An Electron Spin Resonance Study of the Copper(II) Chelates of Cyclobutane-1,1-dicarboxylic Acid and Their Mixed Ligand Chelates

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The *X*-band e.s.r. spectra of the copper(II) chelate of cyclobutane-1,1-dicarboxylic acid formed in dimethylformamide, dimethyl sulphoxide, or trimethyl phosphate show that dimeric species are formed which give rise to magnetic dipole–dipole coupling in dimethylformamide or dimethyl sulphoxide and predominantly exchange coupling when trimethyl phosphate is used as the solvent. The introduction of salicyclic, mandelic, benzilic, malic, or citric acid results in the formation of monomeric mixed ligand complexes though minor amounts of dimeric species are present. The 'triplet' state spectra have been used to extract structural and magnetic parameters of the copper(II) dimeric chelates.

PREVIOUS studies concerned with the use of e.s.r. data in the elucidation of the structure of dimeric chelates of copper(II) have shown a remarkable diversity of structural forms brought about by subtle changes in the structure of the ligand. It is therefore of continuing interest to study dimeric forms of copper(II) chelates where the ligand offers few possibilities for bridging sites, of conformations of the dimeric structure, and of symmetry relationships of the copper(II) ions in the dimers.

A ligand of particular simplicity in this respect is cyclobutane-1,1-dicarboxylic acid. In the present investigation the potential of cyclobutane-1,1-dicarboxylic acid for giving rise to dimeric forms of its copper(II) chelates has been assessed by e.s.r. spectroscopy. In addition the stability of the copper(II) chelate of this acid in the presence of other ligands which included imidazole, salicyclic, mandelic, benzilic, malic, and citric acids has been determined.

A potentiometric study of complexes of cyclopropane-1,1-dicarboxylic acid, cyclopentane-1,1-dicarboxylic acid, and cyclohexane-1,1-dicarboxylic acid with copper(II), nickel(II), zinc(II), and cobalt(II) ions has been reported.[1] For all the ions, the stability of the 1 : 1 complexes was found to decrease with an increase in size of the ligand ring.

RESULTS AND DISCUSSION

The copper(II) chelate of cyclobutane-1,1-dicarboxylic acid has a low solubility in water, but was sufficiently soluble in non-aqueous solvents such as dimethylformamide, dimethyl sulphoxide, or trimethyl phosphate to allow the preparation of 0·1M solutions. The chelate can easily be formed under these conditions by the addition of base, namely triethylamine to a dimethylformamide solution containing copper(II) chloride (0·1M) and the ligand (0·2M). This process leads to a reduction in the intensity of the *X*-band e.s.r. signal due to copper(II) chloride by *ca.* 50% when $n = 1$, where n is the number of moles of triethylamine added per mole of copper(II). For further addition of base up to $n = 4$ the intensity of the signal due to monomeric copper(II) chelate increases and acquires a resolved structure. The spectra observed with sample temperatures of 77 K for the *g ca.* 4 and *g ca.* 2 regions are illustrated by Figures 1A and 1B respectively, for $n = 1$—4. For $n = 1$, a low-field component was observed and attributed to $\Delta M_s = \pm 2$ transitions arising from magnetic dipole coupling in a dimeric form of the copper(II) chelate. The corresponding $\Delta M_s = \pm 1$ transition can be discerned in the *g ca.* 2 region although the signal is composite owing to monomeric and dimeric species. Similar spectra were obtained at 77 K for $n = 2$, though the contribution by the monomeric species in the *g ca.* 2 region was more pronounced. For $n = 3$, although the $\Delta M_s = \pm 2$ signal was of similar intensity, the $\Delta M_s = \pm 1$ signal was much weaker. Higher instrumental gain was required to record the spectrum shown in Figure 1A for $n = 4$, while in the *g ca.* 2 region the dimer $\Delta M_s = \pm 1$ signal was not identified, though it must be a broad weak signal underneath the strong monomer spectrum in that case (Figure 1B, $n = 4$) which cannot be extracted with any certainty.

