.

There is no theoretical reason why, for cupric acetate and its homologues, the g value appropriate to equation (1) should differ appreciably from 2.16 ± 0.03 , a view

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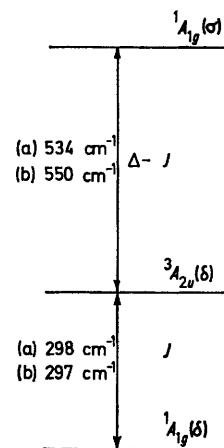
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which finds support in all of the e.s.r. measurements which have been reported for these compounds.^{56,64,75-101} In Table I we present some typical e.s.r. values of g which have been recorded. In our analysis we therefore take $g = 2.16$ when an e.s.r. value is not available and obtain best-fit values of J and Δ (see the Figure).



As we have pointed out,¹ where the Néel temperature is known with some accuracy, it is possible to determine J and Δ uniquely from the two equations that are

available (in χ and $\frac{d\chi}{dT} = 0$). When the results of this

approach are compared with those of the best-fit procedure for cupric acetate monohydrate, excellent concordance is obtained.¹ In the present study of a wide range of isotopes of cupric acetate monohydrate, we have found that the unique-solution method is very sensitive to the value of T_N , a quantity which is difficult to determine to $\pm 5^\circ\text{C}$ unless the bulk-susceptibility data are detailed and precisely determined. This method is therefore of doubtful reliability for general use, and in this paper we will report exclusively the best-fit values obtained for J and Δ by minimising the sum of the squares of $(\chi_{\text{calc}} - \chi_{\text{exp}})$.

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A programme was written which allowed solutions to equations (1) and (2) to be obtained either by the least-squares method or by the method of solution of simultaneous equations. The iterative procedure gave values of J to $\pm 0.1 \text{ cm}^{-1}$, which we have rounded off to the nearest whole number. Values of Δ are less precise, falling within limits of $\pm 1 \rightarrow 10 \text{ cm}^{-1}$ depending upon the magnitudes of Δ and J .

RESULTS

To establish the general effects of errors in the reported experimental data, or in the values chosen for fixed parameters, we submitted the bulk-susceptibility data for cupric acetate monohydrate⁶³ to repeated best-fit analyses using equation (2) to determine the consequent J and Δ values. The input values of g , T_N , and χ_N were altered by $\pm 5\%$; input values of $N\alpha$ were altered by $\pm 25\%$. Overestimating g increases J and decreases Δ , the inverse effect is more marked. However, 5% is a very gross change in g . Altering $N\alpha$ gives rise to small changes in the same sense as those due to g . The differing data reported for the variation of magnetic susceptibility of cupric acetate monohydrate with temperature indicates that some of the samples studied contained impurities. To assess the general importance of this phenomenon, the accepted experimental data was adjusted to values which would be appropriate if the host contained 4% of a diamagnetic or a paramagnetic impurity ($\mu_{\text{eff}} = 1.9$), and the analysis was repeated, unmodified, on the new data. (Such a level of impurity does not manifest itself in any self-evident change in the data.) The effects of these changes on the values of J and Δ [equation (2)] obtained by the best-fit method are recorded in Table 2. A similar study of the two-equation method showed it to be more sensitive to these changes, because of its reliance on an accurate value of T_N . For either method, the effect of a paramagnetic impurity⁸⁰ is to reduce the apparent Néel temperature and the singlet-triplet separation. Conversely, a diamagnetic impurity increases the best-fit value of J . Both diamagnetic and paramagnetic impurities appear to reduce the value of Δ somewhat. In the case of paramagnetic impurities the divergence between experimental and calculated susceptibility data is marked at low temperature and is reflected in the high standard deviation of the best-fit solution. A study using a fit to equation (1) showed that the effects of these changes on the values of J thus calculated parallel those described above. When all of the parameters g , J and $N\alpha$ were varied simultaneously to allow for impurities the results obtained with equation (1) demonstrated that the closeness of fit is not greatly sensitive to large changes in g or $N\alpha$. The exponential quantity, J , essentially dominates the analysis, and experimental errors (assessed by arbitrarily increasing or decreasing a single experimental χ value by

