The Insignificance of Metal–Metal Bonding in the Antiferromagnetism of Copper(II) Carboxylate Dimers

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Summary Magnetic and structural studies on a pair of analogous copper(II) acetate and formate dimers suggest that metal-metal bonding is not important in explaining their antiferromagnetism.

THE antiferromagnetism of copper(II) acetate monohydrate has stimulated much experimental and theoretical work on this, and related compounds, in recent years. Bleaney and Bowers showed[1] that the antiferromagnetism could be explained by spin coupling of the form $-JS_1S_2$. However the coupling *mechanism* has been the subject of controversy, and various theoretical treatments have been advanced. Figgis and Martin suggested[2] a direct metal–metal, δ, bond between the two copper atoms, which are only 2·64 Å apart,[3] but emphasized[2] that this would be weak (in line with subsequent orbital-overlap calculations[4]). Hansen and Ballhausen[5] accounted for the observed g-values and electronic spectrum with a coupled chromophore model, without invoking any direct metal–metal bonding. Comparison with the very short Mo–Mo separation (2·11 Å) in $Mo(OAc)_2$[6] has been used[7] as a basis for ruling out significant metal–metal bonding in the copper analogue, and the idea that the spin coupling proceeds predominantly by super exchange *via* the carboxylate bridges has become increasingly favoured.[8]

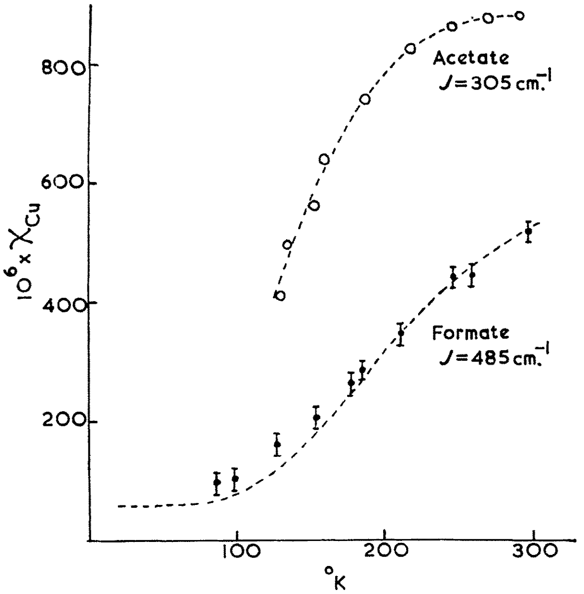

FIGURE 1. *Temperature dependence of the magnetic susceptibilities of* $(Me_4N)_2[Cu(RCO_2)_2(NCS)]_2$, (R = H *or* Me). *Dotted lines represent the calculated curves.*

Direct experimental evidence to correlate the extent of spin exchange with copper–copper distance in strictly analogous compounds has been lacking hitherto. We have isolated the crystalline compounds $(Me_4N)_2[Cu(RCO_2)_2(NCS)]_2$ where R = H or Me. The temperature variations of their magnetic susceptibilities are summarized in Figure 1. Using the Bleaney and Bowers formula,[1] the J values, calculated from the experimental susceptibilities, the g-values determined from e.s.r. spectra, and with N_α = 60 × 10^{-6} c.g.s.u. are: acetate 305 cm.$^{-1}$, formate 485 cm.$^{-1}$. The greater spin exchange observed for the formate correlates well with the results for other dimeric copper(II) formate complexes.[9]

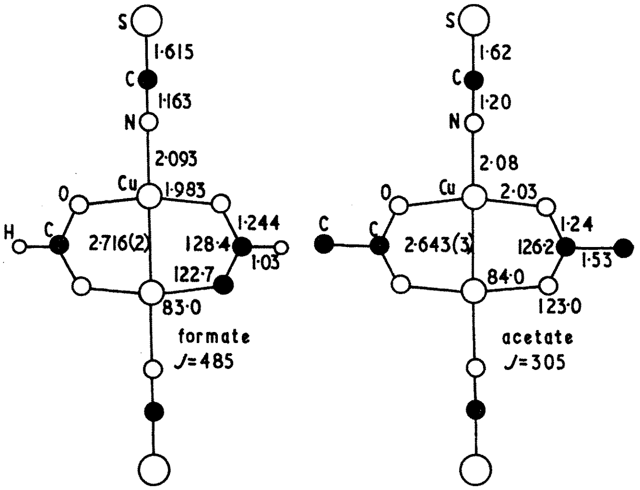

FIGURE 2. *Standard deviations for the formate are*: Cu–Cu, 0·002; Cu–O, 0·004; C–O, 0·008; Cu–N, 0·009; C–N, 0·014; C–S, 0·011 Å; Cu–Cu–O, 0·1; Cu–O–C, 0·3; O–C–O, 0·5°, *and for the acetate*: Cu–Cu, 0·003; Cu–O, 0·01; C–O, 0·02; C–C, 0·04; Cu–N, 0·02; C–N, 0·03; C–S, 0·02 Å; Cu–Cu–O, 0·3; Cu–O–C, 1·3; O–C–O, 1·3°.