A similar sequence of spectra was obtained with dimethyl sulphoxide as solvent; however, the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ signals in this solvent were not as well resolved as those obtained in dimethylformamide. Addition of triethylamine to a solution of copper(II) chloride (0·1M) and cyclobutane-1,1-dicarboxylic acid (0·1M) in trimethyl phosphate produced spectra which, in addition to the resolved signals at *g ca.* 2 and *g ca.* 4, possessed a zero-field line and a high-field component at *ca.* 4600 gauss, indicative of exchange coupling.[2]

The addition of imidazole (0·1M or 0·2M) to dimethylformamide solutions of the copper(II) cyclobutanedicarboxylic acid chelate brought about a marked reduction in the intensity of the low-field (*g ca.* 4) signal. This indicated that mixed ligand chelate formation leading to a monomeric species competes well with the process of dimerisation.

The addition of salicyclic acid plus base to the same copper(II) chelate brought about a similar change. In this case, a well resolved signal was observed at both

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[1] E. Roletto, A. Vanni, and G. Ostacoli, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2817.

[2] J. F. Boas, R. H. Dunhill, J. R. Pilborow, R. C. Srivastava, and T. D. Smith, *J. Chem. Soc.* (*A*), 1969, 94.

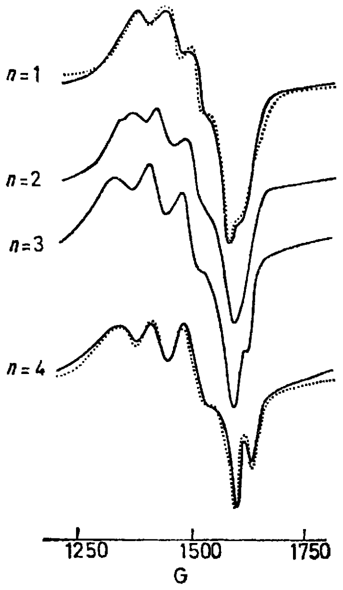

FIGURE 1A Experimental X-band e.s.r. spectra (——) and best-fit theoretical e.s.r. lineshapes (– – – –) for the *g ca.* 4 region due to dimethylformamide solutions of copper(II) (0·1M) and cyclobutane-1,1-dicarboxylic acid (0·2M) at 77 K and 9140 MHz for various n values. Parameters for best-fit theoretical e.s.r. lineshapes are listed in Table 1

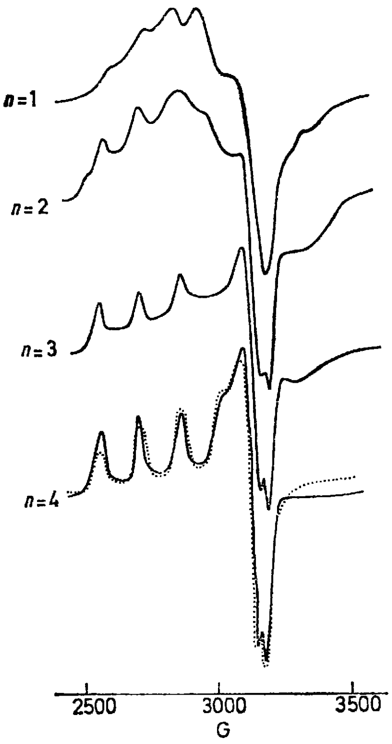

FIGURE 1B Experimental X-band e.s.r. spectra (——) and a best-fit theoretical e.s.r. lineshape (– – – –) for the *g ca.* 2 region due to dimethylformamide solutions of copper(II) (0·1M) and cyclobutane-1,1-dicarboxylic acid (0·2M) at 77 K and 9140 MHz for various values of n. Parameters for the best-fit theoretical monomer e.s.r. lineshape are listed in Table 2

