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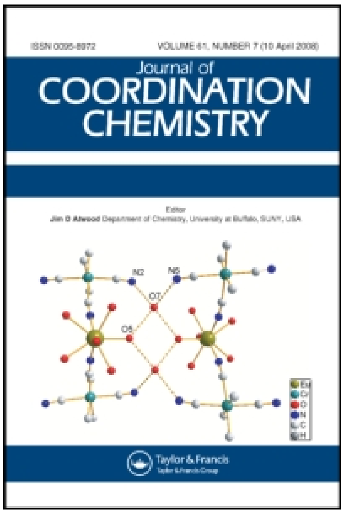

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THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRASODIUM DICOPPER(II)-*dl*-TARTRATE DECAHYDRATE

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THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRASODIUM DICOPPER(II)-*dl*-TARTRATE DECAHYDRATE

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The crystal structure of the complex of Cu^{2+} and racemic tartaric acid formed in basic solution has been determined by X-ray analysis. The crystals of $Na_2[Cu\text{-}d,l\text{-}C_4O_6H_2]\cdot 5H_2O$ are monoclinic, $a = 9.290(4)$, $b = 10.894(5)$, $c = 11.556(5)$ Å, and $\beta = 94.85(6)°$; the space group is $P2_1/n$. The structure has been refined to an *R*-factor of 0.040 on 1852 non-zero structure amplitudes measured on an automatic diffractometer. The structure consists of centrosymmetric dimeric tetranegative anions $[Cu_2$ *d*-tartrate, *l*-tartrate$]^{4-}$, with each Cu^{2+} ion forming a square planar complex with two ionized carboxyl and two ionized hydroxyl oxygen atoms. There is no fifth coordination to the Cu^{2+} ion. The Cu- - -Cu distance within the dimer is 2.9869(7) Å and the Cu^{2+} ions are slightly displaced (0.0617 Å) from the plane through their four coordinating oxygen atoms *towards* the other half of the dimer. The crystal structure is completed by a rather complex organization of Na^+ octahedra and water molecules. All the water molecules form hydrogen bonds in a rather regular fashion to the tetranegative complex anion so as to leave a small hole above the Cu^{2+} ion but which is not large enough to accommodate a fifth coordination to Cu^{2+}.

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INTRODUCTION

The complexes formed in equimolar solutions of Cu^{2+} ions and tartaric acid molecules at various pH values have been the subject of much study.[1] In acid solution, the complexes $Cu[meso\text{-}C_4O_6H_4]\cdot 1.75H_2O$[2] and $Cu[d\text{-}C_4O_6H_4]\cdot 3\,H_2O$[3] have been isolated and characterized as having only the carboxyl groups ionized.[4] A monomeric structure with three water molecules completing a six-fold coordination about Cu^{2+} was proposed for the copper *d*-tartrate trihydrate,[5] although magnetic measurements on powdered samples suggest a polymeric structure.[6] The crystal structures of $Cu[meso\text{-}C_4O_6H_4]\cdot 3\,H_2O$ (presumably the same species as the reported 1.75 hydrate[2]) and of $Cu[d\text{-}C_4O_6H_4]\cdot 3\,H_2O$ have been determined recently.[7] In neutral solutions, complexes with formulae $Na_3[Cu_4C_{12}O_{18}H_{17}]\cdot n\,H_2O$ have been isolated and polymeric structures have been proposed.[6] Of special interest (*e.g.*, in the organic test reagent, Fehling's solution) are the complexes formed in basic solution; these have both carboxyl and hydroxyl protons ionized. Precipitates have been obtained with generally variable composition with the notable exception of the $Na_2[Cu\text{-}dl\text{-}C_4O_6H_2]\cdot 5\,H_2O$ complex.[4] In the analogous oxovanadium-*d,l*-tartrate complex, $Na_2[VO\text{-}d,l\text{-}C_4O_6H_2]\cdot 6\,H_2O$ and also in an oxovanadium-*d,d*-tartrate complex, $(NH_4)_2[VO\text{-}d\text{-}C_4O_6H_2]\cdot H_2O$, Tapscott and Belford[8] proposed dimeric bridged structures on the basis of EPR spectra. The essential features of these structures have been confirmed by X-ray studies of the two complexes.[9,10] Also, on the basis of solution EPR spectra, Chasteen and Belford[11] proposed a dimeric bridged structure in the $Na_2[Cu\text{-}d,l\text{-}C_4O_6H_2]\cdot 5H_2O$ complex with water molecules completing five-fold coordination about the Cu^{2+} ions. Here we report an X-ray single-crystal study of this complex undertaken to assess this proposed structure and to assist in probing relationships between structure and magnetic properties.[12]

EXPERIMENTAL

Opaque, blue needles of $Na_2[Cu\text{-}d,l\text{-}C_4O_6H_2]\cdot 5H_2O$ were generously provided by Dr. N. D. Chasteen.[11] While the faces were well-formed, the edges were somewhat rounded.

Crystal Data: $Na_2[Cu\text{-}d,l\text{-}C_4O_6H_2]\cdot 5H_2O$, $M = 345.6$, monoclinic, $a = 9.290(4)$, $b = 10.894(5)$, $c = 11.556(5)$ Å, $\beta = 94.85(6)°$, $V = 1164 \times 10^{-24}$ cm^3, ρ_{meas} (flotation in iodoform and carbon tetrachloride at 25°C) $= 1.95$ g cm^{-3}, $Z = 4$, $\rho_{calc} = 1.97$ g cm^{-3}, $F(000) = 700$, μ $(CuK_\alpha) = 39.95$ cm^{-1}. Systematic absences, $h0l$ when $h+l=$

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$2n+1$, $0k0$ when $k = 2n + 1$. Space group, $P2_1/n$ (non-standard setting for $P2_1/c$).

Initial cell parameters and the space group assignment were obtained from a precession and Weissenberg photographic examination of the crystal. The final cell data were obtained from a least squares fit to the hand-centred settings for the four angles of twelve reflections on a Picker FACS-1 diffractometer (CuK$_\alpha$, $\lambda = 1.5418$ Å). Intensity data were collected at ambient room temperature (~20°C) on the diffractometer (CuK$_\alpha$ radiation). The crystal used for data collection was a needle 1.08 mm along the *a*-axis and 0.16 and 0.14 mm in cross-section. The intensities were measured with a scintillation counter, employing pulse height analysis and with attenuators being inserted when the count rate exceeded 10,000 counts/sec. The 1989 symmetry-nonequivalent reflections in the 2θ range 0–130° were measured at least once using a moving crystal-moving counter method with a 2θ scan rate of 1°/min. Background measurements for 10 sec. were recorded at the two limits of the scan. The base-width of the scan was 2°, but a dispersion factor was applied to take account of the α_1–α_2 splitting. A standard reflection, 1 4 1, was measured after every fifty reflections and a steady decrease in the intensity to 91% of its original value was noted during the eight-day period of data collection. The intensities were scaled assuming a linear fall-off between the periodic measurements of the standard reflection. Lorentz and polarization corrections were applied to the data and at a later stage of the analysis, absorption corrections were made;[13] the maximum and minimum transmission coefficients to be applied to the intensities were estimated to be 0.62 and 0.38. Of the 1989 unique reflections, 1852 were judged to be above background at the 2σ level.[14]

STRUCTURE SOLUTION AND REFINEMENT

The structure was determined by the heavy atom method based on the copper atom. Two rounds of structure factor and Fourier calculations were necessary to locate the positions of all the non-hydrogen atoms in the crystal asymmetric unit. Several cycles of full-matrix least squares refinement on positional and isotropic thermal parameters gave crystallographic R and R_2[15] factors of 0.082 and 0.087. In this and subsequent least squares refinement, unit weights were employed and the quantity minimized was $\Sigma w||F_{\text{obs}}| - |F_{\text{calc}}||^2$. Anisotropic thermal parameters were now introduced for all the atoms and two cycles of full-matrix least squares refinement reduced R to 0.052 and R_2 to 0.065. At this stage, anomalous dispersion corrections were applied to the Cu^{2+} scattering curve. A three-dimensional difference map was computed and contained twelve peaks with heights greater than 0.40 electrons/Å^3 in positions that could represent the twelve hydrogen atoms in the asymmetric unit. Before the hydrogen atoms were included in a refinement, absorption corrections[13] were applied to the data. Three cycles of full-matrix refinement gave R of 0.043 and R_2 of 0.045. Inspection of the $|F_{\text{obs}}|$ and $|F_{\text{calc}}|$ values for some of the low order data indicated that eight reflections may be suffering from significant extinction effects.

