A NEW INTERPRETATION OF THE ANOMALOUS MAGNETIC AND OPTICAL BEHAVIOUR OF COPPER ACETATE MONOHYDRATE*

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ABSTRACT. Recent attempts to interpret the magnetic and optical behaviour of copper acetate monohydrate on the basis of C_{4v} symmetry are considered to be incomplete as these fail to give satisfactory explanations of many phenomenon.

We have assumed C_{2v} symmetry for electronic states of each half of the complex as shown by e. p. r. observation to find out more accurate and complete expressions for the exchange interaction coefficient (J), spectroscopic splitting factors and magnetic susceptibilities. With the assumption of C_{2v} symmetry we find that the bonding between two halves of the complex is a mixture of α and δ-type instead of pure σ or δ-type as obtained with the assumption of C_{4v} symmetry.

Copper acetate monohydrate is the most extensively studied (Guha 1951, 1965, 1966; Figgs et al, 1965; Mookherji et al, 1959, 1963; Mathur, 1965; Abe et al, 1957; Bleaney et al; 1952; Yamada et al, 1957, 1958; Graddon, 1961; Tonnet et al, 1964) copper salt with subnormal magnetic moment. Apart from its antiferromagnetic behaviour it manifests a characteristic dimeric optical absorption band which is z-polarised (Yamada et al, 1957; 1958; Graddon, 1961; Tonnet et al, 1964). It may be noted, however, that (1) the g-values calculated from the magnetic susceptibility data do not agree with the e.s.r. data; (Mookerji et al, 1963) (2) under C_{4v} symmetry of the complex, as postulated by the previous workers (Figgs et al, 1965; Tonnet et al, 1964; Forster et al, 1964, Hansen et al, 1965; Ross et al, 1959a, b) a δ-bond can account for the observed values of g but not that of J (the singlet-triplet separation 300 cm^{-1}), whereas a σ bond can account for J but results in making $g_z = 2$ as against the observed values of 2.345-2.4² (Abe et al, 1957; Bleany et al, 1952), (3) there is a strong controversy regarding the assignment of the dimeric absorption band (Tonnet et al, 1964; Forster et al, 1964; Hansen et al, 1965) at 28000 cm^{-1}.

In this paper we shall make an attempt to remove these contradictions by assuming that the symmetry of each half of the complex is C_{2v} and the overall symmetry is D_{2h}.

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THEORY

a. *Singlet-triplet separation (J)*

In the following section we shall calculate the effect of direct exchange interaction between the directly linked Cu^{2+} orbitals, which are, in turn, modified by the admixture of water and carboxylate oxygen orbitals (s and p), and shall neglect the interaction through the carbon orbitals (which we call super-exchange). The Hamiltonian for the whole complex, of which each half consists of one Cu^{2+} central ion and five oxygen ligands, can be written as

$$H = H_a + H_b + H_c + H_d + H_e$$

$$= (H_{F1} + H_{F2}) + (H_{V1} + H_{V2}) + \left\{ \frac{Z_{eff}^2}{R} + \frac{1}{r_{12}} - Z_{eff}\left(\frac{1}{r_{B1}} + \frac{1}{r_{A2}} \right) \right\}$$

$$+ (H_{LS1} + H_{LS2}) + \beta \overrightarrow{H}\{(\bar{L}_1 + 2\bar{S}_1) + (\bar{L}_2 + 2\bar{S}_2)\} \qquad \ldots \quad (1)$$

where '1' and '2' refer to the first and the second ion in all the terms except the third where γ_{B1}, γ_{A2}, γ_{12}, Z_{eff} and R have their usual significances.

For each unit the ligand field interaction under the C_{2v} symmetry can be represented by Ross (1959b)

$$H_v = e[D'(x^4 + y^4 + z^4 - \tfrac{3}{5}r^4) - \sigma'(2z^2 - r^2) - \delta'(x^2 - y^2) + \gamma'(2z^4 - x^4 - y^4$$

$$- 6y^2z^2 - 6x^2z^2 + 12x^2y^2) + \epsilon'(x^4 - 6x^2z^2 + 6y^2z^2 - y^4)] \qquad \ldots \quad (2)$$