room temperature and 77 K which accounted for all of the copper(II) being present as a monomeric species. Further, on addition of base to the dimethylformamide solution containing copper(II) chloride (0·1M), cyclobutane-1,1-dicarboxylic acid (0·1M), and salicyclic acid (0·1M) up to $n = 2$, the spectra were closely similar to those obtained in the absence of salicyclic acid. This indicated that the formation of the dicarboxylate chelate is the first step in the mixed ligand chelate formation. For $n = 3$ a spectrum due to the monomeric species was observed in the *g ca.* 2 region at 77 K which became better resolved at $n = 4$. In the *g ca.* 4 region for $n = 3$, the $\Delta M_S = \pm 2$ signal is reduced in intensity, while for $n = 4$ no signal could be observed even at much higher instrumental gain.

When benzilic or mandelic acid was added to a solution containing copper(II) chloride (0·1M) and cyclobutane-1,1-dicarboxylic acid (0·1M) in dimethylformamide the dimeric copper(II) chelate was formed initially and was found to persist up to $n = 3$. For these mixed ligand systems, however, a small amount of copper remains in a new dimeric form for $n = 4$, whose presence is indicated by the appearance of low-intensity low-field lines which could be easily distinguished from those due to the dicarboxylic acid dimer. For the dicarboxylic acid–mandelic mixed ligand case at 77 K, the *g ca.* 4 spectra are shown in Figure 2A and the *g ca.* 2 spectra in Figure 2B. At room temperature the signal intensity increased slightly from $n = 3$ to 4. This observation confirmed that most of the copper(II) was present in a monomeric form when $n = 4$.

The spectra obtained at both room temperature and 77 K from dimethylformamide solutions containing copper(II) chloride (0·1M), cyclobutane-1,1-dicarboxylic acid (0·1M), and malic acid (0·1M) were indicative of the formation of monomeric species arising from mixed ligand chelate formation which accounted for all of the copper(II) present in the system when $n = 4$ or 5. It is more difficult in this case to decide which ligand controls the co-ordination of the copper(II), but a comparison of the signals with those due to malic acid and dicarboxylic acid systems alone indicated that the early stages of combination involve the formation of the cyclobutanedicarboxylic acid chelate. When $n = 1$, 2, or 3, although the intensity of the room-temperature e.s.r. spectra indicated that most of the copper(II) was in monomeric form, there is some modification of the low-field lines when compared with those due to the dicarboxylic acid alone at 77 K.

Spectra obtained from a dimethylformamide solution containing copper(II) chloride (0·1M), cyclobutane-1,1-dicarboxylic acid (0·1M), and citric acid when $n \geqslant 3$ accounted for all of the copper(II) present in monomeric form as determined from e.s.r. measurements at both 77 K and room temperature. At lower n values, however, the spectra at 77 K show the presence of low-field components such that when $n = 1$, a signal centred at *ca.* 900 G occurred along with a broad signal centred at 1500 G. It may be speculated that these low-field components

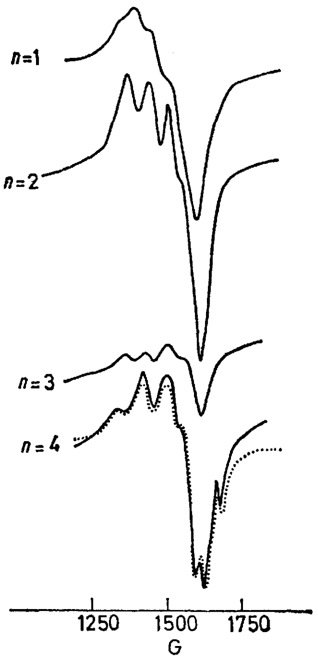

FIGURE 2A Experimental X-band e.s.r. spectra (——) and a best-fit theoretical e.s.r. lineshape (– – – –) for the g *ca.* 4 region due to dimethylformamide solutions of copper(II) (0·1M), cyclobutane-1,1-dicarboxylic acid (0·1M), and mandelic acid (0·1M) at 77 K and 9140 MHz for various values of n. Parameters for the best-fit theoretical e.s.r. lineshape are listed in Table 1