TABLE I

Final positional parameters with estimated standard deviations (× 10^5)[a] in fractions of the unit cell edge[b]

Atom	*x*	*y*	*z*
Cu	0.06846(5)	0.12275(5)	0.02210(5)
Na(1)	0.57554(17)	−0.03886(16)	−0.12442(14)
Na(2)	0.68357(19)	−0.01815(16)	−0.40959(14)
C(1)	0.25599(39)	0.08839(34)	−0.14093(31)
C(2)	0.10817(37)	0.05482(35)	−0.19894(32)
C(3)	0.09811(39)	−0.08710(34)	−0.19698(31)
C(4)	−0.04956(41)	−0.12356(34)	−0.25434(33)
O(1)	0.36579(27)	0.07611(29)	−0.19276(23)
O(2)	0.25869(26)	0.12537(25)	−0.03395(22)
O(3)	−0.00207(26)	0.10682(24)	−0.13777(22)
O(4)	0.11487(26)	−0.13030(25)	−0.08120(22)
O(5)	−0.14518(27)	−0.15188(25)	−0.18303(23)
O(6)	−0.07545(31)	−0.12162(27)	−0.36159(23)
O(7)	0.59753(32)	0.14339(32)	0.01544(27)
O(8)	0.72081(31)	0.09738(27)	−0.23652(25)
O(9)	0.80716(48)	0.11732(34)	−0.52321(35)
O(10)	0.51067(40)	−0.14431(30)	−0.31024(29)
O(11)	0.41779(38)	0.11341(31)	−0.42198(27)
H(2)	0.099(4)	0.081(3)	−0.281(3)
H(3)	0.178(4)	−0.121(4)	−0.249(3)
H(7A)	0.704(6)	0.139(5)	0.032(4)
H(7B)	0.592(9)	0.235(9)	−0.029(7)
H(8A)	0.717(10)	0.189(10)	−0.247(8)
H(8B)	0.811(7)	0.105(6)	−0.201(5)
H(9A)	0.805(6)	0.202(6)	−0.514(5)
H(9B)	0.919(9)	0.120(8)	−0.534(7)
H(10A)	0.516(6)	−0.245(6)	−0.328(5)
H(10B)	0.617(8)	−0.152(7)	−0.269(6)
H(11A)	0.401(6)	0.201(6)	−0.429(5)
H(11B)	0.397(7)	0.098(6)	−0.351(6)

[a] The standard deviations for the hydrogen atoms are only (× 10^3).

[b] Hydrogen atoms are given the number of the atom to which they are attached.

These reflections were removed from the data and two further cycles of least squares refinement produced parameters that gave a final R-value of 0.040 and an R_2-value of 0.041 on all observed data. In the final cycle of refinement none of the shifts were greater than one half of the estimated standard deviation. Although some of the isotropic thermal parameters for the hydrogen atoms were quite large ($B_\theta = 15.0$ Å^2), the O_{water}–H distances were generally reasonable (0.87–1.12 Å) and a final difference map contained only one peak greater than 0.2 electrons/Å^3; this peak was 1.3 Å from the Cu^{2+} ion and could not reasonably correspond to another atomic position. The position for H(10B) is of concern because it is unusually close (~2.2Å; see below) to two Na^+ ions. Difference maps were run on the final model (but excluding H(10B)) both including and excluding the eight reflections believed to suffer from extinction. On the first difference map there were two positive peaks of height 0.3 e/Å^3 that might represent H(10B); one of these was the position determined previously, the other had the O(10)—H(10B) bond pointing into the hole (see below) above the Cu^{2+} ion. On the other difference map, there was one positive peak of height 0.3 e/Å^3 at the position first determined; the rest of the map in this region was quite clear (±0.1 e/Å^3). Nevertheless, a least squares refinement was run on the alternative position indicated by the first difference map. The refinement converged with $R = 0.041$ and $R_2 = 0.042$, the temperature factor of the hydrogen atom included at the new position rose to 25 Å^2 and the position moved erratically. We must conclude that the unusual position determined initially for H(10B) is the one supported by our data.

The final positional and thermal parameters are listed in Tables I and II, while the values of h, k, l, $|F_{obs}|$, and F_{calc} have been deposited.[16] The atomic scattering curves for neutral Cu, C, and O, and for Na^+ were those calculated by Cromer and Mann,[17] with that for Cu corrected for anomalous disper-

TABLE II

Final anisotropic temperature parameters (× 10^4)[a] standard deviations are in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_θ[b, c]
Cu	24.9(.6)	27.3(.4)	28.6(.4)	−2.0(.4)	−0.1(.3)	−0.9(.3)	0.99(3)
Na(1)	71(2)	84(2)	46(1)	−7(1)	0(1)	4(1)	2.59(7)
Na(2)	116(2)	77(2)	44(1)	−29(2)	5(1)	−5(1)	2.91(7)
C(1)	63(4)	39(3)	42(3)	−2(3)	5(3)	5(2)	1.87(14)
C(2)	43(4)	49(3)	37(3)	0(2)	7(3)	0(2)	1.70(13)
C(3)	55(4)	48(3)	35(3)	3(3)	0(3)	−2(2)	1.77(14)
C(4)	75(5)	35(3)	47(3)	−2(3)	−1(3)	−5(2)	2.15(14)
O(1)	48(3)	92(3)	51(2)	1(2)	12(2)	4(2)	2.52(11)
O(2)	54(3)	58(2)	47(2)	−9(2)	1(2)	−6(2)	2.07(10)
O(3)	46(3)	52(2)	48(2)	8(2)	0(2)	−8(2)	1.98(10)
O(4)	57(3)	55(2)	44(2)	0(2)	1(2)	13(2)	2.09(10)
O(5)	57(3)	53(2)	54(2)	−12(2)	1(2)	1(2)	2.28(11)
O(6)	99(4)	70(3)	42(2)	−4(3)	−9(2)	−6(2)	2.77(12)
O(7)	61(4)	93(3)	67(3)	−4(3)	−5(2)	21(2)	2.98(12)
O(8)	59(3)	53(3)	61(2)	4(2)	−6(2)	−4(2)	2.41(11)
O(9)	192(7)	61(3)	114(4)	−6(4)	83(4)	5(3)	4.49(16)
O(10)	140(5)	59(3)	71(3)	−15(3)	23(3)	−10(2)	3.56(14)
O(11)	150(5)	58(3)	47(2)	−17(3)	14(3)	−5(2)	3.16(13)

Final isotropic temperature parameters for the hydrogen atoms[b]

H(2)	1.6(7)	H(8A)	11(3)	H(10A)	7(2)
H(3)	2.6(8)	H(8B)	5(2)	H(10B)	7(2)
H(7A)	4(1)	H(9A)	6(1)	H(11A)	4(1)
H(7B)	13(3)	H(9B)	11(3)	H(11B)	7(2)

---

[a] Anisotropic thermal parameters are expressed in the form $\exp\ [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\,hk\beta_{12} + 2\,hl\,\beta_{13} + 2\,kl\,\beta_{23})]$.