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TABLE 2

The effects of errors in the input data on the calculated values of J and Δ to fit equation (2) for cupric acetate monohydrate

Input data			Calculated data				
g	$10^4 N\alpha$ c.g.s.u.	Notes	$-J/$ cm^{-1}	$\Delta/$ cm^{-1}	$T_N/$ K	$10^4 \chi_N$ c.g.s.u.	$10^6 \sigma$ c.g.s.u.
2.167	150	a, b	297.9	831.9	262	1793	9.31
2.275	150		307.2	399.3	260	1736	11.07
2.059	150		280.3	∞	250	1737	59.4
2.167	188		302.3	687.0	265	1793	11.16
2.167	112		293.3	1207	262	1791	10.13
2.167	150	c	297.3	883.0	262	1799	24.5
2.167	150	d	298.3	775.1	262	1787	22.7
2.167	150	e	297.5	811.3	262	1794	12.35
2.167	150	f	298.1	841.2	262	1792	10.00
2.167	150	g	298.6	∞	268	1801	13.8
2.167	150	h	297.2	684.6	260	1784	25.1
2.167	150	i	286.5	481.3	245	1804	39.6
2.167	150	j	303.1	551.1	260	1725	8.95

^a Published best-fit data¹ for the dimeric molecule. ^b $\sigma = \left[\sum_{T_1}^{T_n} (\chi_{\text{expt}} - \chi_{\text{calc}})^2 / n \right]^{1/2}$. ^c 5% increase in $\chi_N(\text{expt})$ (*i.e.* $\chi_{\text{max}}(\text{expt})$). ^d 5% decrease in $\chi_N(\text{expt})$. ^e 5% increase in χ_{expt} for $T = 93 \text{ K}$. ^f 5% decrease in χ_{expt} for $T = 93 \text{ K}$. ^g 5% increase in χ_{expt} for $T = 396 \text{ K}$. ^h 5% decrease in χ_{expt} for $T = 396 \text{ K}$. ⁱ 4% paramagnetic impurity ($\mu_{\text{eff}} = 1.9$) to modify values of χ_{expt} . ^j 4% diamagnetic impurity to modify values of χ_{expt} .

5%) and/or impurities tend to be reflected in unusual or absurd values of g and $N\alpha$. It is probable that when g and $N\alpha$ are fixed in equation (1) the most meaningful values of J and of the standard deviation, σ , are obtained. Similar considerations apply to the use of equation (2) with an additional reservation, namely that the value of Δ is also somewhat sensitive to such errors (particularly to erroneous susceptibility measurements at *high* temperature and to large paramagnetic or diamagnetic impurities). It is to be noted that when g and $N\alpha$ are fixed, equation (2) has two independent variables, whereas equation (1) has only one. In such cases, it is to be expected that the former will give a better fit with experiment. However, in the majority of cases discussed in this paper, the comparison of goodness of fit is between two two-parameter models, namely the g , J and the J , Δ models, so that any overall improvement may be regarded more confidently as a criterion for the applicability of equation (2). In the tables we have used an e.s.r. value for g when this is available. Those cases where only one parameter (J) has been used to fit equation (1) are those in which this same e.s.r. g value is quoted in column 4 of Tables 3—5.

In Tables 3—5 we present the results for our calculations on the supposedly binuclear copper(II) complexes of alkylcarboxylic acids,^{15, 63, 75, 78, 85, 92, 102–112} arylcarboxylic acids,^{78, 85, 92, 94, 111, 113–119} and unsaturated¹¹¹ and dicarb-

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¹¹⁷ A. Earnshaw and K. S. Patel, *J. Inorg. Nuclear Chem.*, 1965, 27, 1805.

¹¹⁸ W. E. Hatfield and C. S. Fountain, *Inorg. Chem.*, 1965, 4, 1368.

¹¹⁹ V. V. Zelentsov, M. N. Volkov, V. M. Allenov, and T. G. Aminov, *Russ. J. Inorg. Chem.*, 1965, 10, 306.

recorded in Table 1. It is evident that the value of g for the carboxylate complexes of copper(II) rarely differs from its average (2.171) by more than 0.02. Two clear, broad trends may be distinguished: $g(\text{halogenoalkyl-carboxylates}) > g(\text{alkylcarboxylates}) > g(\text{arylcarboxylates})$ and $g(\text{terminal amine}) > g(\text{anhydrous}), g(\text{terminal H}_2\text{O})$.

