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Copper Complex of α-Aminooxyacetic Acid. The Crystal and Molecular Structure of Diaquo-bis(aminooxyacetate)copper(II) Dihydrate, $[Cu(C_2H_4NO_3)_2(H_2O)_2] \cdot 2H_2O$

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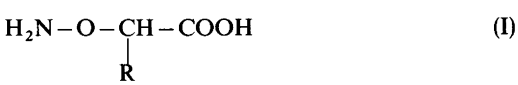
The structure of diaquo-bis(aminooxyacetate)copper(II) dihydrate has been determined by X-ray crystallographic methods, using diffractometer data collected at room temperature. The crystals are orthorhombic, space group *Pbca*, with $a = 5.2092(3)$, $b = 18.8395(9)$, $c = 11.1252(6)$ Å. The structure was solved by the heavy atom method, and refined by full-matrix least-squares to an R of 0.023. The copper ion is situated on a centre of symmetry, and has a 4+2 elongated octahedral coordination. Two aminooxyacetate ions coordinate to each copper ion through the amino nitrogen (Cu–N = 1.978 Å) and a carboxylate oxygen (Cu–O1 = 1.967 Å), forming the equatorial plane, while the axial positions are occupied by water molecules (Cu–O4 = 2.545 Å). The six-membered chelate ring is appreciably puckered.

Certain α-aminooxy acids, (I), are known to possess antibacterial properties. Several papers on chemical



(I)

properties and biological activity of these compounds have been published.[1–5] An early investigation suggested that simple α-aminooxy acids did not form complexes with divalent metals.[6] Shortly afterwards, however, Zilichovsky reported the isolation of a copper(II) complex of α-aminooxyacetic acid[5] and recently a paper on the isolation and characterization of a series of Cu(II), Co(II) and Ni(II) complexes of various α-aminooxy acids appeared.[7] The stability of these complexes in aqueous solutions is reported to be appreciably lower than that of analogous amino acid complexes. This is the first crystal structure to be reported for this class of compounds.

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EXPERIMENTAL

The compound was synthesized according to the procedure described by Zilichovsky.[5] Bright blue prismatic crystals grew upon recrystallization from water by slow evaporation at room temperature. The crystal used for data collection had dimensions $0.45 \times 0.26 \times 0.30$ mm. Data were recorded at room temperature (20 °C ± 1 °C) on an Enraf-Nonius CAD-4 diffractometer using monochromatized Mo$K\alpha$ radiation and the ω-scan technique. Scan widths were $\Delta\omega = 0.50 + 0.35 \tan\theta$, and the scan speed was varied between 3.3 and 0.4° min.$^{-1}$ depending on peak intensity. Three reference reflections were monitored. The strongest one increased by approximately 25 % in the course of the data collection, indicating extinction. Towards the end of the data collection no further increase was observed. Thus, the strong, low order reflections, up to $\theta = 18°$, were recollected, and replaced the corresponding original measurements. The final data set consists of 1884 independent reflections up to $\theta = 30°$, 1390 of these have $I > 2\sigma_I$, and were used in the refinement. The error in the intensity of any one reflection was estimated as $\sigma_I = [\sigma_c^2 + (0.03N_{net})^2]^{\frac{1}{2}}$. The intensities were corrected for Lorentz and polarization effects and for absorption; the maximum and minimum transmission factors being 0.76 and 0.57, respectively.