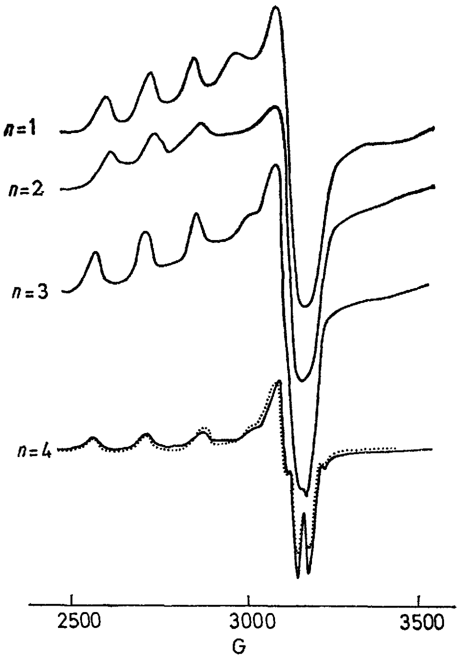

FIGURE 2B Experimental X-band e.s.r. spectra (——) and a best-fit theoretical e.s.r. lineshape (– – – –) for the g *ca.* 2 region due to dimethylformamide solutions of copper(II) (0·1M), cyclobutane-1,1-dicarboxylic acid (0·1M), and mandelic acid (0·1M) at 77 K and 9140 MHz for various values of n. Parameters for the best-fit theoretical e.s.r. lineshape are listed in Table 2

can be attributed to $\Delta M_s = \pm 3$ and $\Delta M_s = \pm 2$ transitions arising from coupling of three copper(II) ions in a trimeric species [3] or from the turning points in a spectrum with $S = 1$ due to coupling between two copper(II) ions with a large value of the zero-field splitting term D.[4] These components may be attributed to $\Delta M_s = \pm 3$ and $\Delta M_s = \pm 2$ transitions arising from the coupling of three copper(II) ions in a trimeric species.[3] For $n = 2$ only a $\Delta M_s = \pm 2$ signal was found in the low-field region.

Interpretation of the E.s.r. Results.—' Triplet ' state spectra arising from purely magnetic dipole–dipole coupled copper(II) dimers can be satisfactorily accounted for by a model which covers axially symmetric cases as well as significant lowering of axial symmetry. The appropriate spin Hamiltonian may be written for cases here as (1) where the nomenclature is identical to that

$$\mathscr{H} = \sum_{i=1,2} \{\beta[g_{\|}H_zS_{iz} + g_{\perp}(H_xS_{ix} + H_yS_{iy})] + AS_{iz}I_{iz} + B(S_{ix}I_{ix} + S_{iy}I_{iy})\} + \mathscr{H}\,(\text{dipolar}) - J\mathbf{S}_1 \cdot \mathbf{S}_2 \quad (1)$$

used previously.[5] It was assumed that $|J| \leqslant$ *ca.* 30 cm^{-1} and that no ' pseudo-dipolar ' contributions arising from exchange in equation (1) are needed. Allowance is made for ' singlet '–' triplet ' transitions which will occur when J *ca.* 0, as well as for the influence of off-diagonal hyperfine interaction matrix elements neglected in our earlier work,[4] but now all allowed for in all our computer programmes.[3,5]

The spectra observed in one case with very low- and very high-field lines, due to the influence of a significant exchange interaction, J *ca.* -300 cm^{-1}, have been treated in terms of a composite D arising from both exchange effects and dipolar coupling, and in terms of the total spin of the pair of ions.[4]

The monomeric signals were accounted for by the use of the well-known axial and orthorhombic spin Hamiltonians.[6]

Best-fit parameters obtained for the dimeric species based on $\Delta M_s = \pm 2$ results alone are in Table 1, while those due to the monomeric species are in Table 2. These examples illustrate that it is often difficult to obtain clear-cut $\Delta M_s = \pm 1$ dimer signals, and so one must rely on $\Delta M_s = \pm 2$ spectra for computer simulation of spectra.

