Inorganica Chimica Acta, 18 (1976) 25–28

The Crystal and Molecular Structure of Diaquobis(2,3-dihydroxy-2-methylpropanoato)copper(II)[a]

J. H. MILLER, J. E. POWELL, R. A. JACOBSON and S. KULPRATHIPANJA
Ames Laboratory-ERDA and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.
Received August 6, 1975

The crystal and molecular structure of diaquobis(2,3-dihydroxy-2-methylpropanoato)copper(II) has been determined by three-dimensional X-ray analysis. The compound crystallizes in the monoclinic space group C2/c, with $a = 5.688 \pm .006$ Å, $b = 20.79 \pm .03$ Å, $c = 10.569 \pm .016$ Å, $\beta = 94.55 \pm .06°$, *and* $Z = 4$. *The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final discrepancy factor* $R = .090$ *for 860 observed reflections* $(I_o > 2\sigma(I_o))$. *The geometry around the copper is distorted octahedral, with the two waters occupying the axial positions. Both ligands coordinate bidently, forming chelate rings incorporating the 2-hydroxy oxygen. The other hydroxy oxygens are not bound to the copper. There appears to be extensive hydrogen bonding in both the a and c directions with long contacts in the b direction.*

Introduction

Solution studies of the copper complexes of some 2- and 3-hydroxycarboxylates have indicated in both cases that the acid anion acts as a bidentate ligand, forming 5- and 6-membered rings, respectively.[1,2] The reported stability constants of the copper isomeric 2- and 3-hydroxypropanoate complexes reveal an expected greater stability of the 5-membered ring.[3] Crystallographic analyses[4] of some 2-hydroxycarboxylates (bis(glycolato)copper(II), aquobis(lactato)copper(II) hemihydrate, diaquobis(2-hydroxy-2-methylpropanoato)copper(II)), have shown the carboxylic acids to be acting in a bidentate fashion, with 2 *trans*-chelate rings around the copper. It has been proposed[2] that in 4-hydroxycarboxylate complexes the acid may act solely as a unidentate ligand.

Recently, the dihydroxy acids, 2,3-dihydroxy-2-methylpropanoic acid (DHMP), and 2,3-dihydroxy-2-methylbutanoic acid (DHMB) have been synthesized in high yields.[5,6] Subsequently, the stability constants of the successive 1 : 1 and 1 : 2 copper complexes of the anions of these acids and the copper complexes of 2-hydroxy-2-methylpropanoate (HMP) were reported.[7] It was proposed that both dihydroxy anions (DHMP, DHMB) act in a bidentate fashion, forming complexes with geometries similar to the tetragonal geometry already reported[4] for the HMP complex. This is in contrast to the behavior exhibited with the lighter rare earths, where both acid anions are thought to bond tridently.[8] Based on the assumption of a bidentate ligand character with an overall tetragonal geometry, the statistical rest term (S) in Bjerrum's statistical ratio theory[9] was estimated and applied to find E, the ligand repulsion effect in the copper complexes of HMP, DHMP, and DHMB. It was found that E increases in the sequence DHMB<DHMP<HMP with the inductive effects on these ligands changing in the reverse order.

The present structural investigation was undertaken to determine the denticity of DHMP in its copper complex, the geometry around the copper, and, if the ligand is acting only in a bidentate fashion, the preferred ring form.

Experimental

Crystals of the complex $Cu(DHMP)_2 \cdot 2H_2O$ were prepared by dissolving one mol of cupric carbonate into an aqueous solution containing two mol of DHMP and allowing the solvent to slowly evaporate at room temperature. The blue platelets which formed were collected by filtration, washed with cold, distilled water, and dried in air at room temperature. Most of the crystals grown were prohibitively large, thus it was necessary to excise a smaller fragment of rough dimensions 0.23 × 0.19 × 0.13 mm for the structure determination.

The crystal was placed on a four-circle diffractometer and initial ω-oscillation photographs were taken. These photographs verified that the crystal was indeed single. From these photographs, seventeen reflections were accurately located on the diffractometer and their

---

[a] Work performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

coordinates were fed into our automatic indexing program.[20] The unsymmetrical cell scalars suggested a C-centered monoclinic cell, and after application of the appropriate transformation matrix and a least-squares refinement,[10] lattice constants of a = 5.688 ± .006 Å, b = 20.79 ± .03 Å, c = 10.569 ± .016 Å and β = 94.55 ± .06° were obtained. Oscillation photographs taken along the three crystal axes showed only the appropriate mirror symmetry perpendicular to the b-axis. The density determined by flotation methods was 1.78 g/cm^3 and the value calculated for $Z = 4$ was 1.80 g/cm^3.

Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory and previously described by Rohrbaugh and Jacobson.[11] Within a 2Θ sphere of 45° ($(\sin\Theta/\lambda) = 0.538\,\text{Å}^{-1}$), all data in the hkl and $hk\bar{l}$ octants were measured using graphite monochromated Mo Kα radiation ($\lambda = 0.70954\,$Å) and the ω-scan technique. The systematic extinctions of hkl, $h+k \neq 2n$ and h0l, $l \neq 2n (h \neq 2n)$, established the space group as Cc or C2/c. The Howells, Phillips, and Rogers[12] statistical test for a center of symmetry indicated the space group was the centrosymmetric C2/c.

The intensity data were then corrected for Lorentz-polarization effects, but no absorbtion correction was made (μ = 18.6 cm^{-1}). The maximum and minimum transmission factors differed by about 9%. The estimated error in each intensity was calculated by

$$\sigma_I = C_T + 2C_B + (0.03C_T)^2 + (0.03C_B)^2$$

where C_T and C_B represent the total count and background count, respectively, and the factor 0.03 represents an estimate of non-statistical errors. The estimated deviations in the structure factors were calculated by the finite difference method.[13] Of the 1268 independent reflections, 860 were considered observed ($I_o > 2\sigma(I_o)$).

The program MULTAN[14] was employed to unambiguously reveal the position of the copper at 1/4, 1/4, 0, indicating $\bar{1}$ molecular symmetry. The remaining atoms were found by successive structure factor[15] and electron density map calculations.[16] With all atoms isotropic, several cycles of full-matrix least-squares procedure (minimizing the function $\Sigma w(|F_o|-|F_c|)^2$, where $w = 1/\sigma_F{}^2$) resulted in an R of 0.237. Refinement with all atoms anisotropic reduced this to a final value of R = 0.090. The largest shift/error for the last cycle was 0.01, and examination of observed and calculated structure factors revealed no appreciable extinction effects. Attempts to include the methylene hydrogens in the refinement had no effect on the final agreement factor.

The atomic scattering factors used were those of Hanson *et al.*,[17] with the copper modified for anoma-

TABLE I. Atomic Coordinates in Crystalline $Cu(C_4O_4H_7)_2 \cdot 2H_2O$[a].

Atom	Fractional Coordinates × 10^4		
	x	y	z
Cu[b]	2500	2500	0
O_1	5351(14)	2967(4)	230(11)
O_2	6925(13)	3935(4)	242(11)
O_3	2774(21)	4012(5)	−2146(10)
O_4	1053(14)	3363(4)	−8(10)
O_5	2422(17)	2370(4)	2388(11)
C_1	5191(20)	3591(6)	205(13)
C_2	2735(21)	3892(5)	136(15)
C_3	2362(24)	4319(6)	−1032(13)
C_4	2409(23)	4242(7)	1411(15)

[a] In this and succeeding tables, standard deviations are given in parentheses for the least significant figures. [b] The copper atom is in a special position so its coordinates are symmetry required.

TABLE II. Anisotropic Thermal Parameters in Crystalline $Cu(C_4O_4H_7)_2 \cdot 2H_2O$[a].

Atom	Anisotropic Parameters, Å^2 × 10^4					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	103(6)	9(1)	200(4)	1(1)	21(4)	−2(1)
O_1	113(27)	13(2)	201(16)	6(6)	22(17)	−2(4)
O_2	84(28)	11(2)	201(16)	−0(6)	37(16)	−0(4)
O_3	410(45)	32(3)	100(14)	11(10)	6(20)	9(5)
O_4	112(25)	10(2)	166(13)	−2(6)	27(15)	−2(4)
O_5	237(30)	24(3)	137(12)	−2(8)	−1(16)	−7(5)
C_1	111(37)	12(3)	113(17)	5(9)	7(20)	−1(5)
C_2	66(34)	11(3)	145(20)	−4(9)	25(21)	2(6)
C_3	214(45)	17(3)	88(16)	−3(10)	13(22)	3(6)
C_4	152(42)	22(4)	129(19)	−3(10)	32(23)	−11(7)

[a] The anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE III. Selected Interatomic Distances (Å) for Cu $(C_4O_4H_7)_2 \cdot 2H_2O$.

Cu–O1	1.890(8)	O3–C3	1.38(2)
Cu–O4	1.974(8)	O4–C2	1.46(1)
Cu–O5	2.542(12)	C1–C2	1.52(2)
O1–C1	1.30(1)	C2–C3	1.52(2)
O2–C1	1.22(1)	C2–C4	1.56(2)

TABLE IV. Bond Angles (deg) for $Cu(C_4O_4H_7)_2 \cdot 2H_2O$.