CRYSTAL DATA

Diaquo-bis(aminooxyacetate)copper(II) dihydrate, $[Cu(C_2H_4NO_3)_2(H_2O)_2]\cdot 2H_2O$, orthorhombic, *Pbca* (No. 61), $a=5.2092(3)$, $b=18.8395(9)$, $c=11.1252(6)$Å, $V=1091.8(2)$Å^3, $M=315.72$, $Z=4$, $D_m=1.93$ g cm^{-3}, $D_X=1.923$ g cm^{-3}, $\mu(MoK\alpha)=21.36$ cm^{-1}, $\lambda=0.71069$Å.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by the Patterson method. Cu and O1 positions were taken from the Patterson map, the remaining non-hydrogen atoms were localized in subsequent Fourier syntheses. The atoms were refined first isotropically, then anisotropically. Hydrogen atoms were localized in a difference Fourier map and were refined isotropically. In the final cycles of full-matrix least-squares refinement an extinction parameter was included and refined, $g=5.99\times10^{-7}$, $[F_{obs}^{corr}=F_{obs}(1+gI_{obs})]$. The weight assigned to each reflection in the refinement is $w=1/\sigma_F^2$, where $\sigma_F=\sigma_I(I\cdot Lp)^{-\frac{1}{2}}$. The refinement converged at an R of 0.023, the weighted R being 0.040 and the standard deviation of an observation of unit weight 2.03.

Atomic scattering factors used were those of Cromer and Waber.[8] All calculations were carried out on a PDP 11/55 computer using the Enraf-Nonius Structure Determination Programs (SDP).[9]

Final atomic parameters are listed in Table 1. An ORTEP drawing of the formula unit, including atomic numbering scheme, bond lengths and angles are shown in Fig. 1. Lists of structure factors may be obtained from the author.

RESULTS AND DISCUSSION

The copper ion is situated on a centre of symmetry and has a 4+2 elongated octahedral coordination. Two aminooxyacetate ions are coordinated in the equatorial plane, each through the amino nitrogen (Cu–N = 1.978 Å) and a carboxylate oxygen (Cu–O1 = 1.967 Å). Due to symmetry requirements the ligand atoms N, N^i, O1, O1^i and the metal ion Cu(II) are exactly coplanar. The axial positions are occupied by two water molecules (Cu–O4 = 2.545 Å). The observed coordination is similar to that found in a number of α-amino acid– and β-amino acid–Cu(II) complexes, *e.g.* Refs. 10–18; the apical ligands being either water molecules and/or carboxylate groups from neighbouring molecules.

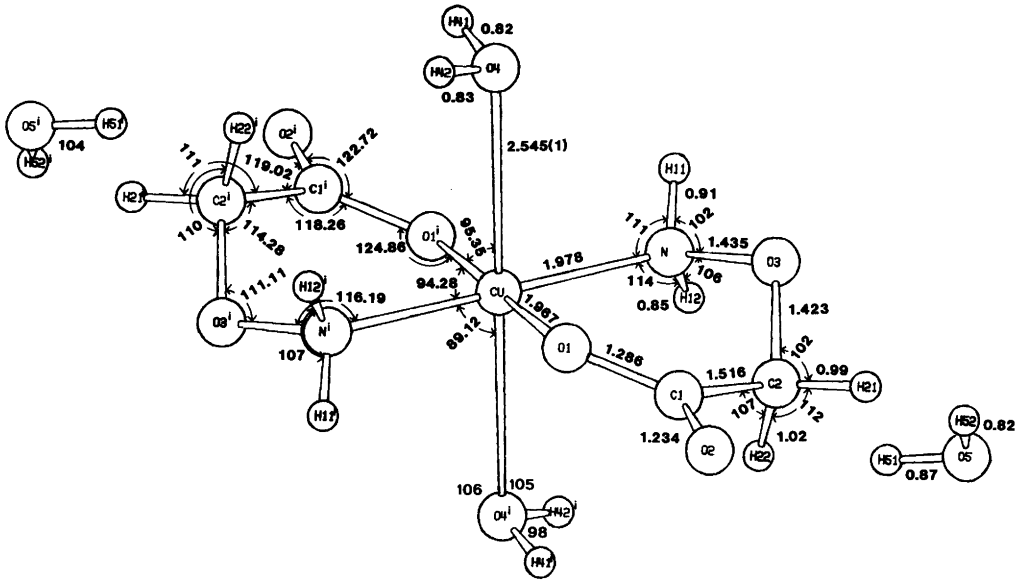

Fig. 1. The formula unit. Standard deviations in bond distances involving non-hydrogen atoms are 0.001 Å, in distances involving hydrogen 0.02 Å. Standard deviations in bond angles at Cu are 0.03°, in other angles involving non-hydrogen atoms 0.05–0.08° and in angles involving hydrogen 1°.