The increments between these classes are of the order of 0.01. Such an increment makes very little difference indeed to the values and J and Δ calculated by equations (1) and (2). The actual trends in the g -values may be

rather smaller values of g . This may correlate partly with stronger ligand-fields, but a rather more important effect is likely to be the presence of rhombic or other low-symmetry co-ordination spheres for these cases. In general, such fields will lead to the admixture of the $|z^2\rangle$ orbital with the ground state. The average value of g will be thus reduced,¹²⁸ because $g_{\parallel} = 2.0$ for an orbital of the $|z^2\rangle$ type. Small rhombic distortions, such as that found for cupric acetate monohydrate³ and copper benzoate⁹⁵ do not appear to lead to a marked reduction in g .

TABLE 5

Magnetic data for miscellaneous copper carboxylates

Compound	Ref. to data	No. of data	Published data [equation (1)]			This work [equation (2)]				Notes	Bridging acid pK_a (room temp.) ^c	Electronic spectrum		Electronic data: e.s.r. data (extra refs.)	
			g	$-J/\text{cm}^{-1}$	$10^6 N\alpha$ c.g.s.u.	$10^6 \sigma$ c.g.s.u.	g	$-J/\text{cm}^{-1}$	Δ/cm^{-1}			$10^6 N\alpha$ c.g.s.u.	$10^6 \sigma$ c.g.s.u.		Band I $\text{cm}^{-1} \times 10^3$
(a) Dibasic carboxylates															
Copper succinate, aniline	122	9	2.20	100	120	481	2.16	76	50	150	14	4.16, 5.61	15.3	26.7	
Copper glutarate, aniline	122	9	2.16	107	120	164	2.16	104	294	150	144	4.34, 5.41	15.2	26.3	
Copper succinate, pyridine	122	8	2.60	342	120	220	2.16	263	∞	150	209	4.16, 5.61	14.9	26.5	
Copper 1,2-phenylene dicarboxylate	120	10	2.12	340	120	600	2.16	266	∞	150	127				
Copper adipate, pyridine	122	8	2.35	342	120	183	2.16	295	∞	150	102	4.43, 5.41	14.6	26.2	
Copper suberate	123	9	2.16	312	120	66	2.16	310	∞	150	50				
Copper glutarate	123	9	2.16	320	120	28	2.16	324	962	150	33	4.34, 5.41	15.3	26.2	122
Copper glutarate	122	9	2.17	320	120	32	2.16	326	789	150	25	4.34, 5.41	15.3	26.2	
Copper succinate	122	8	2.22	331	120	95	2.16	329	500	150	15	4.16, 5.61	15.3	27.1	
Copper succinate dihydrate	122	8	2.12	324	120	71	2.16	329	∞	150	42	4.16, 5.61			
Copper succinate dihydrate	123	9	2.20	336	120	33	2.16	329	∞	150	32	4.16, 5.61			
Copper glutarate, pyridine	122	9	2.23	337	120	29	2.16	331	∞	150	18	4.34, 5.41	14.7	26.5	
Copper succinate	123	9	2.12	320	120	38	2.16	333	844	150	37	4.16, 5.61	15.3	27.1	122
Copper succinate	124	15	2.16	312	120	224	2.16	343	367	150	26	4.16, 5.61	15.3	27.1	122
Copper adipate	122	12	2.04	348	120	34	2.16	372	414	150	14	4.43, 5.41	15.3	26.3	
(b) Unsaturated carboxylates															
Copper phenylacrylate	111	10	2.08	300	120	187	2.16	245	71	150	87				
Copper furlacrylate	111	8	2.08	303	120	180	2.16	268	171	150	84				
Copper acrylate	111	8	2.08	287	120	96	2.16	276	201	150	64	4.25	14.7	26.5	121

* $10^6 \sigma > 50$ c.g.s.u. unreliable data. † $10^6 \sigma > 100$ c.g.s.u. data too unreliable for further consideration.

