Inorganica Chimica Acta, 15 (1975) L15 - L16
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EPR Spectra of Trigonal Bipyramidal Copper(II) Species Cu(R_6tren)X^+

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(Received July 14, 1975)

Very little data exists in the literature on the EPR spectra of trigonal bipyramidal copper(II) species in solution. One of the very few examples for which data has been reported is Cu(OH)tren$^+$ (tren = 2,2′,2″-triamino-triethylamine) in aqueous solution for which the Spin Hamiltonian parameters found[1] (see Table) were interpreted using the first order expressions derived for a d_{z^2} ground state by means of perturbation theory, *viz.*

$$\begin{aligned} g_{\parallel} &= 2.0023 \\ g_{\perp} &= 2.0023 - (6\lambda/\Delta)\alpha^2\beta_1^2 \end{aligned} \tag{1}$$

$$\begin{aligned} A_{\parallel} &= P[-\kappa\alpha^2 + 4/7\alpha^2 - 1/7(g_{\parallel} - 2)] \\ A_{\perp} &= P[-\kappa\alpha^2 - 2/7\alpha^2 + 15/14(g_{\perp} - 2)] \end{aligned} \tag{2}$$

where all the symbols have the meaning given in ref. 1 and where the molecular orbital formalism has been used but only metal orbital coefficients have been retained.

Results and discussion

In order to extend and deepen our understanding of such species we have examined the spectra of a series of complexes Cu(R_6tren)X_2, where R_6tren can be $[(CH_3)_2N(CH_2)_2]_3N$ or $[(C_2H_5)_2N(CH_2)_2]_3N$ and X = Cl, Br, I, NO_3, ClO_4, all of which are believed to give trigonal bipyramidal cations in solution. Solid Cu(Me_6tren)Br_2 is known[2] to contain trigonal bipyramidal cations of C_{3v} symmetry, Cu(Me_6tren)Br^+, in which the Cu(II) ion is displaced out of the equatorial plane away from the axial N donor atom and the Cu–N_{ax} distance is shorter than the Cu–N_{eq} distance as expected for an oblate spheroidal *d*-electron distribution.[3] Ciampolini has shown[4] from conductivity and electronic spectral data that the cation goes into solution in various organic solvents without change of structure and that other salts with different anions give species of very similar structure in solution. We have confirmed that this is also true in methanol. However it should be noted that the EPR spectrum of Cu(Me_6tren)I^+ in methanol shows marked rhombic anisotropy (see Fig. 1) so that this species must depart appreciably from C_{3v} symmetry in this solvent. In order to compare our data directly with those for Cu(OH)tren$^+$ we have also recorded the spectra of Cu(Me_6tren)$^{2+}$ and Cu(Et_6tren)$^{2+}$ obtained by dissolving the bromide and the perchlorate respectively in water to which a little glycerine has been added to facilitate the formation of good glasses at low temperature.

A number of interesting features emerge from the data shown in the Table. Firstly it will be noted that the iodides and bromides have values of $g_{\parallel}$ markedly smaller than the free electron g-factor whilst the nitrate and the species Cu(Me_6tren)$^{2+}$ in H_2O have

TABLE. Spin Hamiltonian Parameters.

Complex[e]	g_{iso}	A_{iso}[a]	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$[a]	$A_{\perp}$[a]	g_{av}[b]	A_{av}[b]
Cu(Me_6tren)I_2	2.110	50	1.889	2.191 2.224	100	–119 –107	2.101	42
Cu(Me_6tren)Br_2	2.109	50	1.945	2.179	82	– 97	2.106	37
Cu(Me_6tren)$(NO_3)_2$	2.140	56	2.017	2.190	73	–108	2.134	48
Cu(Me_6tren)aq^{2+} [c]	2.146	57	2.011	2.181	65	–108	2.137	50
Cu(Et_6tren)I_2	2.123	69	1.978	2.212	90	96	2.134	94
Cu(Et_6tren)Br_2	2.112	83	1.986	2.194	80	85	2.125	83
Cu(Et_6tren)Cl_2	2.122	79	2.000	2.194	75	79	2.129	78
Cu(Et_6tren)$(ClO_4)_2$	2.133	80	1.977	2.218	78	104	2.138	95
Cu(Et_6tren)aq^{2+} [c]	2.133	90	2.002	2.212	98	93	2.142	95
Cu(tren)OH$^+$ [d]	2.137	48	2.006	2.210	68	–111	2.142	51

[a] In units of 10^{-4} cm^{-1}. [b] $g_{av} = 1/3(g_{\parallel} + 2g_{\perp})$, $A_{av} = 1/3(A_{\parallel} + 2A_{\perp})$. [c] In H_2O plus a little glycerol. [d] In H_2O from reference 1.
[e] The spectra were obtained for solutions in methanol except where otherwise indicated.

