Structure and Stability of Carboxylate Complexes. Part XIII.[1] Crystal and Molecular Structure of Aquobis(*NN*-dimethylglycinato)copper(II) Dihydrate

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The crystal and molecular structure of the title compound (orthorhombic, $a = 7{\cdot}05 \pm 0{\cdot}01$, $b = 31{\cdot}7 \pm 0{\cdot}05$, $c = 6{\cdot}51 \pm 0{\cdot}01$ Å, space group $P2_12_12_1$ visual data, 1111 independent reflections) has been determined by three-dimensional *X*-ray methods and refined by least squares to *R* 0·12. The copper atom is five-co-ordinate; a square-based pyramid with the ligand water molecule at the apex (mean Cu–N 2·05, Cu–O 1·97; Cu–OH_2 2·28 Å) and the basal ligands in the *trans*-configuration. The structural relationship between this and similar simple copper aminocarboxylate complexes is discussed.

THE crystal and molecular structures of numerous copper(II) complexes of aminocarboxylates and peptides have been collated.[2] Few structures of *N*-alkylaminocarboxylates appear to have been studied. We report the structure of copper(II) *NN*-dimethylglycinate.

EXPERIMENTAL

Preparation.—Basic copper carbonate was dissolved in the amino-acid and the excess of the carbonate filtered off. The pH was adjusted to 5 to suppress hydrolysis and the solution left to evaporate slowly until crystals appeared.

Crystal data.—$C_8H_{22}CuN_2O_7$, $M = 321{\cdot}8$, Orthorhombic, $a = 7{\cdot}05 \pm 0{\cdot}01$, $b = 31{\cdot}72 \pm 0{\cdot}05$, $c = 6{\cdot}51 \pm 0{\cdot}01$ Å, $U = 1455{\cdot}8$ Å^3, $D_m = 1{\cdot}46$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}47$ g cm^{-3}, $F(000) = 169$; Space group $P2_12_12_1$ (D_2^4, No. 19). Equi-inclination Weissenberg photographs, Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 24·28 cm^{-1}.

Unit-cell dimensions were measured from zero-layer Weissenberg photographs and the intensities of 1111 independent reflections were estimated visually from equi-inclination Weissenberg photographs (*hk*0—4). Data were corrected for Lorentz and polarisation effects but not for absorption.

In the three-dimensional Patterson function there were three well-resolved prominent maxima consistent with a single copper atom in the asymmetric unit in the space group $P2_12_12_1$. The positions of the remaining atoms, except hydrogen, were established from successive F_o syntheses. Preliminary atomic parameters were refined by six cycles of full-matrix least-squares. The first two cycles assumed isotropic and the subsequent four anisotropic thermal motion. Unit weights were used throughout. The refinement converged at *R* 0·121. There were no significant features in the final difference synthesis; hydrogen atoms were not located.

The observed structure amplitudes and the structure factors calculated from the final atomic parameters in Table 1 are given in Supplementary Publication No. SUP 20835 (8 pp. 1 microfiche).* Atomic scattering factors were those for neutral atoms[3] and were corrected for the real part of the anomalous dispertion.

RESULTS AND DISCUSSION

The crystal structure projected down the *c* axis is shown in Figure 1 and the molecule projected along the

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* See Notice to Authors No. 7, *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are sent as full-size copies).

[1] Part XII, K. B. Dillon and F. J. C. Rossotti, *J.C.S. Dalton*, 1973, 1005.

[2] H. C. Freeman, *Adv. Protein Chem.*, 1967, **22**, 257.

[3] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, p. 220.

axis of the C(1)-C(2) and of the C(3)-C(4) bonds is shown in Figure 2. Interatomic distances and interbond angles are given in Table 2.

