1130 computer which were used were written by Drs R. Shiono and G. L. Gartland.

References

ABRAHAMSSON, S. & PASCHER, I. (1966). *Acta Cryst.* **21**, 79–87.

AJO, D., BOSSA, M., DAMIANI, A., FIDENZI, R., GIGLI, S., LANZI, L. & LAPICCIRELLA, A. (1972). *J. Theoret. Biol.* **34**, 15–20.

BEVERIDGE, D. L. & RADNA, R. J. (1971). *J. Amer. Chem. Soc.* **93**, 3759–3764.

CANEPA, F. G., PAULING, P. & SØRUM, H. (1966). *Nature, Lond.* **210**, 907–909.

CULVENOR, C. C. J. & HAM, N. S. (1970). *Chem. Commun.* pp. 1242–1243.

HERDKLOTZ, J. K. & SASS, R. L. (1970). *Biochem. Biophys. Res. Commun.* **40**, 583–588.

HJORTÅS, J. & SØRUM, H. (1971). *Acta Cryst.* B**27**, 1320–1323.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JELLINEK, F. (1957). *Acta Cryst.* **10**, 277–288.

JENSEN, B. (1970). *Acta Chem. Scand.* **24**, 2517–2524.

KIER, L. B. (1967). *Mol. Pharmacol.* **3**, 487–494.

LIQUORI, A. M., DAMIANI, A. & DECOEN, J. (1968). *J. Mol. Biol.* **33**, 445–450.

PARTINGTON, P., FEENY, J. & BURGEN, A. S. V. (1972). *Mol. Pharmacol.* **8**, 269–277.

PULLMAN, B., COURRIERE, P. & COUBEILS, J. L. (1971). *Mol. Pharmacol.* **7**, 397–405.

SHEFTER, E. (1971). *Cholinergic Ligand Interactions*, p. 83–117. Edited by D. J. TRIGGLE, J. F. MORGAN, & C. A. BARNARD. New York: Academic Press.

SUNDARALINGAM, M. (1968). *Nature, Lond.* **217**, 35–37.

SUNDARALINGAM, M. & JENSEN, L. H. (1965). *Science*, **150**, 1035–1036.

Acta Cryst. (1973). B**29**, 1136

The Metal Complexes of Peptides and Related Compounds. VII. The Crystal Structure of Bis-(6-aminohexanoato)copper(II) Dihydrate

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The crystal structure of bis-(6-aminohexanoato)copper(II) dihydrate has been determined from 993 independent, visually estimated reflexions, which were recorded using equi-inclination Weissenberg photographs and Cu $K\alpha$ radiation. The monoclinic, $P2_1/n$ unit cell has the dimensions $a = 8{\cdot}550$ (2), $b = 20{\cdot}068$ (3), $c = 5{\cdot}145$ (1) Å, and $\beta = 106{\cdot}85$ (2)°; it contains four asymmetric units. The structure was solved by using standard Fourier techniques, and refined by the method of least squares ($R = 0{\cdot}066$). Four aminohexanoate molecules are coordinated to a central copper atom, two of them *via* a carboxylate oxygen atom and the other two *via* a nitrogen atom [Cu–O = 1·967 (5) Å, Cu–N = 1·994 (6) Å]. These centrosymmetric ligand atoms form an almost square plane, and they are *trans* with respect to each other. The second oxygen atoms of the two carboxylate groups bound, one above and one below the 'square' plane, complete a distorted octahedron [Cu–O = 2·768 (6) Å]. Each ligand molecule binds two copper atoms, forming a two-dimensional network; the networks are connected by hydrogen bonds formed between the amino nitrogen atoms and carboxylate oxygen atoms, and *via* water molecules which are hydrogen bonded to nitrogen and carboxylate oxygen atoms.

Introduction

As part of a general study on copper–protein interaction, the copper ion complexes of 6-aminohexanoic acid are being investigated. This particular ligand is intended as a model for carboxylate and ε-amino side chains present in proteins. In a solution study, we have previously shown that the carboxylate group rather than the ε-amino group of aminohexanoic acid interacts with copper(II) ions (Österberg & Toftgård, 1972). In the corresponding copper(I) system, on the other hand, our data indicate that copper(I) is bound to the ε-amino group (Österberg & Sjöberg, 1972). Here, we report the crystal structure of bis-(6-aminohexanoato)-copper(II) dihydrate, which clearly demonstrates that copper(II) ions interact with the ε-amino group in the solid state.

