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Binuclear Complexes

I. The Electronic Structure of Copper Acetate

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The electronic structure of the dimeric copper acetate $Cu_2(Ac)_4 \cdot 2H_2O$ is considered using a molecular orbital scheme. It is proposed that a rather strong σ-bond exists between the two copper-units, in contrast to a former proposal of a δ-bond [4]. The form of the molecular orbital scheme is such that all of the experimental features (antiferromagnetism, absorption spectrum and g-factors) are qualitatively explained. It is suggested that the intensity of the dichroic absorption bands is either of vibronic origin or due to a static dissymmetry.

Copper acetate monohydrate is the prototype of a significant class of complexes, the cupric alkanoates. The basic unit in this complex is a dimer held together principally by acetate bridges [1]. The complex is distinguished from the usual monomeric Cu(II) complexes by the appearance of antiferromagnetism [2-5] and of a new ultraviolet band in the absorption spectrum [6]. The antiferromagnetism has been ascribed to the Cu—Cu interaction and the existence of a δ-bond suggested [4,5]. A theoretical treatment along valence bond lines appeared to be consistent with this conclusion [7]. We will in this note reconsider the problem of the electronic structure of copper acetate as seen from a molecular orbital (L.C.A.O.) viewpoint.

ORBITAL SCHEME

If each copper ion were situated in a regular octahedral environment, the highest occupied molecular orbitals would fall into two groups; the antibonding (or non-bonding) t_{2g}-orbitals characterized by their transformation properties (xy), (yz) and (xz) and the antibonding e_g-orbitals designated (x^2-y^2) and (z^2). For a regular octahedral Cu(II) complex with oxygen ions as ligands

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we would expect the separation, $10Dq$, between the e_g and t_{2g} orbitals to be some 10 000 cm^{-1}.

Consider now the actual complex $Cu_2(Ac)_4 \cdot 2H_2O$ where Ac stands for CH_3COO^-. The structure has been given by van Niekerk and Schoening [1]; the four acetate groups make a fourfold bridge holding the complex together (Fig. 1). Furthermore, due to the short Cu—Cu distance (2.64 Å) a direct bond should occur between the two copper atoms. The oxygen atoms in the bridging groups are separated by 2.20 Å.

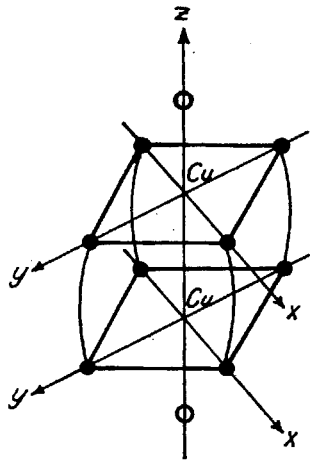

Fig. 1. Molecular structure of $Cu(Ac)_4 \cdot 2H_2O$.

If we now consider the molecule as made up of two units, each containing *one* Cu^{2+} ion we notice that each of these entities has the symmetry C_{4v}. When put together the symmetry of the molecule is D_{4h}. The molecular orbital scheme for the highest occupied levels in the "monomeric complex" $CuO_4 \cdot H_2O$ (pointgroup C_{4v}) would be expected to resemble that of $CuSO_4 \cdot 5H_2O$, that is after Holmes and McClure [8] $E[(xz),(yz)] = 0$, $E(xy) \approx 10\,000$ cm^{-1}, $E(z^2) \approx 13\,000$ cm^{-1} and $E(x^2-y^2) \approx 14\,000$ cm^{-1} (Fig. 2, left and right). Bringing two units of $CuO_4 \cdot H_2O$ together, we would then obtain a molecular orbital scheme as pictured in the middle of Fig. 2.

The reason for the considerable splitting of the two (z^2) molecular orbitals as compared to the other splittings is to be found in the values of the Cu—Cu overlaps. Assuming for a moment that we can consider the molecule as Cu_2^{2+}

Table 1. Overlap integrals for Cu_2^{2+}.