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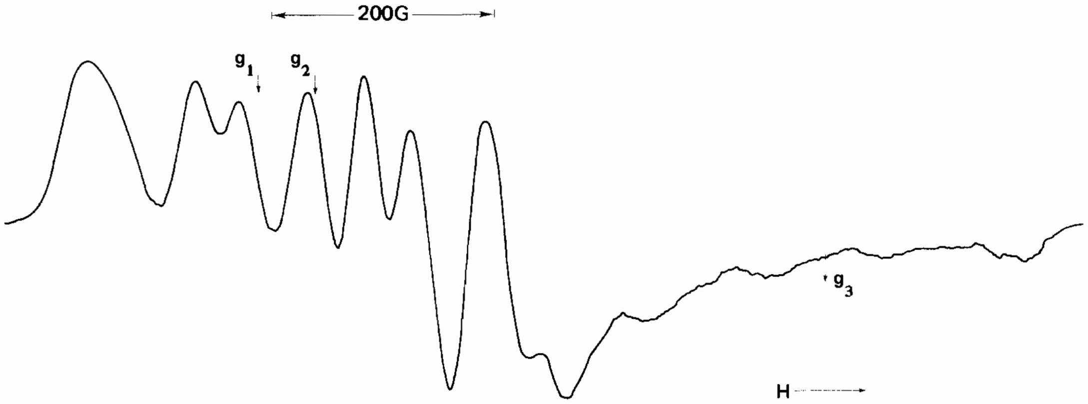

Fig. 1. EPR spectrum of Cu(Me$_6$tren)I$^+$ in frozen methanol solution at −140 °C.

values of $g_\parallel$ slightly larger than the free electron g-factor. Inclusion of the small second order term, $-3\lambda^2/\Delta^2$, which should be added to the expression for $g_\parallel$ obtained from the perturbation treatment is not sufficient to account satisfactorily for the deviations below the free electron value. It is clear that equations (1) do not adequately represent the g-values in the case where a) the ligand spin–orbit coupling constant λ is very large, *e.g.*, Br, 2460 cm^{-1}, I, 5000 cm^{-1},[5] and b) the relatively small size of the crystal field splitting parameter Δ compared with the Cu(II) spin–orbit coupling constant of −829 cm^{-1} makes the use of perturbation theory unsuitable. In order to obtain satisfactory equations for the g-values we consider that it is necessary to solve the appropriate secular equations even though the analysis will be complicated by the presence of odd-order terms in the crystal field potential which mix *p* and *d*-orbitals and of quartic terms Y_4^3, Y_4^{-3} which mix d_{xz},d_{yz} with d_{xy},$d_{x^2-y^2}$ orbitals. The fact that the $g_\parallel$ values found for the species Cu(Me$_6$tren)$^{2+}$ are slightly larger than the free electron value may be explained by a small admixture of d_{xy} or $d_{x^2-y^2}$ into the ground state *via* vibronic coupling.[6]

Secondly the relative signs of the hyperfine coupling constants are also worth noting. In copper (II) compounds the hyperfine coupling constants are largely determined by the core polarisation which is negative.[7] For a $d_{x^2-y^2}$ ground state both $A_\parallel$ and $A_\perp$ are negative with $A_\parallel \gg A_\perp$ in most cases. For a d_{z^2} ground state however, if the equations (2) are at least approximately correct, the absolute values of $A_\parallel$ and $A_\perp$ will be comparable since the spin dipolar contribution to $A_\parallel$ is positive and the orbital contribution though negative is small, whilst the spin dipolar contribution to $A_\perp$ is negative and the relatively large orbital contribution is positive. Taking the free ion value of 0.43 for κ (eq. 2) it seems probable that the sign of $A_\parallel$ will be positive while that of $A_\perp$ will be negative. In fact Senyukova *et al.*[1] found that a) $A_\parallel$ and $A_\perp$ must have opposite signs if the expression $A_{iso} = 1/3(A_\parallel + 2A_\perp)$ is at least approximately valid, and b) it is necessary that $A_\parallel > 0$ and $A_\perp < 0$ if $\alpha^2 > 0$ in equations (1) and (2). However in our case we find this to be true for only some of the species investigated (see Table) while for the others $A_\parallel$ and $A_\perp$ appear to have the same sign with absolute values which increase with the polarisability of coordinated halide. In fact a few percent of 4*s* wave-function mixed into the primarily $3d_{z^2}$ground state – a mixing which is symmetry allowed in the C_{3v} point group – can reduce the value of κ considerably as has been observed in other cases[8] and this could be sufficient to make both $A_\parallel$ and $A_\perp$ positive.

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