Inorganica Chimica Acta, 11 (1974) L31 - L32

Trapping-out of Dynamic Jahn–Teller Distortions in Octahedral Copper(II) Complexes

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(Received September 25, 1974)

Recently, Bertini *et al.* have shown[1] that the e.s.r. spectra of single crystals of $Cu(en)_3SO_4$ at 77 K may be interpreted in terms of three magnetically non-equivalent sites. At room temperature, the signal is isotropic due to the presence of a dynamic Jahn–Teller effect, which "traps-out" in a distorted stereochemistry as the temperature is reduced. The authors make no suggestions as to the distorted geometry which is then present, although illustrations are given of two possible relationships between the g directions and the (regular octahedral) molecular axes. We wish to make comparisons with data on other tris-chelate copper(II) complexes. The regular complex has D_3 symmetry and should distort to remove the degeneracy of the ^2E ground-state. Two modes of vibration have been illustrated[2] which would effect this change, one resulting in an almost tetragonal geometry, while the other leads to the *cis*-distortion shown in Figure 1. Unfortunately, single-crystal data is not available on any distorted tris-chelates in which all the ligands are identical, but information has been published on examples of each of the distortions in mixed-ligand complexes. The *cis*-distortion is illustrated[2] by $[Cu(bipy)_2(ONO)]NO_3$ which has $g_1 = 2.029, g_2 = 2.170$ and $g_3 = 2.205$; the tetragonal distortion is typified by $Cu(hfacac)_2(bipy)$ with $g_1 = 2.072, g_2 = 2.079$ and $g_3 = 2.292$. The observed g-values for $Cu(en)_3SO_4$ were[1] $g_1 = 2.053, g_2 = 2.134$ and $g_3 = 2.159$ and show the same sort of distribution as those of $[Cu(bipy)_2(ONO)]NO_3$ in that g_2 is closer to g_3 than it is to g_1. Also the electronic reflectance spectrum of $Cu(en)_3SO_4$ has[4] at room temperature, a strong peak at 15.7 kK and a weaker 8.7 kK peak and this pattern shows greater similarity to the spectrum of $[Cu(bipy)_2(ONO)]NO_3$ than it does to that of $Cu(hfacac)_2(bipy)$[3]. We should not expect closer identity of the g-values of the two complexes, in view of the all-nitrogen co-ordination of $Cu(en)_3^{2+}$ compared with the presence of some oxygen ligands and also potential π-bonding in $[Cu(bipy)_2(ONO)]^+$. We wish to suggest then that $Cu(en)_3SO_4$ contains *cis*-distorted species which are involved in a dynamic Jahn–Teller effect at room temperature but "trap-out" at lower temperatures; we suppose that the electronic spectrum does "see" the distortion at both temperatures. In this case, little error will result from combining room-temperature electronic spectral data with low-temperature e.s.r. data. Assuming the presence of a predominantly d_{z^2} ground-state the expressions for the g-values in C_{2v} symmetry have been given[3] (note the typographical error in ref. 2) as

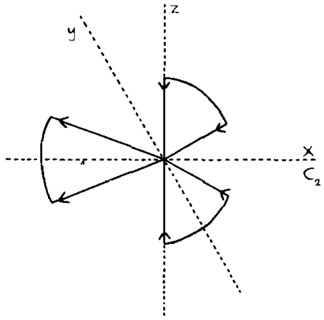

Fig. 1. An E-type mode of vibration yielding a *cis*-distorted tris-chelate complex in $Cu(en)_3^{2+}$.

$$g_1 = g_z = 2 - 8k_\parallel^2\lambda\sin^2\alpha/E(d_{xy} \rightarrow d_{z^2})$$
$$g_2 = g_x = 2 - 2k_\perp^2\lambda(\sin\alpha + \sqrt{3}\cos\alpha)^2/E(d_{yz} \rightarrow d_{z^2})$$
$$g_3 = g_y = 2 - 2k_\perp^2\lambda(\sin\alpha - \sqrt{3}\cos\alpha)^2/E(d_{xz} \rightarrow d_{z^2})$$

The crystal-field splitting diagram suggested for *cis*-distorted complexes leads to the possible assignment of the 8.7 kK band to the $d_{xy} \rightarrow d_{z^2}$ transition and the 15.7 kK band to a superposition of the $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{xz} \rightarrow d_{z^2}$ and $d_{yz} \rightarrow d_{z^2}$ transitions. We then calculate $\sin\alpha = 0.0779$, $k_\perp = 0.673$ and $k_\parallel = 3.32$; these data may be compared with $[Cu(bipy)_2(ONO)]NO_3$ for which $\sin\alpha = 0.0807$, $k_\perp = 0.753$ and $k_\parallel = 2.52$. In both cases the $k_\parallel$ values are absurd (since it is difficult to see how orbital reduction factors can be greater than unity), and this situation has previously[2] been interpreted in the sense that the usual $k_x \approx k_y$ approximation is invalid. The similarity of the results seems to support the suggested stereochemistry and also leads to a preference for the first of Bertini's possible relations between g directions and molecular axes;[1] the C_2 axis of the elongation is the g_2 axis as in $[Cu(bipy)_2(ONO)]NO_3$. The e.s.r. data on $Cu(en)_3SO_4$ are unusual in that magnetically non-equivalent sites can be distinguished (by three signals) in a non-dilute copper(II) complex.