[b] Isotropic thermal parameters are expressed in the form $\exp\ (-B_\theta \sin {}^2\theta/\lambda^2)$.

[c] These values were those obtained from the final cycle of isotropic refinement.

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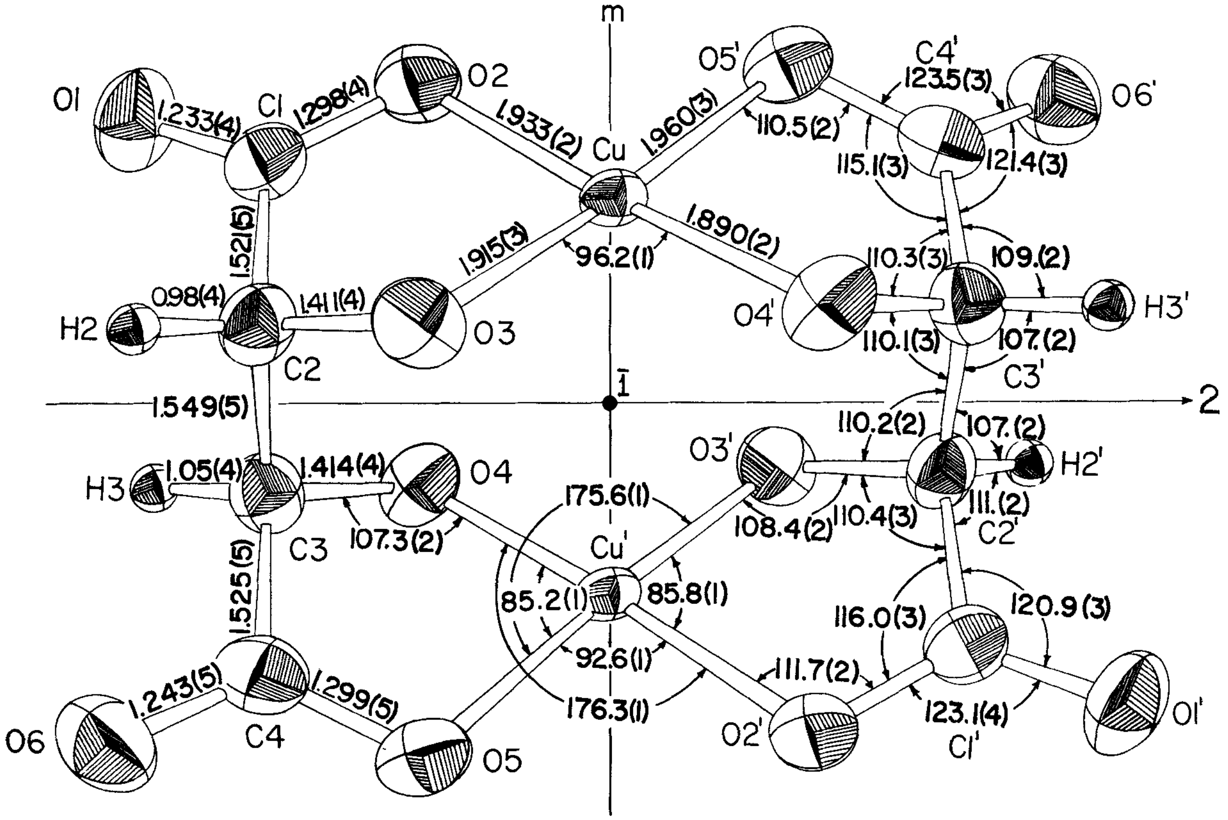

FIGURE 1 Bond lengths and angles in the anion. The ellipsoids show the thermal motion of the atoms with a probability of 50%.

sion.[18] The hydrogen scattering curve used was that calculated by Stewart *et al.*[19]

RESULTS AND DISCUSSION

The crystal structure consists of dimeric tetranegative anions, $[Cu_2^{-}d\text{-}C_4O_6H_2, l\text{-}C_4O_6H_2]^{4-}$, and a fairly complex arrangement of Na^+ ions and water molecules which are linked to both cations and anions.

The Structure of the Copper(II)dl-Tartrate Anion

The dimeric anions have crystallographic $C_i(\bar{1})$ symmetry and approach $C_{2h}(2/m)$ molecular symmetry. The structure of the dimer, together with the bond lengths and angles, is shown in Figure 1.

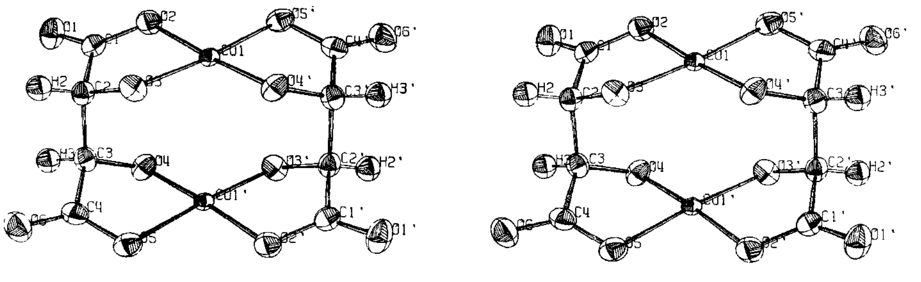

FIGURE 2 Stereoscopic view of the dimeric Cu-tartrate anion. The ellipsoids show the thermal motion of the atoms with a probability of 50%.

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A stereoscopic view of the dimer is shown in Figure 2. For comparison, stereoscopic views of the structures of *meso* and *d*-tartrate complexes of Cu^{2+} as determined by Prout and co-workers[7] are shown in Figure 3. Complete bond lengths and angles are given in Table III. Some details of the coodination are given in Table IV, along with comparative data for the Cu^{2+}-*meso*-tartrate and Cu^{2+}-*d*-tartrate complexes.