The crystals contain aquobis(*NN*-dimethylglycinato)-copper(II) complexes in general positions in the unit cell with two crystallographically distinct *NN*-dimethylglycinato-ligands, and two molecules of water of crystallisation, which link the complexes by hydrogen bonding. The hydrogen bonds associated with oxygen atom O(6) of one water molecule [O(6$^{\text{III}}$) · · · H-O(4) 2·73, O(6)-H · · · O(3) 2·81, O(6$^{\text{II}}$)-H · · · O(3) 2·77 Å] form a helical arrangement around the two-fold screw axis in the zone of the *c* axis, and bond together two molecules of the complex which are also related by this axis, while the hydrogen bonds associated with the oxygen atom O(7) of the second water molecule [O(7$^{\text{I}}$) · · · H-O(4) 2·70, O(7$^{\text{I}}$)-H . . . O(2) 2·73, O(7)-H · · · O(5) 2·77 Å] hold together three adjacent helical stacks. The oxygen atom O(4) of the water molecule in the complex forms hydrogen bonds with both water molecules of crystallisation (Figure 1 and Table 2).

The copper atom is in a five-co-ordinate square-based pyramidal configuration, the base of which is formed from the nitrogen and oxygen atoms N(1), O(1), N(2), and O(2) in the *trans*-configuration. Mean Cu-O and Cu-N bond lengths are 1·97 and 2·05 Å. The copper atom is displaced 0·27 Å from the least-squares best basal plane towards the oxygen atom of the water molecule at the apex, which is 2·28 Å from the metal atom and 2·53 Å from the basal plane. There is no other atom of an

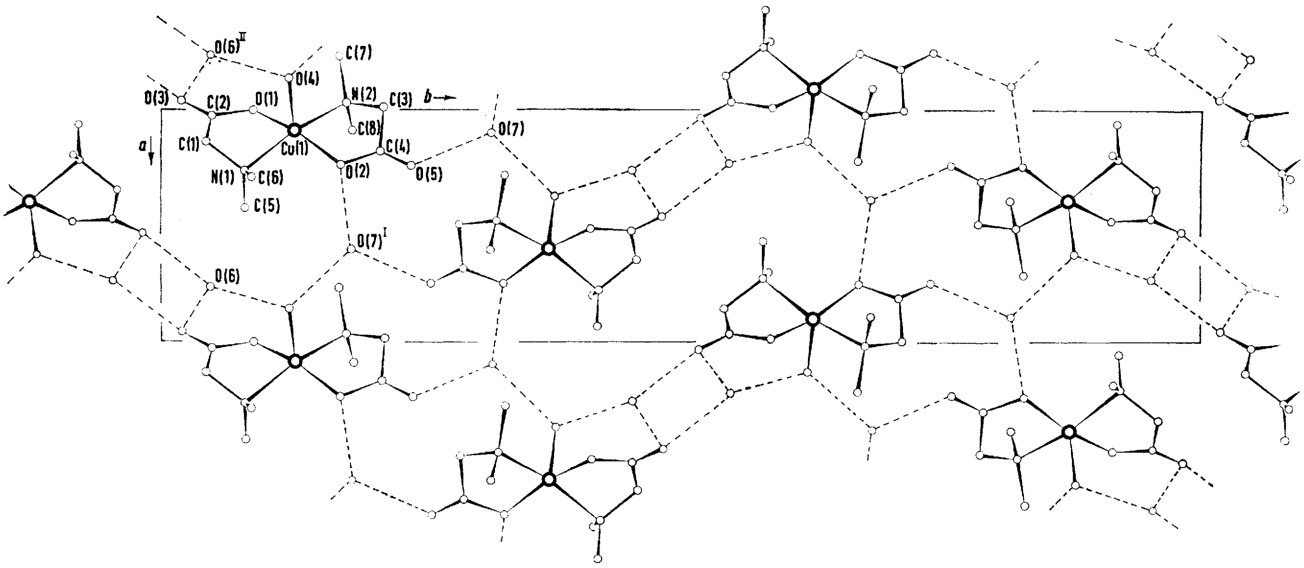

FIGURE 1 Projection of the unit cell of aquobis(*NN*-dimethylglycinato)copper(II) dihydrate along [001]

