# Crystal Structure, Magnetic Susceptibility, and Electron Spin Resonance Studies of a Stereospecific Copper Tartrate Dimer

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*Summary* The crystal structure of $Na_2Cu[(\pm)$-tartrate],$5H_2O$ reveals centrosymmetric $Cu^{2+}$ tartrate dimers with a Cu–Cu distance of 2·9865(9) Å; magnetic susceptibility studies, which reveal a triplet state 18 $cm^{-1}$ above the singlet, and e.s.r. spectra are reported and discussed in terms of that structure.

RECENTLY, Chasteen and Belford[1] reported preparation of the tartrate complex salt $Na_2Cu[(\pm)$-$C_4O_6H_2]$,$5H_2O$ and suggested that the structure exists as dimers with two $Cu^{2+}$ ions, bridged by one (+)- and one (−)-tartrate (4−) anion.[2] The presence of half-field, and the structure of the full-field, e.s.r. features of frozen solutions indicated dimeric triplet states and were interpreted in terms of a large dipolar coupling between electrons. The similarity in the optical spectra of the solutions and solid mulls[1] indicated that the crystal dissolves with retention of important structural features. Here we describe an *X*-ray study of the complex, a magnetic susceptibility study which verifies that assumptions previously made are valid for the solid salt, and auxiliary e.s.r. studies of aqueous solutions which help to clarify the chemistry and the assignments of e.s.r. features.

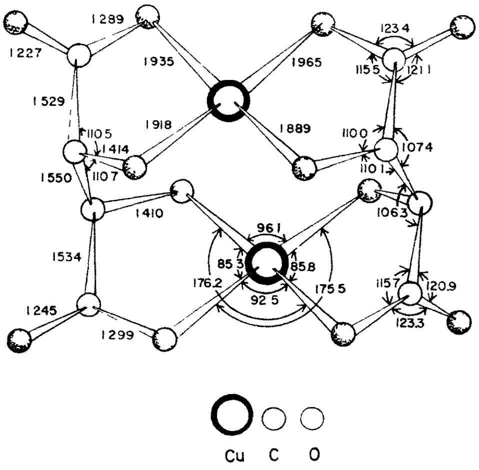

FIGURE 1. *Drawing of the structure of the dimer of* $Cu[(\pm)$-$C_4O_6H_2]^{2-}$ *as found in the crystal. E.s.d. of the* C–C, C–O *and* Cu–O *distances are* 0·006, 0·005, and 0·003 Å, *and the e.s.d. of the angles range from* 0·2—0·4°.

*Crystal data*: Blue needles, $Na_2Cu[(\pm)$-$C_4O_6H_2]$,$5H_2O$, $M = 345{\cdot}59$, monoclinic, $a = 9{\cdot}290(4)$, $b = 10{\cdot}894(5)$, $c = 11{\cdot}556(5)$ Å, $\beta = 94{\cdot}85(6)°$, $U = 1164{\cdot}1 \times 10^{-24}$ $cm^3$, $D_m = 1{\cdot}95$, $Z = 4$, $D_c = 1{\cdot}97$; space group, $P2_1/n$. A total of 1776 independent, non-zero intensities was collected on a Picker FACS-1 computer-controlled diffractometer using Cu-$K_\alpha$ radiation. The structure was solved by the heavy-atom method, and has been refined by full-matrix least-squares methods to a conventional *R*-factor of 0·043 on all observed data.

The structure of the centrosymmetric dimer of $Cu[(\pm)$-$C_4O_6H_2]$ (Figure 1) corresponds to that suggested[1] except that in the crystal reported here the $Cu^{2+}$ ion is involved in square-planar co-ordination to tartrate oxygen atoms with no fifth co-ordination to a water molecule. Each co-ordinated oxygen atom is displaced by only 0·009(3) Å from the best plane through the four co-ordinated oxygen atoms, and the Cu atom is displaced (*toward* two oxygen atoms in the other half of the dimer) by only 0·0617(6) Å.