^c Refs. 126, 127; both dissociation constants given for the dibasic acids.

interpreted by means of the explicit expressions for g_{\parallel} and g_{\perp} in a tetragonal field:⁷¹

$$g_{\parallel} - 2 = -8k_{\parallel}^2 \lambda / t_1 \quad (4)$$

$$g_{\perp} - 2 = -2k_{\perp}^2 \lambda / t_2 \quad (5)$$

where g_{\parallel} and g_{\perp} represent the anisotropic components of g resolved with respect to the fourfold axis $\{g = [\frac{1}{3}(g_{\parallel}^2 + 2g_{\perp}^2)]^{\frac{1}{2}}$, *i.e.* averaging susceptibility values}, λ is the spin-orbit coupling constant of the Cu^{II} ion (-830 cm^{-1}), k_{\parallel} and k_{\perp} are the orbital reduction factors and t_1 and t_2 represent the spectroscopic splittings between the $|x^2 - y^2\rangle$ ground state and the $|xy\rangle$ and $|xz\rangle$, $|yz\rangle$ excited states respectively. We see from these equations that $g - 2$ diminishes with increasing crystal-field strength and/or metal-ligand bonding, as indeed we have noted from Table 1. The changes in g -values are therefore small and correlate with changes in the electronic spectra of the copper(II) carboxylates. On the basis of the data in Table 1, we have chosen to use a value of 2.16 for g in this work for those cases for which e.s.r. data is not available. *a fortiori*, A constant value may be used for $N\alpha$, which is 150×10^{-6} c.g.s.u. for a dimeric copper carboxylate.⁷¹

Some miscellaneous binuclear copper(II) compounds, which are also mentioned in Table 1, tend to exhibit

The Singlet-Triplet Separation, -J.—The magnitude of the singlet-triplet separation, J , dominates the analysis of the bulk-susceptibility data, so that in a comparison between our analyses, based on equation (1) with fixed g and $N\alpha$, and those reported in the literature, the J values are in reasonable agreement. The same is true in a comparison of analyses using equations (1) and (2), where the value of J required to fit equation (2) rarely differs from the published value [equation (1)] by more than 20 cm^{-1} . However, some of these changes, which are generally consequent upon a large change in the value of g , totally alter the pattern observed for a homologous series. Thus we find an identical value of J (318 cm^{-1}) for the three picoline complexes of copper acetate which were reported by Kokot and Martin,¹⁰³ whereas the published data single out the α -picoline compound as showing a stronger coupling than its analogues. The pyridine analogue has a rather higher value for $|J|$. Both sets of data on the hydrate analogues have values of $|J|$ falling in a narrow range, but following a quite different order. These examples are particularly relevant, since our solution placed the second singlet at infinity, *i.e.* our equation (2) reduced to equation (1) in these cases. It is evident that the parameterization

¹²⁸ R. N. Bagchi and P. Sengupta, *Indian J. Phys.*, 1966, **40**, 675.

of g , particularly in a series of closely related compounds, may lead to erroneous trends in the J -values. Although the data for the singlet-triplet separations presented in Tables 3—5 form a much more consistent body of information than has previously been available, the general trends which we observe have been known for some considerable time. Thus, $|J|$ tends to increase along the following exemplifying series of bridging and terminal groups: trichloroacetate < chloroacetate ~ stearate ~ phenylacetate < acetate ~ butyrate < diphenylacetate < formate; aniline < water \lesssim anhydrous < pyridine ~ picolines ~ SCN^- ~ ethanol < dioxan.

There exists in both of these series a general trend for $|J|$ to increase as either the terminal or the bridging ligands become better electron-donors. To this extent there is a clear correlation between the value of J and the $\text{p}K_a$ of the bridging acid (and therefore the position of Band I as discussed above). It is to be noted, however, that the formate ion remains anomalous.