The eigenvalues and eigenfunctions corresponding to $H_v + H_F$ are then (Ghosh et al, 1967)

$$E_{a,b} = 6D \mp \sqrt{(6\sigma + 18\gamma) + 3(2\delta - \epsilon)^2}, \quad E_c = -4D + 6\sigma + 24\gamma$$

$$E_{d,e} = -4D - 3\sigma - 12\gamma \mp (3\delta + 2\epsilon);$$

$$|a> = \mu |\phi_{z^2}> + \nu |\phi_{x^2 - y^2}>, \quad |b> = \nu |\phi_{z^2}> - \mu |\phi_{x^2 - y^2}>$$

$$|c> = |\phi_{xy}>, \quad |d> = |\phi_{xz}>, \quad |e> = |\phi_{xy}>;$$

where

$$D = -\frac{6}{315} eD'\bar{r}^4, \quad \sigma = \frac{2}{21} e\sigma'\bar{r}^2, \quad \delta = \frac{2}{21} e\delta'\bar{r}^2, \quad \gamma = -\frac{2}{63} e\gamma'\bar{r}^4$$

$$\epsilon = \frac{8}{3} \sqrt{\pi} e\rho\epsilon'\bar{r}^4 \text{ (ρ is a numerical constant)}, \quad \mu^2 + \nu^2 = 1$$

$$\text{and } \frac{\nu}{\mu} = \frac{6(D + 3\gamma) - [36(\sigma + 3\gamma)^2 + 3(3\delta - \epsilon)^2]^{\frac{1}{2}}}{\sqrt{3}(3\delta - \epsilon)} \qquad (3)$$

ϕ's are the d-orbitals modified by the appropriate combinations of the ligand and p-orbitals.

The different valence bond configurations will be a_1a_2; a_1b_2, a_2b_1; a_1c_2, a_2c_1, a_1d_2, a_2d_1; a_1e_2; a_2e_1 and there will be ionic configurations a_1a_1, a_2a_2; a_1b_1, a_2b_2; a_1c_1, a_2c_2; a_1d_1, a_2d_2 and a_1e_1, a_2e_2. It can be shown then that J is given by Ross et al, (1959a)

$$J = -2(1-S_{aa}{}^4)^{-1}\{2S_{aa}(Z_3A_3 - Z_2A_2S_{aa}) + S_{aa}{}^2B_2 - B_4\}$$

where

$$S_{aa} = \int a_1(1)a_2(1)dv_1 = \mu^2 \int \phi_{z^2 1}(1)\phi_{z^2,2}(1)dv_1 + \nu^2 \int \phi_{x^2-y^2,1}(1)\phi_{x^2-y^2,2}(1)dv_1$$

$$+2\mu\nu \int \phi_{z^2 1}(1)\phi_{x^2-y^2,2}(1)dv_1 \qquad \ldots \quad (4)$$

and A_2, A_3, B_2 and B_4 are respectively one electron coulomb, one electron exchange, two electron coulomb and two electron exchange integrals respectively. Similar to S_{aa} they involve the mixing coefficients μ and ν.

If in addition we consider the ionic terms, their effect will be to depress the ground singlet. Now one electron integrals involve the mixing coefficients as μ^2, ν^2 and $2\mu\nu$ whereas in the two electron integrals they occur as μ^4, ν^4, $4\nu^3/\mu$, $4\nu\mu^3$ and $2\mu^2\nu^2$. Since in the present case $\mu <\!< 1$ and $\nu \approx 1$ the effect of mixing of ϕ_{z^2} and $\phi_{x^2-y^2}$ states is much more felt in the one electron integrals, and the two electron integrals remain almost unaffected if the integrals involving two different types of orbitals are neglected. The net effect of this will be to depress the singlet by an appreciable amount.

b. *Spectroscopic splitting factors and the gm ionic susceptibilities* :

Expressing the sum of the spin-orbit and the magnetic perturbations in the form of the Spin Hamiltonian it can be shown that

$$g_x = 2\left\{1 - \frac{2(\mu\sqrt{3}+\nu)^2 R_x' k_x' \zeta_d}{E_{ad} - E_{aa}}\right\}$$

$$g_y = 2\left\{1 - \frac{2(\mu\sqrt{3}-\nu)R_y' k_y' \zeta_d}{E_{ae} - E_{aa}}\right\}$$

$$g_z = 2\left\{1 - \frac{8\nu^2 R_z' k_z' \zeta_d}{E_{ae} - E_{aa}}\right\}$$

$$K_x = N\left[\frac{1}{D} g_x{}^2\beta^2 e^{-J'/kT}(1-e^{-D/kT}) - {}^3\alpha_x e^{J'-O'/kT}(2e^{-D/kT}+1)^{-1}\alpha_x\right]\bigg/D'$$

$$K_y = N\left[\frac{1}{D} g_y{}^2\beta^2 e^{-J'/kT}(1-e^{-D/kT}) - {}^3\alpha_y e^{-J'/kT}(2e^{-D/kT}+1)^{-1}\alpha_y\right]\bigg/D'$$

$$K_z = N\left[\frac{g_z{}^2\beta}{kT} e^{-(J'+D)/kT} - {}^3\alpha_z e^{-J'/kT}(2e^{-D/kT}+1)^{-1}\alpha_z\right]\bigg/D'$$

where

$$D' = 1 + e^{-J'/kT} + 2e^{-(J'+D)/kT}, \quad J' = J + D_x + D_y. \qquad \ldots \quad (5)$$

where R_i' and $k_i'(i = x, y, z)$ are the spin-orbit and orbital reduction factors α's the high frequency terms (the super-scripts '1' and '3' indicate whether they originate from the singlet or the triplet state, ζ_d is the $S-0$ coupling coefficient for the dimer, D_i's are the spin-Hamiltonian parameters and $D = D_z - \frac{1}{2}(D_x + D_y)$