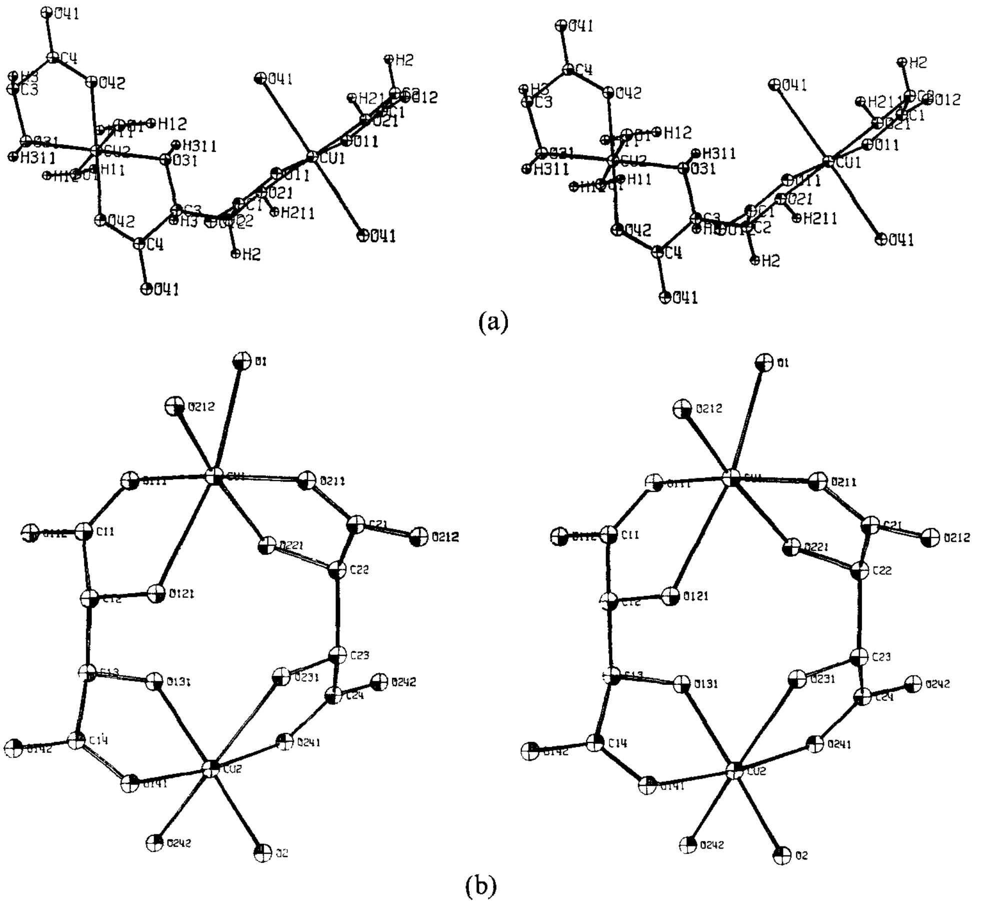

FIGURE 3 Stereoscopic pictures of (a) the Cu^{2+}-*meso*-tartrate complex, and (b) the Cu^{2+}-*d*-tartrate complex drawn from the coordinates in reference 7. We thank Dr. Prout for providing us with the coordinates in advance of publication.

The dimeric tetranegative anions are formed by the coordination of two Cu^{2+} ions by a *d* and an *l*-tartrate ion which have lost the two carboxyl and the two hydroxyl protons. The coordination of the oxygen atoms in the tartrate anion about each Cu^{2+} is *cis*, as was the case in the racemic vanadyl tartrate dimer[9], with the four coordinating oxygen atoms being nearly coplanar; each deviates by 0.009 Å from the plane of best fit through all four atoms (Table V). The Cu^{2+} ion lies 0.0617 Å to the interior of the dimer from this plane. The two Cu^{2+}---O (hydroxyl) lengths (1.890(2) and 1.915(3) Å) are slightly shorter than the two Cu^{2+}---O (carboxyl) lengths (1.933(2) and 1.960(3) Å), in contrast to the situation in the low pH species (see Table IV). The intradimer Cu---Cu distance is 2.9869(7) Å which is considerably shorter than the 3.3 Å deduced from the dipolar electron-electron interaction in frozen aqueous solution,[11] and much shorter than the V---V distance of 4.082(2) Å reported in the racemic vanadyl tartrate dimer, where the vanadium atoms are 0.546 Å above the best plane through the four

TABLE III

Bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses.

Distances and angles around copper ion

Cu——O(2)	1.933(2)	Cu- - -Cu′	2.9869(7)
Cu——O(3)	1.915(3)	Cu- - -O(3′)	2.926(3)
Cu——O(4′)	1.890(2)	Cu- - -O(4)	3.049(3)
Cu——O(5′)	1.960(3)		
O(2)—Cu—O(3)	85.8(1)	O(5′)—Cu—O(4)	117.8(1)
O(4′)—Cu—O(5′)	85.2(1)	O(5′)—Cu—O(3′)	77.2(1)
O(2)—Cu—O(5′)	92.6(1)	C(1)—O(2)—Cu	111.7(2)
O(3)—Cu—O(4′)	96.2(1)	C(2)—O(3)—Cu	108.4(2)
O(2)—Cu—O(4′)	176.3(1)	C(4′)—O(5′)—Cu	110.5(2)
O(3)—Cu—O(5′)	175.6(1)	C(3′)—O(4′)—Cu	107.3(2)
O(2)—Cu—O(4)	73.7(1)		
O(2)—Cu—O(3′)	113.6(1)		

Distances and angles within the tartrate group

C(1)—O(1)	1.233(4)	C(3)—H(3)	1.05(4)
C(1)—O(2)	1.298(4)	C(3)—O(4)	1.414(4)
C(1)—C(2)	1.521(5)	C(3)—C(4)	1.525(5)
C(2)—O(3)	1.411(4)	C(4)—O(5)	1.299(5)
C(2)—C(3)	1.549(5)	C(4)—O(6)	1.243(5)
C(2)—H(2)	0.98(4)		
O(1)—C(1)—O(2)	123.1(4)	C(2)—C(3)—C(4)	107.9(2)
O(1)—C(1)—C(2)	120.9(3)	C(2)—C(3)—O(4)	110.1(3)
O(2)—C(1)—C(2)	116.0(3)	C(2)—C(3)—H(3)	107(2)
C(1)—C(2)—O(3)	110.4(3)	C(4)—C(3)—O(4)	110.3(3)
C(1)—C(2)—C(3)	106.7(2)	C(4)—C(3)—H(3)	109(2)
C(1)—C(2)—H(2)	111(2)	O(4)—C(3)—H(3)	113(2)
O(3)—C(2)—C(3)	110.2(3)	C(3)—C(4)—O(5)	115.1(3)
O(3)—C(2)—H(2)	111(2)	C(3)—C(4)—O(6)	121.4(3)
C(3)—C(2)—H(2)	107(2)	O(5)—C(4)—O(6)	123.5(3)

Environment of sodium ions

Na(1)——O(1)	2.394(3)	Na(2)——O(8)	2.364(3)
Na(1)——O(2$^{\mathrm{I}}$)	2.476(3)	Na(2)——O(9)	2.340(4)
Na(1)——O(7)	2.557(4)	Na(2)——O(11)	2.848(4)
Na(1)——O(8)	2.449(3)	Na(2)——O(10)	2.470(4)
Na(1)——O(10)	2.465(4)	Na(2)——O(6$^{\mathrm{III}}$)	2.526(3)
Na(1)——O(7$^{\mathrm{I}}$)	2.410(3)	Na(2)——O(11$^{\mathrm{II}}$)	2.333(4)
Na(1)- - -O(5$^{\mathrm{III}}$)	3.001(3)	Na(2)- - -O(5$^{\mathrm{III}}$)	3.287(3)
Na(1)- - -H(10B)	2.14(7)	Na(2)- - -H(10B)	2.31(7)
Na(1)- - -Na(2)	3.532(2)	Na(2)- - -Na(2$^{\mathrm{II}}$)	3.867(2)
Na(1)- - -Na(1$^{\mathrm{I}}$)	3.411(2)		
O(1)—Na(1)—O(2$^{\mathrm{I}}$)	151.8(1)	O(8)—Na(2)—O(9)	95.5(1)
O(1)—Na(1)—O(7)	79.7(1)	O(8)—Na(2)—O(11)	80.7(1)
O(1)—Na(1)—O(8)	88.7(1)	O(8)—Na(2)—O(10)	87.6(1)
O(1)—Na(1)—O(10)	79.9(1)	O(8)—Na(2)—O(6$^{\mathrm{III}}$)	89.3(1)
O(1)—Na(1)—O(7$^{\mathrm{I}}$)	81.9(1)	O(8)—Na(2)—O(11$^{\mathrm{II}}$)	164.3(1)
O(2$^{\mathrm{I}}$)—Na(1)—O(7)	79.4(1)	O(9)—Na(2)—O(11)	96.8(1)
O(2$^{\mathrm{I}}$)—Na(1)—O(8)	106.6(1)	O(9)—Na(2)—O(10)	168.9(1)
O(2$^{\mathrm{I}}$)—Na(1)—O(10)	123.9(1)	O(9)—Na(2)—O(6$^{\mathrm{III}}$)	86.4(1)
O(2$^{\mathrm{I}}$)—Na(1)—O(7$^{\mathrm{I}}$)	80.5(1)	O(9)—Na(2)—O(11$^{\mathrm{II}}$)	89.7(1)
O(7)—Na(1)—O(8)	81.1(1)	O(11)—Na(2)—O(10)	73.0(1)
O(7)—Na(1)—O(10)	155.9(1)	O(11)—Na(2)—O(6$^{\mathrm{III}}$)	169.8(1)
O(7)—Na(1)—O(7$^{\mathrm{I}}$)	93.3(1)	O(11)—Na(2)—O(11$^{\mathrm{II}}$)	84.0(1)
O(8)—Na(1)—O(10)	85.8(1)	O(10)—Na(2)—O(6$^{\mathrm{III}}$)	104.4(1)
O(8)—Na(1)—O(7$^{\mathrm{I}}$)	169.8(1)	O(10)—Na(2)—O(11$^{\mathrm{II}}$)	84.7(1)
O(10)—Na(1)—O(7$^{\mathrm{I}}$)	96.3(1)	O(6$^{\mathrm{III}}$)—Na(2)—O(11$^{\mathrm{II}}$)	105.8(1)