The values of $|J|$ for the arylcarboxylate series (Table 5) are generally rather lower than those found in the alkylcarboxylate series. The general trend correlates with the lower $\text{p}K_a$ values of benzoic acids, and within the arylcarboxylate compounds themselves there is a good correlation between $\text{p}K_a$, $|J|$ and the position of Band I, provided that the *ortho*-substituted benzoates are treated separately.^{115,125} The experimental data are generally less precise in the arylcarboxylate series. This reflects mainly the severe difficulties provided by the formation of many compounds in a number of magnetically distinct forms,¹¹⁶ many of which may well turn out not to be binuclear, or else to involve large inter-dimer interactions. In contrast, it should be noted that copper benzoate trihydrate,^{116,129} does not contain dimeric units,¹³⁰ although it does contain copper atoms bridged by benzoate groups (Cu-Cu = 3.15 Å).

The Singlet-Singlet Separation.—The essential difference between the models represented by equations (1) and (2) is the existence of a singlet state at an energy, Δ , above the ground state in the latter. Such a singlet is only important magnetically when it is ap-

* Our comment that equation (2) gives better agreement than equation (1) with the low-temperature experimental susceptibility data for cupric acetate has been criticised on the grounds that the two equations make similar predictions at low temperature but would be expected to differ at high temperatures.^{49,131} This point is well made if it were the practice to obtain J values by some independent method and then substitute these values into equation (1). In practice, however, J values are obtained by a best-fit procedure to equation (1). In this situation, one cannot claim that any defects in equation (1) would only be made manifest at high temperatures. Indeed, since the high-temperature experimental data contain a large number of similar values one would expect a least-squares procedure to fit these points particularly closely so that any defects in the theory would be evident only in the low-temperature region, where the different data differ considerably. Conversely, if a best-fit J is obtained for the low-temperature data on cupric acetate using equation (1), then the predicted high-temperature values are in poor agreement with the experimental, the predicted values being too high. It is arguable that this indicates the applicability of equation (2).

preciably thermally occupied.* Ideally, then, high-temperature magnetic measurements are desirable. Unfortunately, the limited thermal stability of most dimeric copper(II) compounds reduces the range of such data that may be obtained experimentally, although such data should be accessible for some of the anhydrous compounds. Although the experimental evidence for the existence of an additional singlet is very good for cupric acetate monohydrate,¹ we find that the quantity Δ is moderately sensitive to impurities and experimental errors in the bulk-susceptibility measurements. It is therefore, in general, rather imprecisely determined by our analysis. Δ was found to be infinity in 50 cases out of 116 (43%) for the binuclear copper carboxylates which were included in this analysis (omitting all cases where the calculated standard deviation from the observed susceptibility data exceeds 10^{-4} c.g.s.u.).

When the complex nature of Δ is taken into account, it is reasonable that the value should vary widely, and that many of the compounds show no signs of an additional thermally-populated singlet. For those compounds yielding finite values of Δ , the overall trend, which is summarised in Table 6, parallels the trend in

TABLE 6

Overall trends in the value of the singlet-singlet separation, Δ , in binuclear copper carboxylates

Class of compounds	Number of cases ($10^6\sigma \leq 10^{-4}$ c.g.s.u.)	Average value of J cm^{-1}	% of cases for which Δ was infinite
Pyridine derivatives	36	-341	64
Alcohol, ether, acid derivatives	13	-323	62
Hydrates	12	-291	58
Alkylcarboxylates	49	-325	51
Dicarboxylates	7	-296	42
Arylcarboxylates	60	-271	40
Aniline derivatives	7	-171	29
Anhydrous derivatives	34	-267	18
Average for copper(II) carboxylates	116	-296	43

the value of J . Furthermore, this parallel may be found within each of the series investigated. For example, Δ is particularly low for the fatty acid compounds and the unsaturated alkylcarboxylates, just those sub-classes which tend to have a low value of $|J|$ itself. As another example, we find that Δ is greater for pyridine derivatives of binuclear copper carboxylates than it is for hydrated derivatives, and that it is usually small for anhydrous compounds. The latter fact is very marked indeed and the former may be systematically traced in Tables 3—5 for various alkylcarboxylates, naphthoates and less clearly for the dicarboxylates. Rather few pyridine derivatives of the benzoate complexes are known, but the alcohol-substituted derivatives

¹²⁹ M. Inoue, S. Emori, and M. Kubo, *Inorg. Chem.*, 1968, **7**, 1427.