TABLE 1

Final atomic parameters * (× 10^4)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{23}	U_{23}	U_{13}	U_{12}
Cu(1)	936(5)	1284(1)	2020(7)	296(2)	1(1)	210(3)	55(3)	−314(4)	21(3)
C(1)	1430(36)	417(6)	2678(55)	253(15)	21(15)	570(31)	52(23)	−350(31)	−15(17)
C(2)	268(39)	483(7)	645(59)	318(16)	23(10)	431(25)	269(25)	−294(33)	−18(20)
C(3)	−45(41)	2142(7)	1862(60)	493(16)	78(9)	272(25)	46(28)	−203(39)	−22(21)
C(4)	1862(41)	2091(7)	3086(67)	254(16)	26(11)	649(30)	86(30)	34(41)	62(21)
C(5)	4303(41)	800(9)	1779(71)	162(16)	417(16)	904(35)	−366(40)	205(43)	−78(27)
C(6)	2978(42)	816(8)	5273(59)	322(17)	239(14)	375(31)	513(30)	−448(35)	−107(26)
C(7)	−2316(48)	1710(8)	−267(72)	300(19)	238(13)	526(37)	−101(37)	−473(45)	−88(27)
C(8)	989(56)	1830(8)	−1431(58)	592(21)	272(12)	405(32)	425(27)	361(45)	−25(32)
N(1)	2545(30)	796(5)	3095(44)	260(11)	60(8)	351(21)	83(19)	−198(29)	−95(17)
N(2)	−211(32)	1781(5)	411(41)	361(13)	35(8)	203(19)	19(20)	−333(26)	88(17)
O(1)	40(26)	869(4)	−4(35)	427(11)	2(7)	453(19)	238(17)	−276(23)	−171(14)
O(2)	2467(27)	1718(5)	3419(36)	195(9)	48(7)	665(19)	−119(17)	−442(23)	85(14)
O(3)	−364(26)	185(4)	−289(37)	431(11)	11(7)	424(18)	−351(16)	−228(21)	−92(13)
O(4)	8623(25)	1211(5)	4446(36)	300(11)	130(8)	308(16)	−40(17)	33(20)	162(14)
O(5)	260(29)	2405(4)	3902(38)	396(12)	42(7)	824(22)	−208(17)	−329(24)	−211(15)
O(6)	−2734(36)	−456(6)	1225(35)	553(16)	289(11)	714(28)	−612(24)	693(31)	−640(22)
O(7)	1029(37)	3180(5)	4859(43)	399(13)	169(9)	1003(24)	−351(21)	916(34)	−456(20)

* The temperature factor $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{23}klb^*c^* + U_{13}hla^*c^* + U_{12}hka^*b^*)]$ Å^2.

adjacent molecule which might be considered to form a long sixth contact.

The dimensions of the two ligands do not differ significantly from each other or from those of other similar chelating amino-acids. Both chelate rings are significantly non-coplanar, as illustrated by the torsion angles between the bonds within these rings (Figure 2), and the torsion angle N(1)–C(2)–C(1)–O(1), 18°, is significantly less than N(2)–C(4)–C(3)–O(2), 30°. The deviation from planarity of the chelate rings may be explained by a combination of three factors: steric and conformational interactions, the requirements of hydrogen bonding, and the requirements for chelate formation. The twist about the bonds Cu(1)–O(2), C(4)–O(2), and C(2)–O(1) (Table 3) is probably largely determined by the steric requirement of the hydrogen bonds to the oxygen atoms and the twist about the bonds C(1)–C(2), C(1)–N(1), C(3)–C(4), and C(3)–N(2) all relieve the interactions between the methyl groups bonded to the nitrogen atoms, the hydrogen atoms on the adjacent carbon atom and the oxygen atom of the carboxy-group. There may also be some adjustment to the conformation of the rings so that the ligand atoms are in optimum positions for chelate formation. The twist about the bonds Cu(1)–N(1) and Cu(1)–N(2) will relieve the interaction between the methyl groups bonded to the nitrogen atoms and the apical oxygen atom O(4) bonded to the copper atom. This, while increasing the O(4) · · · Me contact distances, brings the two methyl groups below the base of the pyramid close together.