Table 1. Final atomic parameters with standard deviations, as obtained from the inverse least-squares matrix, in parentheses. Anisotropic temperature factor: $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{23}klb^*c^*)]$. Isotropic temperature factor: $\exp[-B\sin^2\theta/\lambda^2]$.

Atom	X	Y	Z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Cu	0.0000(0)	0.0000(0)	0.0000(0)	0.0207(1)	0.0235(1)	0.0275(1)	−0.00260(7)	0.00462(7)	−0.00509(6)
O1	0.2657(2)	0.07418(6)	0.00523(7)	0.0234(4)	0.0264(4)	0.0394(5)	−0.0023(4)	0.0066(3)	−0.0056(3)
O2	0.3867(2)	0.18604(5)	0.02800(10)	0.0313(5)	0.0292(4)	0.0526(5)	−0.0078(4)	0.0073(4)	−0.0035(4)
O3	−0.0804(2)	0.09816(5)	0.19885(7)	0.0295(4)	0.0342(4)	0.0259(4)	−0.0079(4)	0.0009(4)	−0.0061(3)
O4	0.2881(2)	−0.06499(5)	0.14850(8)	0.0334(4)	0.0307(4)	0.0391(4)	−0.0005(4)	0.0054(4)	−0.0011(4)
O5	0.4148(2)	0.29945(5)	0.18780(9)	0.0418(5)	0.0320(4)	0.0427(5)	0.0005(4)	−0.0032(5)	−0.0023(4)
N	−0.1959(2)	0.03935(6)	0.13705(9)	0.0208(4)	0.0275(4)	0.0270(4)	−0.0019(4)	0.0002(3)	−0.0036(4)
C1	0.2319(2)	0.13751(7)	0.0457(1)	0.0209(4)	0.0247(5)	0.0284(5)	0.0005(4)	−0.0025(4)	−0.0001(4)
C2	−0.0098(2)	0.15287(7)	0.1169(1)	0.0261(5)	0.0237(5)	0.0380(6)	−0.0002(4)	0.0047(4)	−0.0042(5)
				B	Atom	*X*	*Y*	*Z*	*B*
H11	−0.210(3)	0.0069(9)	0.197(2)	2.5(3)	H41	0.227(3)	−0.1047(12)	0.156(2)	4.2(4)
H12	−0.347(3)	0.0521(9)	0.119(1)	3.3(3)	H42	0.417(3)	−0.0757(10)	0.109(2)	3.5(3)
H21	0.015(3)	0.1940(10)	0.172(2)	2.5(3)	H51	0.402(4)	0.2658(12)	0.135(2)	4.9(4)
H22	−0.153(3)	0.1614(9)	0.057(2)	3.4(4)	H52	0.564(4)	0.2972(10)	0.210(2)	3.7(4)

In the α-amino acid complexes the ligands form stable five-membered chelates.[10-15] The introduction of an oxygen atom between the α-carbon and the amino group results in a six-membered chelate ring which is appreciably puckered, C1, C2, O3 being displaced by -.48, -.81 and .14Å, respectively, from the equatorial plane. The ring strain is relieved mainly through rotation around the single bonds C1 – C2, C2 – O3, O3 – N, as seen from the torsional angles listed in Table 2. The puckering is comparable to that found in the six-membered chelate rings of β-amino acid – Cu(II) complexes.[16-19]

The difference in chelate ring geometry between the α-aminooxy acid complex and the α-amino acid complexes apparently does not produce significant differences in the metal – ligand bond distances. In recent structure determinations of α-amino acid complexes[12-15] Cu-$O_{carboxyl}$ distances are found in the range 1.944 – 1.970 Å, and Cu – N_{amino} distances in the range 1.970 – 2.035 Å as compared to 1.967 and 1.978 Å, respectively, in the present structure. *A priori* the introduction of an electron withdrawing group adjacent to the amino nitrogen is expected to reduce the bonding ability of the coordinating lone pair. However, the observed comparatively short Cu – N bond is not in accordance with this simple picture of charge distribution. An accurate low temperature study of the compound is being undertaken in order to determine deformation electron density distribution in the complex.