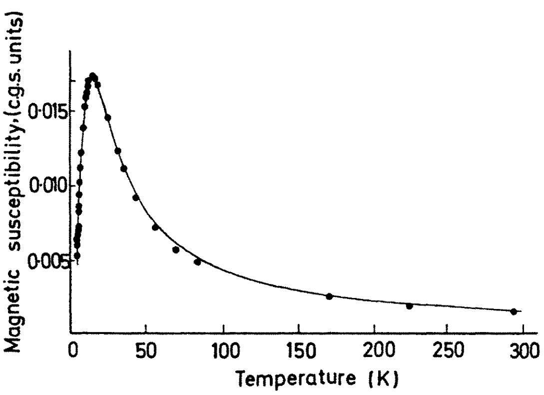

FIGURE 2. *Magnetic susceptibility data for* $Na_2Cu[(\pm)$-$C_4O_6H_2]$,-$5H_2O$. *The solid line represents the best fit of the data (solid circles) to the equation*

$$\chi_m = g^2N\beta^2/k(T - \theta)\{3 + \exp(-2J/kT)\};$$

$$g = 2{\cdot}138,\ \theta = 3{\cdot}35\text{K},\ 2J = -18{\cdot}0\ \text{cm}^{-1}.$$

We find no other published reports of four-co-ordinate $Cu^{II}$ hydroxy-acid structures; however, the Cu–O lengths in the present structure agree with the shorter lengths in several of the reported five- and six-co-ordinate $Cu^{II}$ hydroxy-acid structures.[3] While the Cu ⋯ Cu distance [2·9865(9) Å] is shorter than the 3·3 Å deduced from the dipolar electron–electron interaction in frozen aqueous solution and much shorter than the V ⋯ V distance of 4·082(2) Å in the corresponding vanadyl (±)-tartrate,[4] it is much longer than the values of 2·61—2·65 Å found in the dimeric copper acetate-type structures,[5] and it appears unwarranted to describe either it or the intracomplex

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Cu · · · O linkages [2·927(3) and 3·050(3) Å] as out-of-plane co-ordination bonds. However, these weak linkages with their unusual geometry may significantly affect the intradimer exchange energy and thus the magnetic properties. The Cu–Cu vector is 31° from the normal to the co-ordination plane and is 27° from the *b*-axis. The resulting non-coincidence of the principal axes of the *g* and *D* tensors makes interpretation of the frozen-solution e.s.r. spectra uncertain; the 31° angle could be only moderately altered in aqueous solution, where axial co-ordination may occur.

Figure 2 shows the magnetic susceptibility of powdered $Na_2Cu[(\pm)\text{-}C_4O_6H_2],5H_2O$ as a function of temperature, 4—300K, together with a least-squares fit to the usual equation for a thermal equilibrium between a non-magnetic singlet and a magnetic triplet characterized by $\langle g \rangle = 2{\cdot}138$.[1] The best fit indicates that the triplet lies 18·0 cm$^{-1}$ above the singlet; the simple fact that the susceptibility has a maximum about 14K indicates a similar value. Clearly, an 18 cm$^{-1}$ exchange splitting is not large enough to suggest that the anisotropy in the exchange energy competes with the dipolar coupling. However, it is large enough to allow singlet–triplet mixing to be ignored in interpretation of e.s.r. spectra. The sign of the exchange interaction is of particular interest; although there are strong similarities in the geometry of this system and that of the copper–pyridine *N*-oxide dimer,[6,7] which has a Cu-Cu distance of 3·46 Å and an angle between the Cu-Cu line and the normal to the co-ordination plane of *ca.* 41°,[7] the signs of the exchange coupling constants (*J*) for the two compounds are opposite.[6]