Experimental

The crystals used in this study were prepared by one of the methods developed by Sjöberg (doctoral dissertation, to be published): bis-(1,5-cyclooctadiene)-

copper(I) perchlorate, synthesized as described by Manahan (1966), was dissolved in a neutral water solution of 6-aminohexanoic acid; the cyclooctadiene was removed by extraction with ether; when oxygen from the air was gradually introduced, oxidation occurred and violet crystals of bis-(6-aminohexanoato)-copper(II) dihydrate separated. The results of chemical analyses are:

Found: Cu = 17·9, C = 40·1, N = 7·8, H_2O = 10·0 %
Calc.: Cu = 17·7, C = 40·0, N = 7·8, H_2O = 10·0 %.
$C_6H_{12}O_2N.\frac{1}{2}Cu.H_2O$. F.W. 179·96. Monoclinic, a = 8·550 ± 0·002, b = 20·068 ± 0·003, c = 5·145 ± 0·001 Å, β = 106·85 ± 0·02°, D_m = 1·40, D_c = 1·41 g cm^{-3}, U = 844·9 Å^3, Z = 4, $F(000)$ = 382, λ(Cu $K\alpha_1$) = 1·5405 Å, λ(Cu $K\alpha_2$) = 1·5443 Å.

Table 1. *Guinier powder data of bis-(6-aminohexanoato)copper(II) dihydrate*

The reflexions indicated by an asterisk (*) coincided with the reflexions from the internal standard, $Pb(NO_3)_2$. In the table heading m means the multiplicity factor.

h	k	l	d_o (Å)	d_c (Å)	I_o	mF_c^2	h	k	l	d_o (Å)	d_c (Å)	I_o	mF_c^2
0	2	0	10.0338	10.0340	vs	16222	2	7	-1	*	2.2711	*	20244
1	1	0	7.5796	7.5769	vs	16231	1	8	-1	2.2312	2.2321	m	15396
1	2	0	6.3477	6.3413	m	4065	1	5	-2	2.1644	2.1658	w	11798
1	3	0	5.1804	5.1789	m	4417	2	8	0		2.1386		11054
0	4	0	5.0171	5.0170	m	2926	3	0	1	2.1359	2.1377	m	15513
0	1	1	4.7833	4.7823	vs	27166	3	6	-1	2.1214	2.1230	m	24593
1	2	-1	4.3986	4.3972	s	21182	3	3	-2	2.0606	2.0612	w	6311
2	1	0	4.0074	4.0088	s	19477	4	3	-1	2.0185	2.0203	w	12104
0	3	1	*	3.9656	*	3464	0	6	2		1.9828		10617
1	3	-1	*	3.9487	*	13614	2	6	-2	1.9737	1.9744	m	23342
1	0	1	3.7648	3.7644	vs	36992	1	7	-2		1.9146		13680
1	1	1	3.6994	3.6999	vs	24706	2	9	-1	1.9123	1.9127	s	19707
1	5	0	3.6022	3.6034	w	4009	3	5	-2		1.9065		12321
1	2	1	*	3.5246	*	7225	4	5	-1	1.8731	1.8741	vw	6926
1	4	-1	*	3.5024	*	11890	3	8	-1		1.8525		11364
2	2	-1	*	3.4893	*	14213	2	2	2	1.8502	1.8499	m	10169
0	5	1		3.1111		6432	4	2	-2	1.8289	1.8296	w	9526
1	5	-1	3.1030	3.1029	vs	14602	1	11	0	1.7798	1.7806	vw	6093
1	6	-1	2.7589	2.7610	s	10514	2	4	2	*	1.7623	*	5544
2	1	1	2.7471	2.7498	s	16028	2	8	-2	*	1.7512	*	11642
1	7	0		2.7056		6371	4	4	-2	*	1.7446	*	8656
3	1	0	2.7010	2.7027	s	37025	1	7	2	1.7437	1.7398	vw	9231
2	6	0	2.5883	2.5895	vw	5773	4	1	1	1.7108	1.7143	vw	8306
2	3	1	2.5616	2.5640	vw	11067	2	1	-3	1.6971	1.6975	vw	8431
3	3	-1	2.5395	2.5414	vw	5405	1	9	-2	1.6846	1.6849	vw	12620
3	3	0	2.5217	2.5256	vw	7389	2	3	-3	1.6514	1.6509	vw	5550
0	7	1		2.4775		9495	2	6	2		1.6403		3188
1	7	-1	2.4725	2.4734	m	13741	2	11	-1	1.6369	1.6381	vw	4251
1	3	-2	2.4024	2.4010	vw	9094	3	10	-1	1.6189	1.6205	vw	7935
0	2	2	*	2.3911	*	7493	2	10	-2	1.5508	1.5515	m	16323