$S(d_{z^2},d_{z^2})$	$S(d_{xy},d_{xy})$ $= S(d_{x^2-y^2},d_{x^2-y^2})$	$S(d_{xz},d_{xz})$ $= S(d_{yz},d_{yz})$
0.019	0.002	0.012

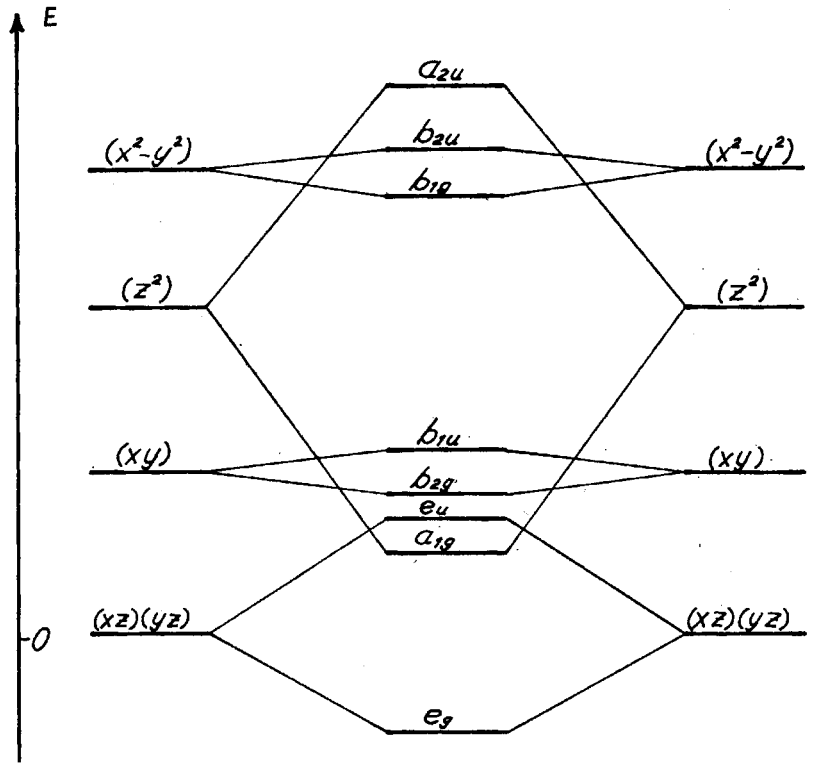

Fig. 2. Highest molecular orbitals for $Cu(Ac)_4 \cdot 2H_2O$. Not drawn to scale. Point group symmetry D_{4h}.

we can calculate the overlap integrals using the analytic SCF $3d^{10}$ (Cu^{+1}) functions given by Watson [9]. These are given in Table 1.

We have assumed some charge neutralization due to the ligand electrons. Whether the effective charge on the copper atom is + 1 or zero is immaterial if the configuration involves $3d^{10}$. Watson [9] has shown that electrons in $3d$ orbitals are not appreciably affected by $4s$ electrons, *i.e.* the $3d$ orbital calculated from $3d^{10}(Cu^{+1})$ is nearly the same as that calculated from $3d^{10}4s(Cu^{\circ})$. Although the SCF orbitals are considerably more contracted than the customary Slater orbitals, in the region of the "tail" the overlap integrals were found to be roughly the same for both sets of orbitals.

The splitting Δ between a given bonding orbital and its antibonding counterpart can be simply expressed as

$$\Delta = \frac{2H_{11}S - 2H_{12}}{1 - S^2} \approx kS$$

where H_{11} and H_{12} has their usual meaning and k is a constant. Hence the greater the overlap S, the greater the magnitude of Δ.

Any direct computation of Δ is however nearly impossible to perform since the orbitals one should use in the calculation of H_{11}, H_{12} and S are molecular orbitals of the form

$$\sigma_1 = ad_{Cu^{2+}} + b\Sigma\sigma_{ligand}$$

where the constants a and b have been determined by a variational calculation for the monomeric molecular unit $CuO_4 \cdot H_2O$. Nevertheless, if we *assume* that no π-bonding takes place, and that $a \approx 1$ (corresponding to *antibonding* e orbitals that are nearly pure metal orbitals) a bonding scheme for the "united" dimer emerges as pictured in Fig. 2.