RESULT AND DISCUSSIONS

With the theory outlined above it was found that by a suitable choice of the parameters $D, \sigma, \gamma, \delta, \epsilon, R_i$'s and k_i's the observed e.s.r., susceptibility and the optical absorption data could be correlated to a good extent with one another. This is shown in table 1.

Table 1

Ligand field coefficients and the observed and the calculated values of
g_i's, K_i's and the optical absorption

Salt : Copper acetate monohydrate

**[$\sigma = -1425$ cm^{-1}, $\gamma = -252$ cm^{-1}, $\delta = 583$ cm^{-1}, $\epsilon = -750$ cm^{-1},
   $D = 17$ cm^{-1},
   $R'z = 0.84$, $k'_z = 0.69$, $R'_x = 0.77$, $k'_x = 0.77$, $R'_y = .69$, $k'_y = 0.69$,
$E_b - E_a = 27000$ cm^{-1} (28000 cm^{-1}), $E_c - E_a = 11000$ cm^{-1} (11000 cm^{-1}),
$E_d - E_a = 14500$ cm^{-1} (14400 cm^{-1}), $E_e - E_a = 15000$ cm^{-1} (14400 cm^{-1});]
   $J' = 300$ cm^{-1} (300 cm^{-1})

Temp.	$g_{\|}$ (obs)	$g_{\|}$ (cal)	$=g_\perp$ $(g_x+g_y)/2$ (obs)	$g_\perp$ (cal)	$K_{\|}-\overset{+}{K_\perp}$ (obs)	$K_{\|}-K_\perp$ (cal)	$\bar{K}$ (obs)	$\overset{\pm}{\bar{K}}$ (cal)
300°K	2.344 (±.01)	2.345	2.073 (±.005)	2.065	279	284	863	845
240°K		2.345		2.065	275	283	840	851
200°K		2.355		2.075	265	270	801	807
140°K		2.370		2.080	204	209	538	550
90°K	2.42 (±.03)	2.445	2.08 (±.03)	2.085	129	124	207	207

**The values within the square bracket refer to 300°K only. The values within the parentheses refer to the observed values.

+The anisotropies and susceptibilities have been redetermined in this laboratory and are in good agreement with earlier values.

Now μ and ν calculated from the values of σ, δ, γ and ϵ by using eqn.(3) come out to be 0.124 and 0.984 respectively. Using these values and the table of integrals calculated by Ross and Yates (1959) we find $J = -138$ cm^{-1} for $Zeff_z^2 = 7.3$ and $Zeff_{x^2-y^2} = 7$. Thus the calculated value of J is still nearly 50% off from the observed one. However it may be noted that J has been calculated under certain limitations. These are : (1) the integrals used for the calculation correspond to pure d-orbitals, whereas the orbitals actually involved contain admixtures of the ligand s and p orbitals; (2) the integrals of the type (dz^2/dx^2-y^2) are not available and have been neglected; (3) the effect of super exchange which is transmitted through the carbon π—orbitals have not been considered. In C_{4v} symmetry they do not mix with the ground ionic states but they do so under C_{2v} symmetry.

It is here seen that the effect of orthorhombicity on J is quite considerable and the anomaly between g and J can be removed by considering it. In this connection it may be pointed out that the abnormally large J of copper thioacetate may be due to the large orthorhombicity introduced by replacing two oxygen ligands by sulphur. Of course the reduction of Z_{eff} due to larger electron donation capacity of sulpher atoms may be another factor.

In the present calculation the dimeric band has been assigned to either $3_{abg} \leftarrow 3_{aau}$ and $1_{abu} \leftarrow 1_{aag}$ transitions, the latter being stronger at low temperature. We make the following justifications for it :

(1) the band is weak;

(2) the ligand field parameters σ, δ, γ, ϵ are quite large compared to ordinary copper salts, as can be expected due to comparetively shorter ligand distances so that a large separation between the components of the orbital doublet appear to be quite reasonable and

(3) under C_{2v} symmetry both the ground state $|a\rangle$ and the excited state $|b\rangle$ span A_1 representation so that an electric dipole type transition between them should be z-polarised as has been actually observed.

Thus it is reasonable to assume that the dimeric band originates from a Laporte forbidden type transition.

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