All internal bond angles are somewhat larger in the α-aminooxy acid chelate than in the α-amino

Table 2. Torsional angles in the chelate ring. Angle *I, J, K, L* is defined as the angle between vectors *J,I* and *K,L* when viewed down *J,K*; positive values denote clockwise rotation of *KL*.

I, J, K, L	Torsional angles (°)
Cu,O1,Cl,O2	−166.6
Cu,O1,C1,C2	12.8
O1,C1,C2,O3	41.0
C1,C2,O3,N	−76.6
C2,O3,N,Cu	52.1
O3,N,Cu,O1	−6.2
N,Cu,O1,C1	−26.9

[a] The asymmetric units are marked as follows:

i:	$1-x,-y,-z$	v:	$-\frac{1}{2}+x,y,\frac{1}{2}-z$
ii:	$1+x,y,z$	vi:	$\frac{1}{2}-x,\frac{1}{2}+y,z$
iii:	$\frac{1}{2}-x,-\frac{1}{2}+y,z$	vii:	$-1+x,y,z$
iv:	$\frac{1}{2}+x,y,\frac{1}{2}-z$	viii:	$-x,y+\frac{1}{2},\frac{1}{2}-z$

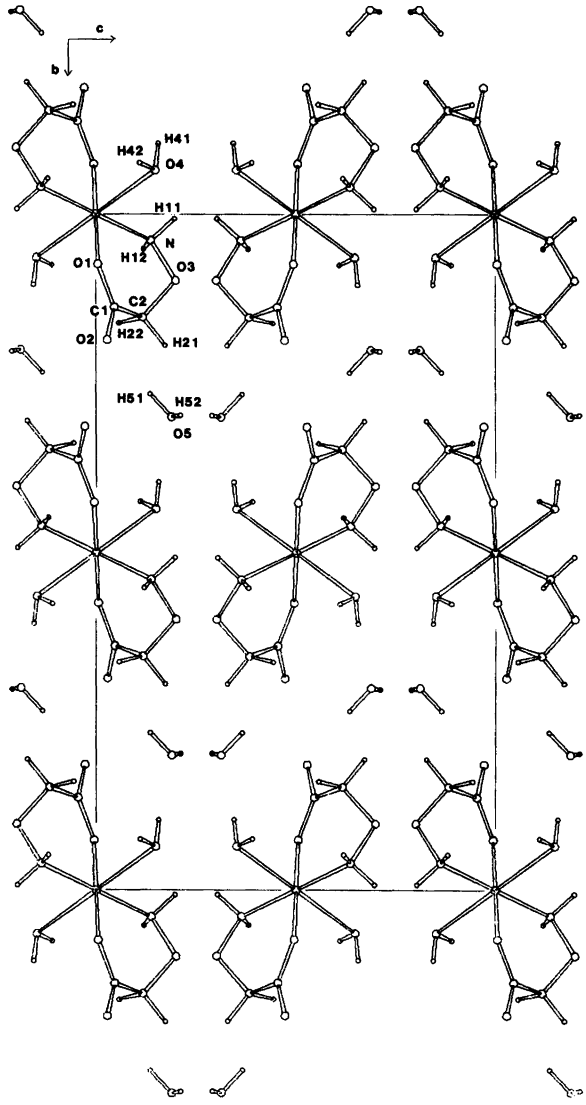

Fig. 2. Crystal packing as viewed down the *a*-axis.

acid chelates, the major differences being in the angles at O1, N and Cu. The N–Cu–O1 angle in the present compound is 94.28° as compared to the range 82.4–86.9° in the α-amino acid complexes referred to above. Corresponding values for Cu–O1–Cl are 124.86 and 112.8–117.7°, and for Cu–N–O3(C2) 116.19 and 105.5–110.3°. In β-amino acid complexes bond angles similar to those in the present structure have been found.[16-19]