¹³⁰ H. Koizumi, K. Osaki, and R. Watanabe, *J. Phys. Soc. (Japan)*, 1963, **18**, 117.

¹³¹ A. K. Gregson, R. L. Martin, and S. Mitra, *Proc. Roy. Soc.*, 1971, **320A**, 473.

of these behave similarly with respect to their aquated or anhydrous counterparts.

In general, the experimental data indicate that the value of Δ increases as we move the terminal ligand higher up the spectrochemical or nephelauxetic series. In this context the low values of Δ for anhydrous compounds may be correlated with the fact that the terminal position is occupied by a relatively distant (oxygen) atom of another dimeric unit. (The appropriate distance in cupric propionate²⁰ is 2.28 Å, which may be compared with the four in-plane distances (average 1.95 Å) for this compound and the Cu-OH₂ distance of 2.20 Å in cupric acetate monohydrate³).

An explicit expression for Δ was given in Part III of this series.¹ Thus omitting minor terms we may write

$$\Delta \simeq 2t_3 + J_\sigma \quad (6)$$

where t_3 is the energy difference between $|x^2 - y^2\rangle$ and $|z^2\rangle$ antibonding metal orbitals of an individual copper(II) ion, and J_σ is given by equation (7).

$$J_\sigma \simeq -(2\sigma)^2/(J_{AA} - J_{AB}) \quad (7)$$

In equation (7) J_{AA} and J_{AB} are repulsion integrals between two 'holes' in $|z^2\rangle$ orbitals on the same copper atom and between a hole on each copper atom respectively; 2σ is the splitting between the bonding and anti-bonding combinations of these $|z^2\rangle$ metal-orbitals. Thus we anticipate that the value obtained for Δ should depend on the tetragonality of the ligand field. As we vary the terminal ligand of any binuclear carboxylate we would expect the value of Δ to decrease for a ligand higher in the spectrochemical series, provided that J_σ remains constant. The observed trend in Δ has an opposite sense to that required by the variation of the tetragonality of the field, and we must therefore conclude that J_σ is the dominant term in equation (6).

J_σ should vary as the square of the relevant overlap integral, S_σ ; we would expect that the electronic factors which would tend to increase S_σ and hence σ would be just those that would decrease the repulsion integrals, so that the two effects would co-operate and be manifest in an increase of $|J_\sigma|$ and thereby a reduction in the value of Δ . Yet, in accord with the orbital-expanding properties of the terminal ligands, we might expect the trends in J_σ to parallel those in J_δ , and, from the above discussion of the values of the singlet-triplet separation, $J(=J_\delta)$, we would then expect higher values of $|J_\sigma|$ for copper(II) carboxylates substituted with pyridine and its analogues than for the corresponding hydrates or anhydrous compounds. However, this argument again leads one to conclude that the value of Δ should follow the sequence: H₂O, anhydrous < pyridine, picolines. It seems more probable from our results that $|J_\sigma|$ decreases, rather than increases, when we substitute a terminal ligand by one higher in the spectrochemical or nephelauxetic series and, indeed, a more detailed examination of the prob-

lem, taking the geometry of the whole complex into account, fully supports this conclusion without reversing the predictions for J_δ at the same time. The structure of these complexes suggests that any metal-metal interaction between the $|z^2\rangle$ orbitals which lie along the Cu-Cu axis, must be mainly of a direct nature. The nephelauxetic effect of the whole set of ligands provides the possibility of increasing the overlap between these $|z^2\rangle$ orbitals to a sufficient value to generate the additional thermally populated singlet required by our model. As a result of metal-ligand σ -bonding, empty orbitals of $|z^2\rangle$ and $|x^2 - y^2\rangle$ type would involve a dispersal of the 'holes' from the metal onto the terminal and bridging ligands respectively for appropriate electronic states. If we now consider the arrangement of the terminal ligands, we see that, compared with the pure metal d orbitals, there is a radial dispersal of the metal-ligand molecular orbitals. This dispersal will reduce the 'metal-metal' σ -overlap. Thus, as we move toward more strongly bonding terminal ligands, despite the general nephelauxetic effect, there is a reduction in the value of $|J_\sigma|$ and a consequent increase in the value of Δ . Axial substitution does not influence $J_\delta (=J)$ specifically, so we conclude that the sole, nephelauxetic effect of the axial substitution is to increase the singlet-triplet separation. If we now turn our attention to the parallel effect of the bridging ligands on J_δ , we note that any dispersal of holes of type $|x^2 - y^2\rangle$ is angular rather than radial and this would not be expected to lead to a large decrease in the metal-metal δ overlap integral. Indeed this integral may well be enhanced by dispersal of the 'holes' onto the bridging ligands as a result of 'superexchange' (*i.e.* mixing of metal wavefunctions with the same ligand functions). Thus the observed increase in J_δ as a result of the substitution of a more strongly bonding bridging ligand may be rationalised principally in terms of the nephelauxetic effect of these ligands. Overall, we conclude that it is mainly the absence of ligands lying directly *between* the copper atoms which leads to opposing trends in J_δ and J_σ and thereby the observed parallel trends in $|J|$ and Δ .