(continued)

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TABLE III—*continued*

Dimensions involving water molecules

O(7)——H(7A)	0.99(5)	H(7A)——O(7)——H(7B)	98(5)
O(7)——H(7B)	1.12(9)	O(4$^{\mathrm{I}}$)- - -O(7)- - -O(6$^{\mathrm{V}}$)	102.6(1)
O(7)- - -O(4$^{\mathrm{I}}$)	2.719(4)	O(7)——H(7A)- - -O(4$^{\mathrm{I}}$)	172(4)
O(7)- - -O(6$^{\mathrm{V}}$)	3.114(4)	O(7)——H(7B)- - -O(6$^{\mathrm{V}}$)	168(5)
H(7A)- - -O(4$^{\mathrm{I}}$)	1.73(5)		
H(7B)- - -O(6$^{\mathrm{V}}$)	2.01(9)		
O(8)——H(8A)	1.01(11)	H(8A)——O(8)——H(8B)	89(7)
O(8)——H(8B)	0.90(6)	O(5$^{\mathrm{V}}$)- - -O(8)- - -O(3$^{\mathrm{III}}$)	106.7(1)
O(8)- - -O(5$^{\mathrm{V}}$)	2.951(4)	O(8)——H(8A)- - -O(5$^{\mathrm{V}}$)	156(5)
O(8)- - -O(3$^{\mathrm{III}}$)	2.728(4)	O(8)——H(8B)- - -O(3$^{\mathrm{III}}$)	174(5)
H(8A)- - -O(5$^{\mathrm{V}}$)	2.00(10)		
H(8B)- - -O(3$^{\mathrm{III}}$)	1.83(6)		
O(9)——H(9A)	0.93(7)	H(9A)——O(9)——H(9B)	91(6)
O(9)——H(9B)	1.06(8)	O(2$^{\mathrm{V}}$)- - -O(9)- - -O(6$^{\mathrm{II}}$)	95.9(1)
O(9)- - -O(2$^{\mathrm{VI}}$)	2.840(5)	O(9)——H(9A)- - -O(2$^{\mathrm{VI}}$)	163(2)
O(9)- - -O(6$^{\mathrm{II}}$)	2.924(5)	O(9)——H(9B)- - -O(6$^{\mathrm{II}}$)	149(6)
H(9A)- - -O(2$^{\mathrm{VI}}$)	1.94(7)		
H(9B)- - -O(6$^{\mathrm{II}}$)	1.97(8)		
O(10)——H(10A)	1.12(7)	H(10A)——O(10)——H(10B)	87(5)
O(10)——H(10B)	1.07(8)	O(3$^{\mathrm{IV}}$)- - -O(10)- - -O(5$^{\mathrm{III}}$)	94.5(1)
O(10)- - -O(3$^{\mathrm{IV}}$)	2.777(4)	O(10)——H(10A)- - -O(3$^{\mathrm{IV}}$)	173(5)
O(10)- - -O(5$^{\mathrm{III}}$)	3.405(5)	O(10)——H(10B)- - -O(5$^{\mathrm{III}}$)	175(3)
H(10A)- - -O(3$^{\mathrm{IV}}$)	1.66(7)		
H(10B)- - -O(5$^{\mathrm{III}}$)	2.34(8)		
O(11)——H(11A)	0.96(6)	H(11A)——O(11)——H(11B)	103(6)
O(11)——H(11B)	0.88(7)	O(4$^{\mathrm{V}}$)- - -O(11)- - -O(1)	96.1(1)
O(11)- - -O(4$^{\mathrm{V}}$)	2.809(4)	O(11)——H(11A)- - -O(4$^{\mathrm{V}}$)	171(3)
O(11)- - -O(1)	2.763(4)	O(11)——H(11B)- - -O(1)	174(5)
H(11A)- - -O(4$^{\mathrm{V}}$)	1.85(6)		
H(11B)- - -O(1)	1.89(7)		

In this Table, the superscripts,

I refers to transformation	$1-x$,	$-y$,	$-z$
II refers to transformation	$1-x$,	$-y$,	$-1-z$
III refers to transformation	$1+x$,	y,	z
IV refers to transformation	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$-\frac{1}{2}-z$
V refers to transformation	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$-\frac{1}{2}-z$
VI refers to transformation	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
′ refers to transformation	$-x$,	$-y$,	$-z$

Other Superscripts

VII	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
VIII	$-1+x$,	y,	z
IX	$-\frac{1}{2}+x$,	$-\frac{1}{2}-y$,	$\frac{1}{2}+z$
X	$-1+x$,	y,	$1+z$
XI	x,	y,	$-1+z$
XII	$-x$,	$-y$,	$-1-z$
XIII	x,	y,	$1+z$
XIV	$1+x$,	y,	$1+z$
XV	$1-x$,	$-y$,	$1-z$

coordinating tartrate oxygen atoms.[9] The Cu—Cu vector makes an angle of 31.8° with the normal to the coordination plane. Because of this lateral displacement of one Cu^{2+} ion from the position perpendicular to the other Cu^{2+} ion in the coordination plane (Figures 4a and b) and the long Cu- - -Cu distance, we do not consider that there is a coordination bond between the two Cu^{2+} ions.

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TABLE IV

Structural data for Cu(II)-*d,l*-tartrate complex compared with those for Cu(II)-*d*-tartrate and Cu(II)-*meso*-tartrate complexes.