A second case of a room-temperature dynamic Jahn–Teller effect is postulated[5,6] in $K_2Pb[Cu(NO_2)_6]$ and here again "trapping-out" appears at lower temperatures. In view of the point made above, it is worth noting that separate signals are again found in a non-dilute copper(II) complex, again with no observable hyperfine structure (hyperfine structure has been noted in some non-dilute copper complexes, for example[7] $Cu(NO_3)_4^{2-}$ and $Cu(NCO)_4^{2-}$). Paoletti *et al.* have given a qualitative interpretation of partial data on a single crystal. They suggest the existence of two magnetically non-equivalent sites, implying that the unit cell of $K_2Pb[Cu(NO_2)_6]$ contains three molecules, since the intensity of site A is twice that of site B. However, the authors venture the unlikely suggestion that at low temperature one site (B) is distorted while the others remain regular octahedral.

A more plausible explanation is that *all* sites are distorted in the same way, their orientations conspiring to produce the observed effects in the rotation of the crystal. This would be feasible if two of the sites were inclined at identical angles to the rotation axis. Suppose the principal molecular axes (z) of both sites A are inclined at angle θ to the rotation axis (R) and are coplanar with this axis, as in Figure 2. Then the signals due to the 2A sites would vary in the same way, from $g_\perp$ to $(g_\parallel^2 \sin^2\theta + g_\perp^2 \cos^2\theta)^{1/2}$; if θ is small then g (A) varies little, as observed. Now if the z axis of site B is orientated perpendicularly to the plane containing the z (A) axes, the observed spectra can be accounted for in that the B signal varies over the larger range of $g_\perp$ to $g_\parallel$. In particular, the maximum value is shown for site B when sites A exhibit the minimum value (and *vice versa*), as observed. The attraction of this scheme is that it is based on the "trapping-out" of sites orientated in three mutually perpendicular directions, as typified by the $Cu(en)_3SO_4$ case; the difference here is that $2\theta < 90^\circ$ in accordance with the lower crystal symmetry at this temperature.[8]

Although Paoletti *et al.* give no g-value data, the apparent absence of exchange-coupling (witness the separate signals from the sites observed in the single-crystal data) suggests that the powder data of Elliott *et al.*[8] may correspond with the molecular g-values. We then have values at 77 K of $g_\parallel = 2.061$ and $g_\perp = 2.155$, which suggest again the presence of a predominantly d_{z^2} ground state. However, the trapped distortion cannot have an exact axial symmetry, otherwise $g_\parallel$ would equal 2.002. We suppose then that the symmetry is derived from a rhombic perturbation of a basically compressed tetragonal geometry. It then seems likely that the electronic reflectance spectrum[3] can be assigned with the broad weak band at 7.0 kK ascribed to the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition with the other three transitions superposed under the sharper peak at 16.5 kK.

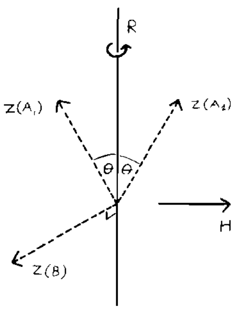

Fig. 2. A possible orientation, relative to the crystal rotation axis, of the principal axes of the three sites present in the unit cell of $K_2Pb[Cu(NO_2)_6]$ at low temperatures.

References

1 I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chim. Acta, 11,* L17 (1974).
2 I. M. Procter, B. J. Hathaway, D. E. Billing, R. Dudley and P. Nicholls, *J. Chem. Soc (A),* 1192 (1969).
3 B. J. Hathaway and D. E. Billing, *Co-ordin. Chem. Rev., 5,* 143 (1970).
4 C. K. Jörgensen, *Acta Chem. Scand., 9,* 1362 (1955).
5 B. J. Hathaway, R. J. Dudley and P. Nicholls, *J. Chem. Soc. (A),* 1845 (1969).
6 P. Paoletti, C. H. L. Kennard and G. Martini, *Chem. Commun.,* 768 (1971).
7 D. E. Billing, Abstract C8, *Autumn Meeting of the Chemical Society,* Imperial College, London, 1970.
8 H. Elliott, B. J. Hathaway and R. C. Slade, *Inorg. Chem., 5,* 669 (1966).