O1–Cu–O4	83.5(3)	O3–C3–C2	113.6(11)
O1–Cu–O5	90.5(4)	O4–C2–C1	106.6(9)
O4–Cu–O5	93.5(3)	O4–C2–C3	107.9(11)
Cu–O1–C1	116.9(7)	O4–C2–C4	108.7(11)
Cu–O4–C2	114.5(6)	C1–C2–C3	110.3(13)
O1–C1–C2	118.2(10)	C1–C2–C4	108.7(11)
O1–C1–O2	122.1(10)	C3–C2–C4	114.3(10)
O2–C1–C2	119.7(10)		

lous dispersion.[18] The final positional and thermal parameters are listed in Tables I and II. The standard deviations were calculated from the inverse matrix of the final least-squares cycle. Bond lengths and bond angles are listed in Tables III and IV, respectively.[19] A table of structure factors is available from the Editor upon request.

Discussion

As can be seen from an illustration of the molecule (Figure 1), the DHMP anion acts as a bidentate ligand, with chelation occurring through a carboxyl oxygen O(1) and the 2-hydroxy oxygen O(4). The distance of 3.90 Å between copper and the 3-hydroxy group O(3) rules out any bonding interaction between them. In comparison, the distances from copper to the carboxyl oxygen and the 2-hydroxy oxygen are 1.89 Å and 1.97 Å, respectively. Other selected bond distances and angles are given in Tables III and IV.

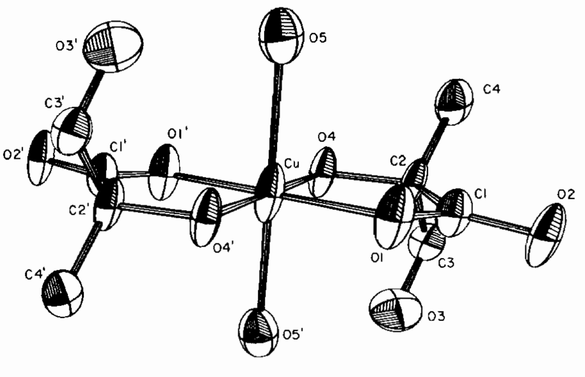

Figure 1. The molecular structure of $Cu(C_4O_4H_7)_2 \cdot 2H_2O$, with thermal ellipsoids drawn at the 50% probability level.

The molecule has a crystallographic center of symmetry about the copper. The geometry around the copper is a distorted octahedron with the axial bonds elongated, a structure common to most six-coordinate copper complexes. The two water molecules occupy the axial positions. As is dictated by symmetry, the four equatorial oxygens are coplanar. The chelate ring itself is nearly planar, with the greatest deviation from the least-squares plane being 0.05 Å for the copper.

The sum of the interior angles around the five-membered ring is 539.7°, compared to 540° for an ideal planar ring.

The hydrogen bonding between molecules in the crystal is extensive. In the *a* direction each molecule forms four hydrogen bonds (two to each molecule related by a translation in either direction in *a*). Both bonds involve interaction between the hydrogen on the chelating 2-hydroxy oxygen O(4) and the free carboxyl oxygen O(2) of the neighboring molecule. The distance between the hydrogen bonded oxygens is 2.66 Å. The direction of the bonding is indicated in Figure 2.

The molecules are joined together in the *c*-direction by another network of hydrogen bonds. Each molecule is hydrogen bonded to the two nearest molecules in each row above and below it. The axial water O(5) extending above the molecule interacts with a water molecule extending down from one of the molecules situated in the row 1/2 a unit cell away in the *c* direction. The oxygen–oxygen distance involved is 2.78 Å. Hydrogen bonding to the other molecule is implied by an oxygen–oxygen distance of 2.70 Å between 3-hydroxy groups O(3) on each molecule. The other water–water and 3-hydroxy–3-hydroxy distances are 2.92 and 3.18 Å, respectively. These distances and the proposed hydrogen bonding are indicated in Figure 2. Interaction between molecules in the *b*-direction involves only weak van der Waals forces as the closest inter-molecular contact is 5.69 Å, and nicely accounts for the mica-like nature of the crystals.