	Cu-*d, l*-tartrate	Cu-*d*-tartrate[a]	Cu-*meso*-tartrate[a]
Extent of ionization of tartrate group	4 protons lost	2 protons lost	2 protons lost
Structural unit	Dimer (C_i crystallographic symmetry)	Dimer (no crystallographic symmetry)	Polymeric Chain linked by tartrate groups.
Coordination of copper ion	4 (approximately square planar)	6 (axially-elongated octahedron)	6 (axially-elongated octahedron)
Types and distances of coordinating oxygen atoms (equatorial)	2 ionized carboxyl Cu---O 1.933–1.960(3)Å 2 ionized hydroxyl Cu---O 1.890–1.915(3)Å	2 ionized carboxyl [b] Cu---O 1.89–1.93(2)Å 1 unionized hydroxyl Cu---O 2.00–2.01(2) Å 1 water molecule Cu---O 1.95(2)Å, or [d] 1 carbonyl Cu---O 1.97(2) Å	2 ionized carboxyl[c] Cu---O 1.918–1.920(3)Å 2 unionized hydroxyl Cu---O 1.955–1.975(3)Å
(axial)	none	1 unionized hydroxyl Cu---O 2.40–2.43(2) Å 1 water molecule Cu---O 2.40(2) Å, or [d] 1 carbonyl Cu---O 2.37(2) Å	2 water molecules Cu---O 2.479(3)Å, or [e] 2 carbonyl Cu---O 2.536(3) Å
Shortest Cu---Cu distance	2.9869(7) Å	5.42(1) Å	5.870(5) Å[f]
Average deviation from coplanarity of four equatorial coordinating oxygen atoms	0.009 Å	0.012 Å[b] 0.004 Å	planar[g]
Deviation of Cu^{2+} from above plane	0.0617 Å	0.032 Å[b] 0.077 Å	0.0 Å[g]

[a] Data taken from reference 7.

[b] There are two crystallographically-independent Cu^{2+} ions and their coordinating groups in this structure.

[c] In this structure, there are two crystallographically-independent Cu^{2+} ions, each of which occupies a center of symmetry in the crystal.

[d] In the case of one Cu^{2+} ion, the equatorial coordination is by two ionized carboxyl, one uionized hydroxyl, and a carbonyl oxygen atom, while the axial coordination is by an unionized hydroxyl group and a water molecule; for the other Cu^{2+} ion, the equatorial coordination is by two ionized carboxyl, one unionized hydroxyl, and a water molecule, while the axial is by an unionized hydroxyl and a non-coordinating carbonyl group.

[e] One of the Cu^{2+} ions is axially coordinated by two centrosymmetrically-related water molecules; the other is coordinated by two centrosymmetrically-related carbonyl groups.

[f] In reference 7, the Cu---Cu distance is given as 6.065 Å; this distance, however, does not correspond to the separation of Cu^{2+} ions within coordinated chains.

[g] By symmetry.

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In contrast, the distances of 2.61–2.65 Å between Cu^{2+} ions found in dimeric copper acetate-type structures most probably represent significant Cu- - -Cu interactions.[20] The lateral displacement of the Cu^{2+} ions leads to relatively short intracomplex Cu- - -O(3′) and Cu- - -O(4) distances of 2.926(3) and 3.049(3) Å. While it is also unreasonable to consider them as coordination bonds to Cu^{2+}, these weak linkages may significantly affect the intradimer exchange energy and thus the magnetic properties. A Cu- - -O distance of 2.85 Å in bis(8-hydroxyquinolinato)Cu^{2+} was considered a very weak coordination, but in that case the oxygen atom lay directly above the Cu^{2+} ion.[21]

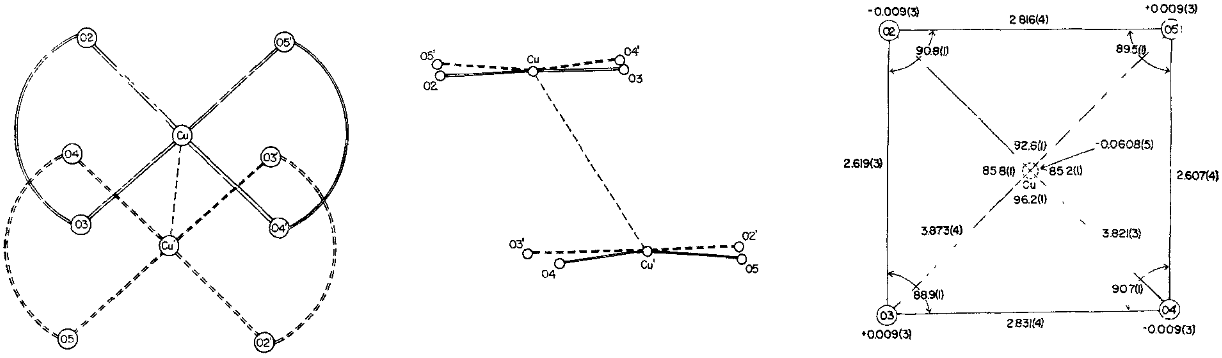

FIGURE 4 (a) Exact projection of the atoms Cu, Cu′, O(2), O(3) and O(4′) and O(5′) onto the best plane through the atoms O(4), O(5), O(2′), and O(3′). This view shows the displacement of two CuO_4 groups. (b) Exact projection of the atoms Cu, Cu′, O(2′), O(3′), O(4′), and O(5′) onto the best plane through the atoms O(2), O(3), O(4), and O(5). (c) Schematic representation of distances (Å) and angles (deg.) describing the copper coordination. The distances marked beside an atom represent the deviation of that atom from the best plane through O(2), O(3), O(4′), and O(5′).

Most α-hydroxy, α-alkoxy, or α-aryloxycarboxylate-Cu^{2+} complexes have octahedral or distorted octahedral coordination around the metal ion.[22] Usually there are four equatorial Cu^{2+}- - -O distances in the range 1.89–2.01 Å, with longer (2.30–2.56 Å) axial Cu^{2+}- - -O contacts.[22] In the present structure, there is neither axial coordination within the dimer nor a fifth coordinating ligand above the Cu^{2+} ion. This is rather unusual, especially in cases where there is no intramolecular steric effect to prevent a fifth coordination. A related situation may pertain here as does in the case of the Cu^{2+} complex of 1-aminocyclopentanecarboxylic acid, where the unionized amino group and the ionized carboxyl group coordinate to the metal ion, and there is only fourfold coordination.[23,24] In that structure, the authors[23] attributed the lack of axial coordination of a water molecule to the unfavorable perturbation in packing energy among the hydrophobic groups that would result from the presence of a water molecule in the crystal. However, in view of the generally hydrophilic environment in the crystal it is rather difficult to make exactly the same argument in the presen case. It is possible, of course, that the energy requirements for the packing of the octahedra around the Na^+ ions preclude a water molecule being situated above Cu^{2+}, and that the complex exists in solution with a coordinating water molecule.

Figure 4c shows the distances and angles that describe the copper coordination. The O- - -O distances within a chelate ring are ~0.2 Å shorter than those between chelate rings. The O—Cu—O angles within the chelate rings are 85.2–85.8(1)°, while those between chelate rings are wider, that between hydroxyl oxygen atoms being 96.2(1) and that between carboxyl oxygen atoms being 92.6(1)°.

The four atoms of a tartrate anion within each chelate ring do not lie on an exact plane (Table V), and the corresponding two planes of best fit through the two such groups of atoms linked by a Cu^{2+} ion make angles of 18° 20′ and 24° 44′ with the plane of best fit through the four oxygen atoms coordinated to that Cu^{2+} ion.