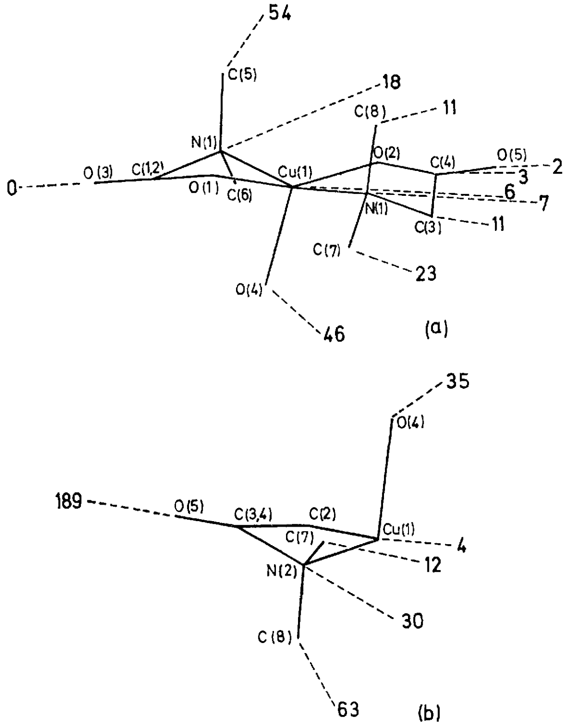

FIGURE 2 Angular bearing of the atoms with respect to the axis of (a) the C(1)–C(2) bond, and (b) the C(3)–C(4) bond

TABLE 2

Distances (Å) and angles (deg)

(*a*) Distances

Cu(1)–N(1)	2·04(2)	N(2)–C(3)	1·49(3)
Cu(1)–N(2)	2·06(2)	N(2)–C(7)	1·56(4)
Cu(1)–O(1)	1·97(2)	N(2)–C(8)	1·48(4)
Cu(1)–O(2)	1·97(2)		
Cu(1)–O(4)	2·28(2)	C(1)–C(2)	1·57(4)
		C(2)–O(1)	1·30(3)
N(1)–C(1)	1·46(3)	C(2)–O(3)	1·21(3)
N(1)–C(5)	1·51(4)	C(3)–C(4)	1·57(4)
N(1)–C(6)	1·45(4)	C(4)–O(2)	1·28(3)
		C(4)–O(5)	1·25(3)

(*b*) Hydrogen bond distances

O(2) · · · O(7^{I})	2·73(2)	O(4) · · · O(6^{III})	2·73(3)
O(3) · · · O(6)	2·81(3)	O(4) · · · O(7^{I})	2·70(2)
O(3) · · · O(6^{II})	2·77(3)	O(5) · · · O(7)	2·77(2)

(*c*) Angles

N(1)–Cu(1)–N(2)	166·6(8)	C(5)–N(1)–C(6)	112·5(23)
N(1)–Cu(1)–O(1)	84·3(8)	N(1)–C(1)–C(2)	109·4(18)
N(1)–Cu(1)–O(2)	93·9(9)	C(1)–C(2)–O(1)	117·6(23)
N(1)–Cu(1)–O(4)	94·7(8)	C(1)–C(2)–O(3)	120·6(24)
N(2)–Cu(1)–O(1)	92·6(7)	O(1)–C(2)–O(3)	121·7(26)
N(2)–Cu(1)–O(2)	85·1(8)		
N(2)–Cu(1)–O(4)	98·6(8)	Cu(1)–N(2)–C(3)	103·6(15)
O(1)–Cu(1)–O(2)	162·3(8)	Cu(1)–N(2)–C(7)	114·0(16)
O(1)–Cu(1)–O(4)	99·5(7)	Cu(1)–N(2)–C(8)	105·6(16)
O(2)–Cu(1)–O(4)	98·2(8)	C(3)–N(2)–C(7)	111·4(21)
		C(3)–N(2)–C(8)	112·9(21)
Cu(1)–N(1)–C(1)	105·1(14)	C(7)–N(2)–C(8)	109·3(21)
Cu(1)–N(1)–C(5)	104·8(18)	N(2)–C(3)–C(4)	108·0(23)
Cu(1)–N(1)–C(6)	114·7(18)	C(3)–C(4)–O(2)	117·9(27)
C(1)–N(1)–C(5)	110·1(21)	C(3)–O(4)–C(5)	119·4(27)
C(1)–N(1)–C(6)	109·4(20)	O(2)–C(4)–O(5)	122·1(29)