The present structure verifies that the DHMP is acting only in a bidentate manner, with chelation through the 2-hydroxy group to form a 5-membered ring. It seems that the steric strain which would be imposed on the 6-membered ring by an approximate octahedral geometry around the copper is great enough to prevent the 3-hydroxy group from chelating, to form such a ring. In view of the greater coordination numbers and diverse geometries seen for the rare earths, it is entirely possible that such strain would be absent in the $Ln(DHMP)_3$ species, allowing the ligand to act in a tridentate fashion. Efforts to grow single crystals of the lanthanide–DHMP complexes have been, thus far, unsuccessful.

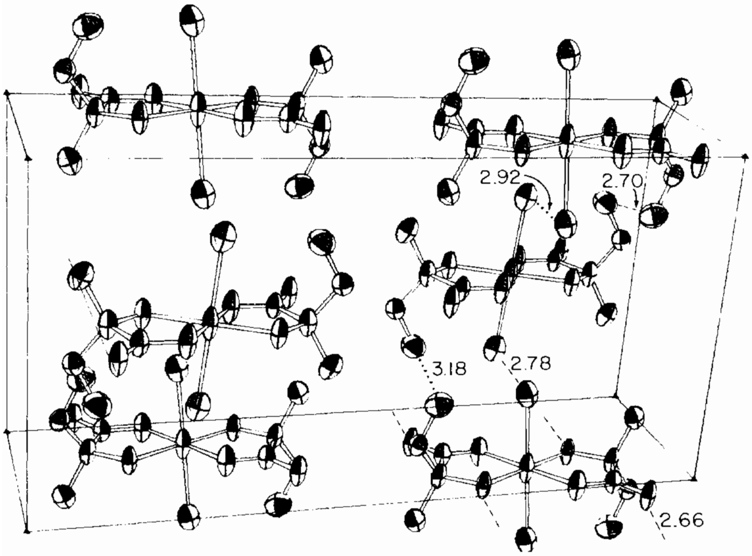

Figure 2. Three dimensional diagram of crystal structure of $Cu(C_4O_4H_7)_2 \cdot 2H_2O$ viewed down the x axis. The z axis is vertical.

References

1 K.D. Dillon and F.J.C. Rossotti, *Chem. Commun.*, 768 (1966).

2 K.D. Dillon and F.J.C. Rossotti, *J. Chem. Soc. Dalton,* 1005 (1973).

3 Z. Warnke and E. Kwiatkowski, *Roczniki Chem., 47,* 467 (1973).

4 C.K. Prout, R.A. Armstrong, J.R. Carruther, J.G. Forest, P. Murray-Rust and F.J.C. Rossotti, *J. Chem. Soc. A, 11,* 2791 (1968).

5 J.E. Powell, H.R. Burkholder and J.L. Farrell, *J. Chromatogr., 57,* 309 (1971).

6 J.E. Powell, S. Kulprathipanja, D.A. Johnson and H.R. Burkholder, *ibid., 74,* 265 (1972).

7 J.E. Powell and S. Kulprathipanja, *Inorg. Chim. Acta, 11,* 31 (1974).

8 J.E. Powell, J.L. Farrell and S. Kulprathipanja, *Inorg. Chem., 14,* 786 (1975).

9 J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Haase, Copenhagen, 1941.

10 D.E. Williams, "LCR-2, a Fortran Lattice Constant Refinement Program," U.S. Atomic Energy Commission Report IS-1052, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1964. The Nelson-Riley extrapolation function was used in the refinement.

11 W.J. Rohrbaugh and R.A. Jacobson, *Inorg. Chem., 13,* 2535 (1974).

12 E.R. Howells, D.C. Phillips and D. Rogers, *Acta Crystallogr., 3,* 210 (1950).

13 S.L. Lawton and R.A. Jacobson, *Inorg. Chem., 7,* 2124 (1968).

14 P.M. Main, M.M. Woolfson and G. Germain, "MULTAN: A Computer Program for the Automatic Determination of Crystal Structures," Department of Physics, Univ. of York, York, England, 1960.

15 W.R. Busing, K.O. Martin and H.A. Levy, "ORFLS, a Fortran Crystallographic Least Squares Program," U.S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

16 C.R. Hubbard, C.O. Quicksall and R.A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT, and FRIEDEL," U.S. Atomic Energy Commission Report IS-2625, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1971.

17 H.P. Hanson, F. Herman, J.D. Lea and S. Skillman, *Acta Crystallogr., 17,* 1040 (1960).

18 D.H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

19 W.R. Busing, K.O. Martin and H.A. Levy, "ORFEE, a Fortran Crystallographic Function and Error Program," U.S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

20 R.A. Jacobson, "An Algorithm for Automatic Indexing and Bravais Lattice Selection. The Programs BLIND and ALICE," U.S. Atomic Energy Commission Report IS-3469, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1974.