Metal-Metal Bonding.—It is clear that the weak σ -component of the metal-metal interaction is of a direct bonding nature, whereas the nature of the dominant δ -interaction remains unresolved for the binuclear copper(II) carboxylate systems. Indeed Goodgame, *et al.* have shown that, for the SCN derivatives,¹⁵ the Cu-Cu distance in the formate is 2.72 Å, which is significantly longer than the 'normal' distance of 2.64 Å found for the acetate.¹⁵ Conversely, the bond-length in copper monochloroacetate α -picoline is 2.75 Å, which is in accord with the lower value of $|J|$ for this compound relative to its acetate analogue.⁸ We also incline to the opinion that the effective spin-coupling arises mainly from an indirect metal-metal bonding, which is consequent upon an effective overlap that arises from mutual overlap of the metal orbitals with suitable orbitals of the bridging ligand.

CONCLUSIONS

We have shown that values of g , $N\alpha$ and, probably, fraction of paramagnetic impurity,¹³² determined together by least-squares fits of experimental susceptibility measurements for binuclear copper species are commonly misleading. On the other hand, J values obtained in this way are in fair agreement with values obtained when g and $N\alpha$ are not parameterized although trends within series may be changed. We found that in 94% of the acceptable cases which we have analysed the new standard deviation was smaller than that calculated from the published values of g , J , and $N\alpha$. In part this was due to the use of the additional singlet, but, in a few compounds, the improvement was also due to more precise iteration of J .

Amongst the possible effects which are neglected in our approach are questions of a significant temperature variation in J or g .^{133,134} As these quantities are derived from electronic quantities they are not expected to vary widely with temperature, unless the compound undergoes a phase change. Secondly, rhombic or lower symmetry components of the ligand field have not been taken into account explicitly in the calculation. It should be noted that copper acetate monohydrate itself, unlike other structurally studied homologues, has a marked rhombic distortion.³ The influence of this distortion and consequent $(z^2)-(x^2 - y^2)$ mixing on the

magnetic properties has been discussed.^{64,128} Finally vibrational and other ligand effects have not been included here.¹³⁵

The trends in the corrected values of the singlet-triplet separation J , obtained in this work may be firmly correlated with the electronic properties of the ligands.¹³⁶ It is more difficult to make a general and unequivocal comment on the Δ values, which have been determined less precisely. Nevertheless the trends in Δ do appear to parallel the trends in the $|J|$ values. This implies that the exchange integrals J_δ and J_o vary in an opposite sense along a series of compounds, and such a phenomenon may only be correlated with the unique features of the geometry of the binuclear copper(II) carboxylates.

All of the detailed treatments of these binuclear copper(II) complexes suggest that the effective exchange integral should be proportional to the square of the relevant metal-metal overlap integral, or, for a superexchange mechanism, to the fourth power of the relevant metal-ligand overlap integral, and inversely proportional to the difference between one- and two-centre electron-repulsion integrals. The very similar values of $|J|$ (ca. 300 cm⁻¹) found for so many copper(II) carboxylates suggest a subtle balancing of effects between related compounds. Evidently, rather similar comments apply to the Δ values.

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