The compounds formed green tetragonal crystals with the following unit-cell dimensions: $[Me_4N]_2[Cu(HCO_2)_2(NCS)]_2$, a = 8·917, c = 15·800 Å, U = 1256·3 Å^3, Z = 2; $(Me_4N)_2[Cu(MeCO_2)_2(NCS)]_2$, a = 8·873, c = 18·087 Å, U = 1424·0 Å^3, Z = 2. The space group for both is $I4/mmm$.

Three-dimensional X-ray data were collected on a Siemens four-circle automatic diffractometer using Cu-K_α radiation. The structures were solved by standard methods and least-squares refinement of the formate has reached R = 0·049 for 381 reflections. For the acetate the refinement has been complicated by disorder among the acetate groups, and R is currently 0·099 for 421 reflections.

Figure 2 shows the main distances and angles of the two dimeric anions (in each case two of the bridging groups have been omitted for clarity). In both cases the copper atoms and the thiocyanate ligands lie on fourfold axes. In the acetate the Cu ··· Cu separation of 2·643 Å (σ = 0·003 Å) is typical of dimeric cupric acetate complexes.[3,10] In the formate the Cu ··· Cu separation is 2·716 Å (σ = 0·002 Å). Despite this, however, the path length *via* the bridging ligands is shorter in the formate, with a concomitant readjustment of the relevant angles. There are no significant differences between the thiocyanate ligands in the two anions.

The formate-bridged complex therefore has a higher J value, more spin exchange, and yet the Cu · · · Cu separation is very significantly greater.

The above results suggest that any contribution to the spin exchange from a direct metal–metal bond is insignificant, as such an interaction would be expected to *decrease* rapidly with increasing copper–copper separation. It therefore seems probable that the carboxylate bridges play a major role in the spin-exchange process. This might be by a superexchange mechanism, as mentioned above, but, unfortunately, it is difficult to predict the magnitude or the effects of the structural differences on this process.

On the other hand it may be noted that all the models invoking a direct copper–copper bond (which are reviewed briefly in ref. 11), depend among other things on an energy difference between a pair of molecular orbitals of symmetry b_{1g} and b_{2u}, but this difference is not, as hitherto assumed, necessarily dependent on the existence of direct metal–metal bonding. These are antibonding orbitals involving $d_{x^2-y^2}$ orbitals and suitable molecular orbitals of the carboxylate ligands. The ligand orbitals involved in the b_{1g} and b_{2u} molecular orbitals of a copper(II) carboxylate are not the same; they belong to the irreducible representations A_1 and B_1, respectively of C_{2v}, the point group of a carboxylate ion (neglecting the alkyl group). There is, therefore, no reason to believe that the copper–oxygen or oxygen–carbon bonding energies of b_{1g} and b_{2u} are identical. We may expect that there will therefore be an energy difference between these states, even in the absence of a direct copper–copper interaction. Furthermore the splitting might conceivably increase with the copper–copper separation.

Such molecular orbital models have been criticized as being too simple.[2,5] Interelectronic repulsion must be taken into account, in which case wave functions related to those of the "coupled chromophore" model are obtained There will then be a singlet–triplet splitting due to electrostatic configuration interaction, and the effects of covalency will appear as a perturbation on the coupled chromophore states making an addition to the singlet–triplet splitting. Incidentally, this model is incompatible with a "six-level" theory for magnetic susceptibility such as was suggested by Jotham and Kettle.[11] The temperature dependencies of the susceptibilities predicted by their theory are insufficiently different from those predicted by the "four-level" theory for it to be possible to discriminate decisively between the theories on experimental grounds.

Whatever the relative importance of the contributions arising from the coupled chromophore model, or from the superexchange process, we conclude from our experimental evidence that direct metal–metal bonding plays only an insignificant role in determining the magnetic properties of these compounds.

We thank Professor D. Rogers for his interest in this work.

(*Received, March* 31*st*, 1969; *Com.* 448.)

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