(*d*) Hydrogen bond angles

C(4)–O(2) · · · O(7^{I})	105	Cu(1)–O(4) · · · O(6^{III})	123
C(2)–O(3) · · · O(6)	128	Cu(1)–O(4) · · · O(7^{I})	122
C(2)–O(3) · · · O(6^{II})	110	C(4)–O(5) · · · O(7)	130

Roman numeral superscripts denote atoms in the following equivalent positions, relative to the reference molecule at x, y, z:

I $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ III $\frac{1}{2} - x, -y, \frac{1}{2} + z$
II $-\frac{1}{2} - x, -y, -\frac{1}{2} + z$

TABLE 3

Torsion angles (deg)

O(1)–Cu(1)–N(2)–C(3)	−10·6	O(2)–Cu(1)–N(1)–C(1)	−13·5
Cu(1)–N(2)–C(3)–C(4)	36·2	Cu(1)–N(1)–C(1)–C(2)	33·0
N(2)–C(2)–C(4)–O(2)	−30·5	N(1)–C(1)–C(2)–O(1)	18·1
C(3)–C(4)–O(2)–Cu(1)	−6·0	C(1)–C(2)–O(1)–Cu(1)	−8·4
C(4)–O(2)–Cu(1)–N(1)	−0·2	C(2)–O(1)–Cu(1)–N(2)	−9·5

In the analogous glycine [4] complex, where the chelate rings are nearly planar, the N–C–C–O torsion angle is 4°. The aquo-ligands at the apex of the essentially square-based pyramidal co-ordination polyhedron repel the hydrogen atom from each amino-group which is above the basal plane, and cause the amino-groups to turn with respect to the Cu–N bonds with a consequential twist about the C–C bond to preserve the tetrahedral configuration about the nitrogen atom. The other pair of

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[4] H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *Acta, Cryst.*, 1944, **17**, 1463.

amino-hydrogen atoms below the basal plane partially block access to the sixth co-ordination position of the potentially octahedral co-ordination sphere. The complex has a $Cu-OH_2$ contact of 2·40 Å and a long Cu · · · O–C–O contact to a neighbouring molecule of 2·74 Å. When the amino-hydrogen atoms are replaced by the more bulky methyl groups in the present compound this effect is enhanced. The greater repulsion between the methyl groups and the aquo-ligands causes a yet larger twist about the Cu–N bond and consequently the greater N–C–C–O torsion angles. This results not only in much greater non-planarity of the chelate rings but also the *N*-methyl groups below the basal plane block access to the sixth co-ordination site. This complex is therefore truly five-co-ordinate whereas Freeman was able to describe [2] the glycine complex as being five-and-a-half-co-ordinate. In a hypothetical *NN*-diethylglycine complex the increased bulk of the diethyl as compared with the dimethyl substituents cannot in itself be expected to increase the twist about the Cu–N bond and the complex would be expected to be five-co-ordinate. However the *NN*-diethylalanine [5] complex is truly square-planar. Here the twist about the ring C–C bond is on average still greater (*ca.* 30°) to relieve strain between the ring methyl group and the *N*-substituted methylene group. Further, for one of the two ligands, repulsion between the 2-methyl group and one of its two *N*-ethyl groups causes the methyl of this *N*-ethyl substituent to turn towards the copper atom to block the fifth co-ordination position and the methylene $-CH_2-$ of its other *N*-ethyl group is similarly placed to one of the methyl groups in the *NN*-dimethylglycine complex and blocks the sixth co-ordination position. (The situation at the other ligand is inverted by the centre at the copper.) It appears also that the ring methyl groups themselves in the *cis*-D- [6] and the *trans*-L-alanine [7] complexes of copper are relatively effective in blocking one or both of the axial co-ordination sites.

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[5] C. P. Nash and W. P. Schaefer, *J. Amer. Chem. Soc.*, 1969, **91**, 1319.

[6] R. D. Gillard, R. Mason, N. C. Payne, and G. B. Robertson, *J. Chem. Soc.* (*A*), 1969, 1864.

[7] A. Dijkstra, *Acta Cryst.*, 1966, **20**, 588.

[8] J. S. Rollett and G. Ford, unpublished work.