As was found in the racemic vanadyl tartrate dimer[9] and in several other tartrate dimers,[1] the four carbon atoms (C(1), C(2), C(3), and C(4)) of the tartrate group are coplanar (maximum deviation 0.001 Å), as are the four coordinating oxygen

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atoms of a tartrate ion (maximum deviation 0.004 Å) (Table V). These two planes are parallel to the Cu—Cu vector. The four carbon atoms of the *meso*-tartrate ion in the Cu^{2+}-*meso*-tartrate do not lie in a plane, whereas the four coordinating oxygen atoms of a tartrate ion in the *d*-tartrate dimer are not coplanar while the four carbon atoms are coplanar. The torsion angles about the C—C bonds in the tartrate ions in the racemic complex are compared in Table VI with those found in the racemic vanadyl tartrate dimer[9] and in uncomplexed *d*-tartaric acid.[25] (A more nearly complete tabulation is given in reference 1.) The O(hydroxyl)—C(2)—C(3)—O(hydroxyl) torsion angle is always within 2° of the staggered value of 60°, but there are differences in the O(hydroxyl)—C(2)—C(1)—O(carboxyl) torsion angles in the two complexes. In the Cu^{2+}-tartrate complex these two torsion angles are almost equal, 18.7–19.5°, whereas in the vanadyl complex one torsion angle is 15° and the other is only 1°. It is a general feature of all tartrate groups, whether coordinated or uncoordinated and whether ionized or unionized, that the five non-hydrogen atoms at one end of the residue exhibit approximate coplanarity,[1] although this coplanarity is less marked in the present structure than in several others. In the coordinating tartrate dimers, the hydroxyl oxygen atom and the *carboxyl* oxygen atom are nearly eclipsed, while, by contrast, with only one known exception,[26] in tartrate compounds containing unionized carboxyl groups the *carbonyl* oxygen atom of the carboxyl group is adjacent to the α-hydroxyl oxygen atom.[1]

TABLE V

Details[a] of some planes of best fit in the structure.

Plane #	1	2	3	4	5
Cu	−0.0608	−0.503			
Cu′	−2.6135		−0.647		
O(1)		0.332			
O(2)	**−0.009**	**−0.031**			**−0.004**
O(3)	**0.009**	**0.026**			**0.004**
O(4)			**0.027**		**0.004**
O(5)			**−0.033**		**−0.004**
O(6)			0.362		
O(4′)	**−0.009**				
O(5′)	**0.009**				
C(1)	−0.260	**0.104**		**−0.001**	
C(2)	−0.500	**−0.097**	−1.521	**0.001**	
C(3)		−1.523	**−0.099**	**0.001**	
C(4)			**0.113**	**−0.001**	
C(3′)	−0.641				
C(4′)	−0.368				
χ^2	44.9	1692	1904	0.5	11.2
P[b]	<0.005	<0.005	<0.005	0.005	~0.005

[a] Each column gives the perpendicular distance (Å) from the atom to the least-squares plane through a set of four atoms. Distances of atoms included in the plane calculation are given in bold type.

[b] Probability that the distances from the plane describe a normal distribution.

TABLE VI

Torsion angles[a,b] in the Cu^{2+} *d,l*-tartrate complex[c] compared with those found in the vanadyl *d, l*-tartrate complex[c,d] and in *d*-tartaric acid.[e]

	Cu–tartrate Complex τ (deg.)	VO–tartrate Complex τ (deg.)	*d*-tartaric Acid τ (deg.)
O(2)—C(1)—C(2)—O(3)	18.7	15.0	4.4
O(1)—C(1)—C(2)—O(3)	−163.9	−170.6	−177.8
O(2)—C(1)—C(2)—C(3)	−101.1	−104.5	−115.7
O(1)—C(1)—C(2)—C(3)	76.3	69.9	62.0
C(1)—C(2)—C(3)—C(4)	179.8	177.1	−175.3
C(1)—C(2)—C(3)—O(4)	59.3	58.6	60.0
O(3)—C(2)—C(3)—C(4)	59.9	56.9	66.5
O(3)—C(2)—C(3)—O(4)	−60.6	−61.5	−58.5
O(4)—C(3)—C(4)—O(5)	19.5	1.0	4.9
O(4)—C(3)—C(4)—O(6)	−162.8	−178.6	−174.4
C(2)—C(3)—C(4)—O(5)	−100.8	−116.5	−119.3
C(2)—C(3)—C(4)—O(6)	76.9	63.9	61.3

[a] The angle A–B–C–D is considered positive if, when looking along the B–C bond, atom A has to be rotated clockwise to eclipse atom D.

[b] The atom numbering in the other two structures has been changed to conform to that used in the present investigation.

[c] The basic coordinates listed in both the present structure and that of the vanadyl *d,l*-tartrate correspond to the *d*-enantiomorph. The coordinates for *d*-tartaric acid given in reference 25, however, in fact correspond to *l*-tartaric acid.

[d] Calculated from the coordinates in reference 9.

[e] Calculated from the coordinates in reference 25.

Pauling's bent-bond conception of a double bond has been invoked to explain the eclipsing of the carbonyl and α-hydroxyl oxygen atoms in unionized molecules.[27,28] Comparing the tartrate anions in the copper complex with *d*-tartaric acid[25] one sees that the two C—O distances in the carboxyl group have become less disparate, (1.238(5) and 1.299(5) Å) as compared to (1.200(7) and 1.317(7) Å), and that the carboxylate carbon is more nearly equiangular (i.e., O=C—O, O=C—C, and O—C—C angles are 123.3(4), 121.2(3), and 115.6(3)° as compared to 125.7, 124.4 and 109.9°).

The Sodium Octahedra

The arrangement of atoms around each sodium ion is shown in Figure 5. Both sodium ions have distorted octahedral coordination by oxygen atoms with Na$^+$---O distances ranging from 2.394(4) to 2.557(4) Å for Na(1) and from 2.333(4) to 2.848(4) Å for Na(2). Na(1) is coordinated by four water molecules, a carbonyl and a carboxyl oxygen atom, while Na(2) is coordinated by five water molecules and a carbonyl oxygen atom. All the octahedra share two coordinating water oxygen atoms with each of the two adjoining octahedra. Four octahedra are linked in a linear fashion, then there is a single step at right angles to this arrangement, followed by a repeat of the four linear octahedra; it is a 3:1 stepping pattern. The unique Na(1)---Na(2), Na(1)---Na(1), and Na(2)---Na(2) distances between adjacent octahedra are 3.532(2), 3.411(2), and 3.867(2) Å, respectively. The atom O(5), a carboxyl oxygen atom coordinating to Cu^{2+}, lies between two octahedra at distances 3.001(3) from Na(1) and 3.287(3) Å from Na(2). These contacts, however, are almost perpendicular to two of the triangular faces of the octahedra and we do not describe them as real Na$^+$ -- O coordination linkages; it should be noted, however, that the approach to Na(1)$^+$ is quite open at that point with the O(8)Na(1)O(2$^{\text{I}}$) and O(10)Na(1)O(2$^{\text{I}}$) angles being 106.6(1) and 123.9(1)°. Thus, some readers may prefer to regard this as a case of sevenfold coordination to the sodium ion.

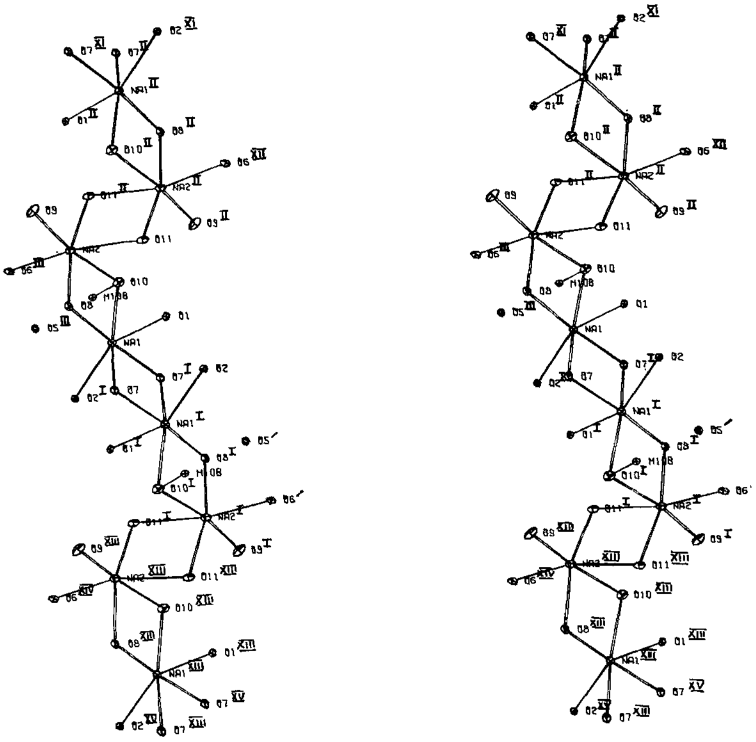

FIGURE 5 Stereoscopic view of the chain of sodium octahedra in the crystal. Roman superscripts refer to the transformations listed in Table III.