The coordinated carboxylic oxygen, O1, participates in two hydrogen bonds, one to the coordinated water molecule and one to the amino group in neighbouring units (Table 3 and Fig. 2). Although the latter contact is rather long (O1---N^{ii} = 3.233 Å), it has been included in the list of hydrogen bonds as the angle at $H12^{ii}$ is 161°. The other carboxylic oxygen, O2, participates in one hydrogen bond to the water of hydration. O3 does not form hydrogen bonds, but has short contacts to symmetry related O3 atoms; O3---$O3^{iv}$ and O3---$O3^{v}$ = 2.843(1)Å),

Table 3. Hydrogen bonds.[a]

	A---H (Å)	A---D (Å)	∠A---H–D (°)
a. Hydrogen bond distances and angles at H-atoms			
O1---H42^{i}–O4^{i}	2.09(2)	2.891(1)	164(1)
O1---H12^{ii}–N^{ii}	2.42(2)	3.233(1)	161(1)
O2---H51–O5	1.92(2)	2.781(1)	175(2)
O4-H41---O5^{iii}	1.98(2)	2.796(1)	175(1)
O4---H11^{iv}–N^{iv}	2.19(2)	3.090(1)	174(1)
O5---H52^{v}–O5^{v}	2.15(2)	2.950(1)	166(1)
b. Hydrogen bond angles at A and D			
∠Cu-N$_H$---O1^{vii}	100.06(2)	∠Cu-O4$_H$---O1^{i}	96.88(2)
∠Cu-N$_H$---O4^{v}	111.74(2)	∠Cu-O4$_H$---O5^{iii}	108.47(3)
∠O3-N$_H$---O1^{vii}	115.12(5)	∠Cu-O4---$_H$N^{iv}	102.18(2)
∠O3-N$_H$---O4^{v}	97.60(5)	∠O1^{i}---$_H$O4$_H$---O5^{iii}	110.00(3)
∠O1^{vii}---$_H$N$_H$---O4^{v}	117.08(5)	∠O1^{i}---$_H$O4---$_H$N^{iv}	118.19(3)
		∠O5^{iii}---$_H$O4---$_H$N^{iv}	118.01(3)
∠Cu-O1---$_H$O4^{i}	120.41(3)		
∠Cu-O1---$_H$N^{ii}	118.71(3)	∠O2---$_H$O5---$_H$O4^{vi}	125.49(4)
∠Cl-O1---$_H$O4^{i}	111.87(5)	∠O2---$_H$O5---$_H$O5^{v}	104.65(4)
∠Cl-O1---$_H$N^{ii}	98.54(5)	∠O2---$_H$O5$_H$---O5^{v}	110.25(4)
∠O4$^{i}_H$---O1---$_H$N^{ii}	63.76(5)	∠O4$^{vi}_H$---O5---$_H$O5^{v}	74.88(3)
		∠O4$^{vi}_H$---O5$_H$---O5^{iv}	114.04(3)
∠Cl-O2---$_H$O5	120.04(5)	∠O5$^{v}_H$---O5$_H$---O5^{iv}	124.09(6)

< O3^{iv}---O3---O3^{v} = 132.84(6)°. The coordinated water molecule participates in three hydrogen bonds, and the water of hydration in four, giving both water molecules somewhat distorted tetrahedral environments.

The hydrogen bonds described above, lace the molecules together in a three-dimensional network. Complex units related by the lattice translation *a* are linked by hydrogen bond O1---H42^{i}–O4^{i}. Units related by the *a*-glide are connected through N1–H11---O4^{v} and through the water of hydration, O2---H51-O5---H52^{v}–O5^{v}–H51^{v}---O2^{v}. Units related by the *b*-glide and the *c*-glide are also connected through water of hydration, by the sequences O2---H51-O5---H41–O4^{vi} and O2---H51-O5---H52^{v}–O5^{v}---H41^{viii}-O4^{viii}, respectively.

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