There are three sets of data that must be rationalized by any model: antiferromagnetism, spectra and g-factors. These will now be considered in that order.

ANTIFERROMAGNETISM

The wavefunction for the ground state of the complex can be written as a determinental wavefunction containing 18 electrons; nine from each Cu^{2+} ion:

$\psi(^1A_{1g}) = |(e_g)^4(a_{1g})^2(e_u)^4(b_{2g})^2(b_{1u})^2(b_{1g})^2(b_{2u})^2|$. The first excited triplet state is then (See Fig. 2) $\psi(^3B_{1g}) = |(e_g)^4(a_{1g})^2(e_u)^4(b_{2g})^2(b_{1u})^2(b_{1g})^2(b_{2u})^1(a_{2u})^1|$ No other deep lying singlet or triplet state is expected to occur.

As first shown by Bleaney and Bowers [2] the magnetic behaviour can be explained in terms of a triplet state lying some 300 cm^{-1} above the ground singlet state. Formally it is of course easy to write down the energies of the above two states in terms of the orbital energies plus the relevant Coulomb (J) and Exchange (K) integrals. Since, however, these latter cannot be calculated with any accuracy, we can only note that the difference in the repulsion energies between the two states must be fairly small.

ABSORPTION SPECTRUM

The crystal absorption spectrum of $Cu(Ac)_4 \cdot 2H_2O$ has been measured by Yamada *et al.*[6] using polarized light. The measurements were presumably performed at room temperature. With a triplet state lying some 300 cm^{-1} above the singlet ground state, we might expect that some of the reported bands were due to transitions from this state to other triplets. Assuming a Boltzmann distribution about 40 % of the molecules should be in the triplet state at room temperature; at $\sim$ 77°K, however, this number has fallen to virtually zero. Consequently one would expect the band intensity of any transition starting from the triplet state to vanish completely by cooling to 77°K. However, measurements indicate that only small intensity changes occur for the "major" bands located at 14 300 cm^{-1} and 27 000 cm^{-1}. We have thus assigned these as singlet-singlet transitions.

In the crystal spectra of cupric acetate monohydrate and several cupric alkanoates, three bands are clearly resolved [6]. The band at 14 300 cm^{-1} has an extinction coefficient in solution of about 200 based upon monomer concentration and therefore the molecular extinction coefficient for the dimer

is about 400. The absorption is more intense in x,y than is z polarization; Yamada *et al.*[6] state that the former is 10 times more intense than the latter. The electric dipole vectors transform like $A_{2u}(\parallel)$ and E_u ($\perp$) with respect to the four-fold axis. The polarization of the band at 14 000 cm^{-1} does therefore correspond to that of an allowed transition $^1A_{1g} \rightarrow {}^1E_u$.

The second band at 27 000 cm^{-1} is somewhat less intense with a molar extinction coefficient of about 100 and ten times stronger in z than in x,y polarization. This band could be assigned to an allowed $^1A_{1g} \rightarrow {}^1A_{2u}$ transition. However, such an assignment as well as the previous one we shall show below to be untenable.

A third band appears at 33 700 cm^{-1} in x,y and at 35 000 cm^{-1} in z polarization. It is difficult to estimate the intensity of this band, since it appears as a shoulder on a more intense band. The origin of this band is unknown.

One electron promotion to the empty a_{2u} orbital from the filled orbitals b_{1g}, b_{2u}, b_{2g}, b_{1u}, e_u, e_g and a_{1g} corresponds to the transitions from the ground state $^1A_{1g}$ to $^1B_{2u}$, $^1B_{1g}$, $^1B_{1u}$, $^1B_{2g}$, ^1E_g, ^1E_u, and $^1A_{2u}$, respectively. It is seen from the level scheme (Fig. 2) that the "parallel" band at 27 000 cm^{-1} in our tentative assignment corresponds to what Mulliken[10] calls a $N \rightarrow V$ transition, that is a transition from a bonding to the corresponding antibonding orbital. With a wavefunction for the excited $^1A_{2u}$ state equal to