Hydrogen Bonding and Water Coordination

The arrangement and structure of the water molecules in the crystal (Figures 6 and 7) show several interesting features. Every water molecule coordi-

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nates to at least one sodium ion (Figure 6). All the hydrogen atoms on the water molecules form hydrogen bonds to oxygen atoms of tartrate groups (Figure 7); there is no O(water)—H- - -O (water) hydrogen bonding. O(7), O(8), O(10), and O(11) complex to two Na$^+$ ions and form hydrogen bonds to two tartrate oxygen atoms in distorted tetrahedral geometry, while O(9) complexes to one sodium ion and forms a hydrogen bond to two tartrate oxygen atoms in a distorted trigonal arrangement. The details of the hydrogen bond distances and angles are in Table III. A hydrogen bond O(11)—H(11B)- - -O(1) of length 2.763(4) Å links two adjacent vertices of the octahedra around Na(1) and Na(2) (Figure 6). There is also a rather weak hydrogen bond O(10)—H(10B)- - -O(5$^{\text{III}}$) of length 3.405(5) Å from O(10), which is shared by two sodium octahedra, to O(5$^{\text{III}}$), which is not part of either sodium coordination octahedron (see preceding section) but which is situated almost midway between the vertices (apical to O(1) and O(11)) of the octahedra. These two structural features cause significant distortion of the octahedra, particularly that around Na(1) as described previously.

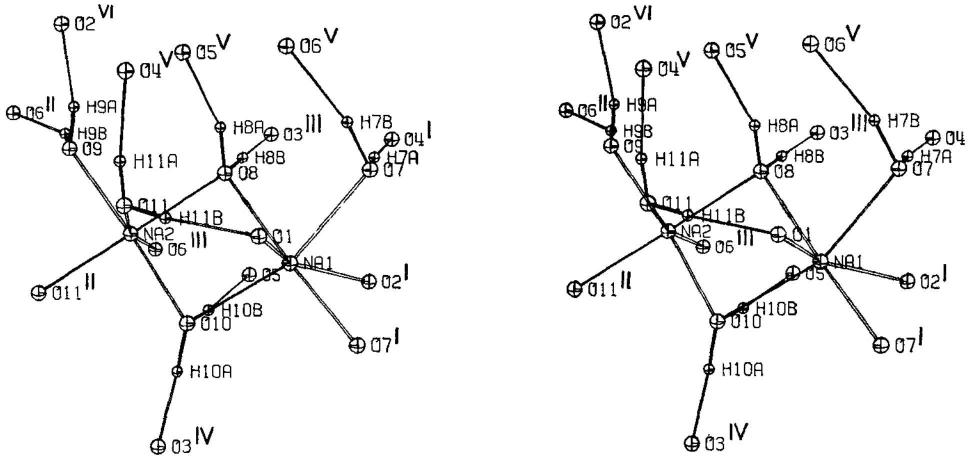

FIGURE 6 Stereoscopic view of the environment of the two sodium ions and their coordinating water molecules. Roman superscripts refer to transformation listed in Table III.

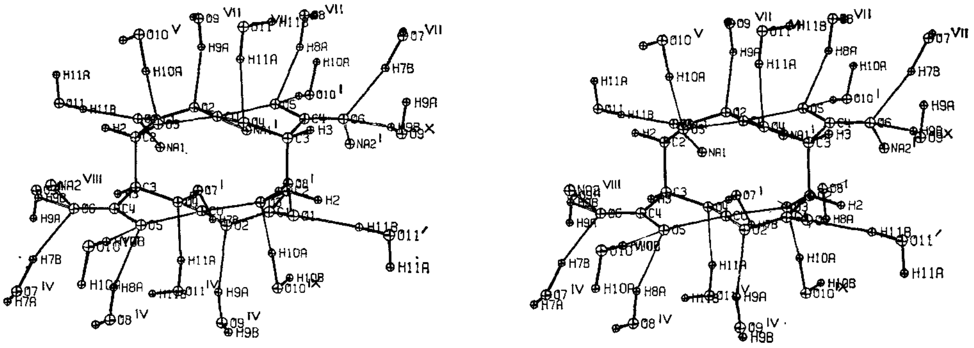

FIGURE 7 Stereoscopic view of the Cu-tartrate anion and surrounding water molecules. Roman superscripts refer to the transformation listed in Table III.

The complex tartrate anion is effectively surrounded by hydrogen-bonding water molecules (Figure 7). As the oxygen atoms in the complex lie in planes (*e.g.*, the four oxygen atoms coordinating to a single Cu^{2+} ion, and the four coordinating

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oxygen atoms in a single tartrate group), so there is a tendency for the oxygen atoms in the surrounding water molecules to lie in planes. The oxygen atoms O(7^{VII}), O(8^{VII}), O(9^{VII}), O(10^{V}), and O(11^{VII}) that lie above the copper-coordination plane and the atoms O(10^{VIII}), O(8^{IV}), O(11^{IV}), O(7^{I}), O(9^{VII}), O(10^{V}), and O(8^{VII}) that complex O(5), O(3), O(2), and O(4) are also approximately coplanar (Figure 7). As the oxygen atoms in the water molecules act as hydrogen bond donors to oxygen atoms in the tartrate groups, there are a large number of O—H bonds pointing inward to the anion. The regularity of the hydrogen bonding creates a hole above the Cu^{2+} ion that is, however, not large enough to accommodate another water molecule to complex the metal ion. While it is geometrically reasonable to postulate a different hydrogen bonding scheme, *e.g.*, H(10B) being donated to O(9^{II}) across the hole (see Experimental Section), the location of H(10B) in a position to hydrogen bond to O(5^{III}) seems reasonably certain. While the O(10)- - -O(5^{III}) distance is long for a hydrogen bond (3.405(3) Å), the H(10B)- - -O(5^{III}) contact (2.34(8) Å) is within the sum of the appropriate van der Waals radii and the O(3^{IV})- - -O(10)- - -O(5^{III}) angle supports this assignment. The other two possible hydrogen bond assignments for H(10B), to either O(9^{II}) or O(11), would also involve long O- - -O distances (3.398(6) and 3.179(5) Å, respectively) and in the case of the latter possibility would involve placing a hydrogen bond along the edge of the Na^+ coordination octahedron. This type of arrangement is unlikely.[29]

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    $R_2 = [\Sigma w(|F_{\mathrm{obs}}| - |F_{\mathrm{calc}}|)^2/\Sigma w|F_{\mathrm{obs}}|^2]^{1/2}$.
16. The final values of h, k, l, $|F_{\mathrm{obs}}|$, and F_{calc} are available (order Document No. NAPS–01872) from National Auxiliary Publications Service, c/o CCM Information Corporation, 866 3rd Avenue, New York, N.Y. 10022; remit $2.00 for microfiche or $5.00 for photocopies.
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