The e.s.r. spectra of solutions of copper(II) chloride (0·1M) and cyclobutane-1,1-dicarboxylic acid (0·1M) in dimethylformamide with benzilic or mandelic acid added showed evidence of a large pseudo-dipolar contri-

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[3] P. D. W. Boyd, T. D. Smith, J. H. Price, and J. R. Pilbrow, *J. Chem. Phys.*, 1972, **56**, 1253.

[4] J. H. Price, J. R. Pilbrow, K. S. Murray, and T. D. Smith, *J. Chem. Soc.* (*A*), 1970, 968.

[5] P. D. W. Boyd, A. D. Toy, and T. D. Smith, *J.C.S. Dalton*, 1973, 1549.

[6] A. D. Toy, S. H. H. Chaston, J. R. Pilbrow, and T. D. Smith, *Inorg. Chem.*, 1971, **10**, 2219.

TABLE 1

Calculated magnetic parameters for dimeric species $\Delta M_s = \pm 2$ spectra only). Errors listed give range of parameters over which theoretical curves compatible with the observed e.s.r. lineshapes are obtained

n	Transition	r/Å	ξ/°C	$g_{\parallel}$	$g_{\perp}$	$\frac{10^{-4}A}{\text{cm}^{-1}}$	$\frac{10^{-4}B}{\text{cm}^{-1}}$	σ/G	Dimer *symmetry* deduced
0·1M-Cu^{II}, 0·2M-cyclobutane-1,2-dicarboxylic acid									
1	$\Delta M_s = \pm 2$	4·0 ± 0·2	—	2·290 ± 0·005	2·060 ± 0·005	110 ± 5	5 ± 5	$\sigma_{\parallel}$ = 15, $\sigma_{\perp}$ = 17	Axial
4	$\Delta M_s = \pm 2$	4·0 + 0·2	15 ± 5°	2·395 ± 0·005	2·015 ± 0·005	170 ± 5	10 ± 10	$\sigma_{\parallel}$ = 10, $\sigma_{\perp}$ = 15	Monoclinic
0·1M-Cu^{II}, 0·1M-cyclobutane-1,1-dicarboxylic acid, 0·1M-mandelic acid									
4	$\Delta M_s = \pm 2$	4·4 ± 0·3	—	2·300 ± 0·005	2·070 ± 0·005	165 ± 5	40 ± 10	$\sigma_{\parallel}$ = 10, $\sigma_{\perp}$ = 15	Axial
0·1M-Cu^{II}, 0·1-cyclobutane-1,1,dicarboxylic acid, 0·1M-benzilic acid									
4	$\Delta M_s = \pm 2$	3·8 ± 0·2	—	2·140 ± 0·005	2·090 ± 0·005	40 ± 5	10 ± 5	$\sigma_{\parallel} = \sigma_{\perp}$ = 10	Axial

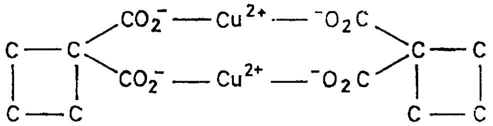
TABLE 2

Calculated magnetic parameters for monomeric species. Errors listed give range of parameters over which theoretical curves compatible with the observed e.s.r. lineshapes are obtained