$$\psi(^1A_{2u}) = \frac{1}{\sqrt{2}}\Big\{ |\, (e_g)^4(a_{1g}^+)\,(e_u)^4(b_{2g})^2(b_{1u})^2(b_{1g})^2(b_{2u})^2(a_{2u}^-) \,| - |\, (e_g)^4(a_{1g}^-)\,(e_u)^4(b_{2g})^2 (b_{1u})^2(b_{1g})^2(b_{2u})^2(a_{2u}^+) \,| \Big\}$$

we get for the transition moment $P = \int \psi(^1A_{2g})\, \vec{r}\, \psi(^1A_{2u}) \mathrm{d}\tau$

$$P = \sqrt{2} \int a_{1g}\, \vec{r}\, a_{2u}\, d\tau$$

Neglecting all overlaps we have

$$a_{1g} = \frac{1}{\sqrt{2}}\Big[(z^2)\,(1) + (z^2)\,(2)\Big]$$

$$a_{2u} = \frac{1}{\sqrt{2}}\Big[(z^2)\,(1) - (z^2)\,(2)\Big]$$

with

$$(z^2) = \alpha d_{z^2} + \sqrt{1-\alpha^2} \sum_1^5 \sigma_{\mathrm{lig}}$$

These wavefunctions lead to the approximate expression

$$P \approx \frac{1}{\sqrt{2}}\Big[\alpha^2 R_1 + (1-\alpha^2) R_2\Big]$$

where R_1 is the distance Cu—Cu and R_2 the distance O—O in a bridge. With $R_1 = 2.6$ Å and $R_2 = 2.2$ Å this expression yields an oscillator strength, f, for the band $f \approx 0.8$. With the molar extinction coefficient $\varepsilon \approx 100$ and $\nu_{1/2} \approx 8 \times 10^3$ cm^{-1} the experimental value of f is about 0.5×10^{-4}.

g-FACTORS

The low-lying triplet state $^3B_{1g}$ is appreciably populated at room temperature and the g-factors have been determined [2], $g_{||} = 2.42 \pm 0.03$, $g_{\perp} = 2.08 \pm 0.03$ ($g_z = 2.34$, $g_x = 2.05$, $g_y = 2.09$) [11]. The configuration of the $^3B_{1g}$ is $(a_{1g})^2(e_u)^4(e_g)^4(b_{2g})^2(b_{1u})^2(b_{2u})\,(a_{2u})$. This state can interact via spin-orbit coupling with $^3E_g(1)$: $(a_{1g})^2(e_u)^3(e_g)^4(b_{2g})^2(b_{1u})^2(b_{2u})^2(a_{2u})$, $^3E_g(2)$: $(a_{1g})^2(e_u)^3(e_g)^4(b_{2g})^2(b_{1u})^2(b_{2u})\,(a_{2u})^2$ and $^3B_{2g}$: $(a_{1g})^2(e_u)^4(e_g)^4(b_{2g})^2(b_{1u})\,(b_{1g})^2(b_{2u})^2(a_{2u})$.

If the L.C.A.O. wave functions for these states are used the expressions for the g-factors are with neglect of overlap effects

$$g_{||} = 2\left(1 - \frac{4\lambda}{E(^3B_{2g}) - E(^3B_{1g})}\right)$$

$$g_{\perp} = 2\left(1 - \frac{\lambda}{E(^3E_g(1)) - E(^3B_{1g})} - \frac{3\lambda}{E(^3E_g(2)) - E(^3B_{1g})}\right)$$

The free Cu^{2+} ion value of $\lambda = -830$ cm^{-1} is too large to use. It is more appropriate to take the spin-orbit coupling parameter for Cu^{+1}, of some -750 cm^{-1}. Using this value we find $E(^3B_{2g}) - E(^3B_{1g}) \approx 14\,000$ cm^{-1}. Due to delocalization effects and state repulsions we would expect the energy of $^3E_g(2)$ to be much higher than the energy of $^3E_g(1)$ and hence we estimate *approximately* $E(^3E_g)\,(1) - E(^3B_{1g}) \approx 17\,000$—$30\,000$ cm^{-1}. In view of the uncertainty of the formula and the values of $g_{||}$ and $g_{\perp}$ these numbers are only reliable to within several thousand cm^{-1}.