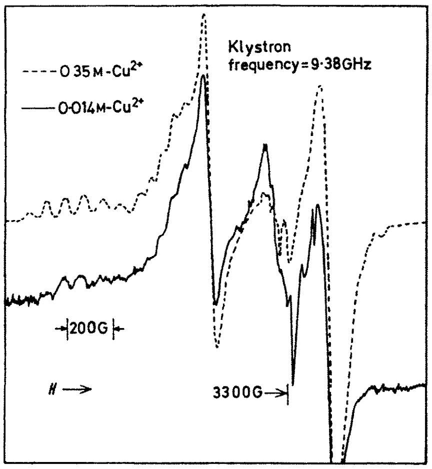

FIGURE 3. *Concentration dependence of the "full field"* $\Delta M_S = \pm 1$, *first-derivative e.s.r. spectrum of* $Na_2Cu[(\pm)\text{-}C_4O_6H_2],5H_2O$, pH 11·4 *in* 1 : 1 *ethylene glycol–water frozen glass at* 77K.

Previously reported e.s.r. spectra confirmed the existence of binuclear racemic copper tartrate species in aqueous solution, but certain spectral features remained anomalous. A new series of e.s.r. studies, for which representative results are given in Figures 3 and 4, show that small but significant amounts of other species also exist in solution. Firstly, an equilibrium between species is indicated by the disappearance of the three small peaks on the broad band of the room-temperature spectrum upon reducing the concentration from 0·70 M to 0·035 M (Figure 4, pH = 11·4). Furthermore, as the pH is reduced, the three small peaks grow into a set of dominant features (Figure 4) which appear identical to the spectrum of copper (+)-tartrate at high pH (*cf.* Figure 5 of ref. 1). Secondly, addition of NaOH produces a spectrum characteristic of copper hydroxide species. Thirdly, concentration dependence of the frozen-solution e.s.r. spectra (Figure 3) shows that the lines in the vicinity of 3300 G are due to monomers (or some related species) as previously suggested.[1] By comparing the dimer and "monomer" line intensities and assuming a simple monomer–dimer equilibrium, we estimate a p*K* for dimer formation in frozen solutions of about 3·0 (probably an underestimate). A p*K* value of 3·0 has been reported[8] for dimerization of racemic copper tartrate in acid solutions. The evidence strongly suggests that the room-temperature e.s.r. spectrum of $Na_2Cu[(\pm)\text{-}C_4O_6H_2],5H_2O$ in aqueous solution at pH *ca.* 11 is largely due to a dimer structurally similar to that in the solid salt, with lesser features attributable to copper tartrate monomers, copper hydroxide species, and the species of basic solutions of the copper (+)-tartrate salt.

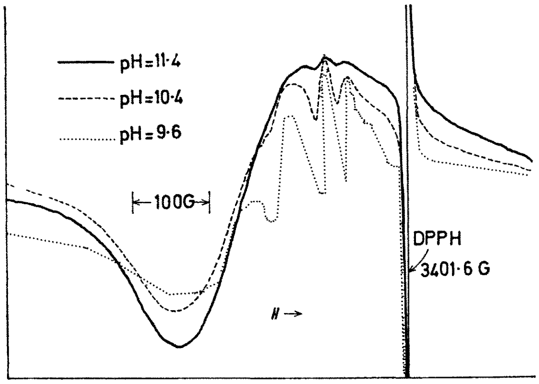

FIGURE 4. pH-*Dependence of the first-derivative e.s.r. spectrum of* 0·70 M-$Na_2Cu[(\pm)\text{-}C_4O_6H_2],5H_2O$ *aqueous solution at room temperature. A precipitate formed in the* pH = 9·6 *solution and was filtered off before the spectrum was obtained.*

We thank the National Science Foundation, National Institutes of Health, Advanced Research Projects Agency, and Materials Research Center at the University of North Carolina for supporting research grants and Professor M. W. Hanha at the University of Colorado, Boulder, for use of e.s.r facilities.

(*Received, January 4th,* 1971; *Com.* 005.)

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