[Cu^{II}]/M	[C$_4$H$_6$(CO$_2$H)]/M	n	g-Values	$10^4 \times$ Coupling constants/cm^{-1}	Line widths/G
0·1	0·2	4	$g_{\parallel}$ = 2·315 ± 0·005 $g_{\perp}$ = 2·055 ± 0·005	A 175 ± 5 B 5 ± 10	σ = 20
With 0·1M-mandelic acid					
0·1	0·1	4	$g_{\parallel}$ = 2·305 ± 0·005 $g_{\perp}$ = 2·060 ± 0·005	A 165 ± 5 B 10 ± 5	σ_z = 15
With 0·1M-benzilic acid					
0·1	0·1	4	g_z = 2·300 ± 0·005	A_z 165 ± 5	σ_z = 10
			g_x = 2·060 ± 0·005	A_x 10 ± 5	σ_x = 5
			g_y = 2·055 ± 0·005	A_y 15 ± 5	σ_y = 5
With 0·1M-salicylic acid					
0·1	0·1	4	g_z = 2·305 ± 0·005	A_z 160 ± 5	σ_z = 15
			g_x = 2·050 ± 0·005	A_x 10 ± 5	σ_x = 5
			g_y = 2·045 ± 0·005	A_y 10 ± 5	σ_y = 5
With 0·1M-malic acid					
0·1	0·1	5	g_z = 2·305 ± 0·005	A_z 165 ± 5	σ_z = 15
			g_x = 2·065 ± 0·005	A_x 10 ± 5	σ_x = 5
			g_y = 2·055 ± 0·005	A_y 10 ± 5	σ_y = 5
With 0·1M-citric acid					
0·1	0·1	6	g_z = 2·305 ± 0·005	A_z 165 ± 5	σ_z = 15
			g_x = 2·055 ± 0·005	A_x 10 ± 5	σ_x = 5
			g_y = 2·045 ± 0·005	A_y 10 ± 5	σ_y = 5

bution to the zero-field splitting owing to exchange. The best-fit parameters obtained were $D = 0{\cdot}345$ cm^{-1}, $g_{\parallel} = 2{\cdot}39 \pm 0{\cdot}01$, $g_{\perp}$ *ca.* 2·07 and the component line-width, $\sigma = 20$ G. The zero-field and high-field lines observed are 'z'-lines and thus $g_{\perp}$ may not be determined accurately from these results. Table 1 shows that $g_{\perp} = 2{\cdot}015 \pm 0{\cdot}005$ and $g_{\perp} = 2{\cdot}395 \pm 0{\cdot}005$ for 0·2M-cyclobutane-1,1-dicarboxylic acid with $n = 4$. These results were based on an analysis of the $\Delta M_s = \pm 2$ spectrum only for which $g_{\perp}$ cannot usually be obtained with high precision.

The essential framework of the copper(II) cyclobutane-carboxylic acid dimeric chelate is illustrated by structure (I). The construction of a space-filling molecular model confirmed that the copper–copper separation distance for this structure was compatible with that obtained from the e.s.r. data. In addition, the structure of this chelate agrees with the 1 : 1 ratio indicated by the room-temperature and 77 K e.s.r. spectra. For this case the structure of the ligand and in particular the CO_2H–C–CO_2H angle controls the overall form of the dimer.



Exceptional behaviour was noted for two of the mixed acid systems. These were the cyclobutanedicarboxylic acid–benzilic and –mandelic acid chelates. In both these cases although room-temperature and 77 K spectra in the g *ca.* 2 region confirmed a breakdown to monomeric species, in the g *ca.* 4 region at 77 K $\Delta M_s = \pm 2$ signals were observed. The parameters obtained for the copper(II) cyclobutanedicarboxylic acid–benzilic acid chelate indicated a copper–copper separation distance of 4·4 Å and a low A value of 40×10^{-4} cm^{-1}. Small A values have been noted previously and interpreted in terms of distortion about the copper(II) even though the overall dimer symmetry remained axial.[7] This $\Delta M_s = \pm 2$ signal was found to be exactly the same as that due to copper(II) benzilate alone. For the copper(II) cyclobutanedicarboxylic acid–mandelic acid chelate the g-values and separation distance are in substantial agreement with those published for copper(II) mandelate.[7] The programme used to obtain the parameters listed in Table 1 uses the more complete theory as explained earlier and so small differences between the present copper(II) cyclobutanedicarboxylic acid–mandelic acid case and the copper(II) mandelate can be accounted for.

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[7] A. D. Toy, T. D. Smith, and J. R. Pilbrow, *J. Chem. Soc.* (*A*), 1971, 2952.