We would expect, since the singlet-triplet splitting for these configurations must be small that

$$E(^3B_{2g}) - E(^3B_{1g}) \approx E(^1B_{2g}) - E(^1A_{1g}).$$

Hence we would expect the orbitally forbidden transition $^1A_{1g} \rightarrow {}^1B_{2g}$ to occur at some 14 000 cm^{-1}, and similarly that $^1A_{1g} \rightarrow {}^1E_g(1)$ would occur at some 17 000 to 30 000 cm^{-1}.

DISCUSSION

It should again be stressed, that our proposed molecular orbital scheme is tentative. We can only observe that our model is reasonably consistent with the experimental data. Of course, alternative schemes may also be consistent with the rather limited data. The most conspicious feature in our level scheme is the large splitting of (z^2) in the dimer. This seems certainly reasonable, but this proposal differs from the model considered by Martin *et al.*[4,5] and Ross [7].

The spectral assignments are uncertain. Due to the observed polarizations we have above tentatively assigned these to orbitally allowed transitions. The fact that the orbitally *forbidden* $^1A_{1g} \rightarrow {}^1B_{2g}$ transition arrived at from the g-factor apparently corresponds to the "perpendicular" band in the measured spectrum is, however, suggestive. The experimental values of the band intensities are also much too small for supposedly allowed transitions as demonstrated by the calculated f-value for an allowed $N \rightarrow V$ transition.

If we abandon the idea that the levels are of pure parity, and consider other intensity giving mechanisms, a static dissymmetry or a vibronic mechanism should suffice [12]. Indeed, for use in a vibronic mechanism all possible even and odd vibrational normal modes (with the exception of α_{2g}) are present. Consider for instance the "perpendicular" band at 14 000 cm^{-1}. We now assign this band to the transition $^1A_{1g} \rightarrow {}^1B_{2g}$, but in order to get the observed polarization of the transition the wavefunction for the excited state must be of the type $^1B_{2g} + \lambda^1E_u$. Such a scrambling can be performed via a vibration of ε_u symmetry.

All in all we are inclined to believe that the observed absorption bands are of the latter kind, *i.e.* that the low excited states are predominantly "even", contaminated with "odd" states via a dissymmetry or vibrational scrambling. This proposal also explains that the band at 14 000 cm^{-1} clearly corresponds to the usual copper band [13]. It is thus due to a transition within half of the complex. On the other hand the second band at 27 000 cm^{-1} must involve the whole complex.

Furthermore the triplets and singlets of nearly all configurations are expected to fall approximately on top of each other. Such a feature would explain the absence of temperature effects in the measured spectra.

X-Ray studies have shown that when crystals of Cr(II), Cu(II), Ni(II), and Co(II) acetates are grown from aqueous solution only the chromium and copper acetates dimerize. The heat of hydration of the Ni complex is about the same as that of the Cu complex while the hydration energy of the Co complex is definitely smaller. The explanation for the stability of the dimers could be found in the strength of the metal-metal bond. It is reasonable to assume that the strength of this bond is roughly proportional to the overlap between the metal orbitals. However, calculation of the overlap from Slater or S.C.F. orbitals does not reveal any striking anomaly in the chromium and copper cases. A possible explanation may however be advanced if we examine the electronic configurations of the single species.

An octahedral or pseudo-octahedral configuration of Cr(II) and Cu(II) both possess an E_g ground state. Such a state is subjected to a rather violent Jahn-Teller distortion [14], and it then seems possible that dimerization is the energetically favorable way of lowering the symmetry. It is however well known, that stability criteria and molecular configurations are nearly impossible to infer from *a priori* considerations.

The main result of this note is thus that it is not necessary to postulate a δ-bond between the two copper atoms to account for the electronic features, but that a σ-bond will suffice. Thus, even though the calculations of Ross [7] indicates that a δ-bond would lead to a value for the interaction of the two molecular species of the right order of magnitude we feel that his result does not necessary prove this mechanism, due to his use of approximate wavefunctions. A direct σ interaction seems to us to be more plausible in view of the overlap criteria.

In addition to the direct interaction it is of course also possible to have a "super-exchange" interaction, working through the oxygen bridges. Such a mechanism seems, however, to the present authors to be less likely than the one considered here.

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