The space group, $P2_1/n$, was determined from systematic extinctions: $0k0$, absent for odd k; $h0l$, absent for odd $h+l$. (The setting differs from those given in *International Tables for X-ray Crystallography*, 1952.)

The density was measured by the flotation method, using a mixture of carbon tetrachloride and 1,2-dimethylbenzene. The unit-cell dimension was obtained from a powder photograph taken with a Guinier camera at 21°, using $Pb(NO_3)_2$ as an internal standard. The parameters, λ(Cu $K\alpha_1$) = 1·54051 Å and $a[Pb(NO_3)_2]$ = 7·8566 Å, were those listed in *International Tables for X-ray Crystallography* (1962). The cell parameters are based on a least-squares refinement using 41 d values and a modified version of the computer program *LETAGROP* (Ingri & Sillén, 1965); the observed and calculated d values, and the corresponding intensities are listed in Table 1.

Equi-inclination, multiple-film Weissenberg data were recorded by rotating the crystal about the a axis ($0kl$) and the c axis ($hk0$–$hk4$). A crystal with the dimensions 0·3 × 0·3 × 0·4 mm was used. The intensities were visually estimated. They were corrected for the Lorentz and polarization factors, and placed upon a common scale by correlation among equivalent reflexions recorded on the two axes; a total of 993 independent reflexions were recorded.

Structure determination and refinement

For the space group $P2_1/n$ there are four equivalent positions: $\pm(x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$, and, since there are only two copper atoms in the unit cell they were assigned the positions 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. A three-dimensional Fourier synthesis, using phases calculated from the copper atom, revealed the remaining non-hydrogen atoms, except the oxygen atoms of the water molecules. Those positions of the atoms first found were refined using block-diagonal least-squares calculations and isotropic temperature factors. Then a difference

Table 2. *The fractional coordinates* (× 10^4) *of the atomic positions and the anisotropic parameters* (× 10^4) *for non-hydrogen atoms*

Anisotropic temperature factor: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	95 (2)	10 (0)	212 (7)	−3 (2)	132 (5)	5 (2)
N	9407 (9)	756(3)	2044 (14)	119 (11)	11 (1)	307 (33)	−4 (6)	213 (29)	7 (10)
C(1)	9460 (13)	1454 (4)	1188 (18)	200 (18)	16 (2)	336 (42)	0 (9)	367 (42)	11 (13)
C(2)	8883 (12)	1950 (4)	2892 (18)	182 (18)	18 (2)	339 (45)	14 (9)	297 (41)	7 (13)
C(3)	9095 (12)	2666 (4)	2150 (19)	163 (17)	17 (2)	314 (44)	9 (9)	268 (38)	−12 (13)
C(4)	8424 (12)	3164 (4)	3747 (18)	194 (18)	16 (2)	339 (45)	21 (9)	327 (42)	−1 (13)
C(5)	8588 (12)	3883 (4)	2975 (20)	165 (17)	15 (2)	339 (46)	13 (9)	297 (38)	−12 (13)
C(6)	7614 (10)	4338 (3)	4278 (14)	149 (14)	14 (2)	222 (35)	4 (7)	210 (32)	4 (11)
O(1)	6103 (6)	4418 (2)	3007 (10)	98 (8)	13 (1)	332 (24)	1 (5)	165 (22)	−7 (8)
O(2)	8237 (7)	4600 (3)	6503 (11)	154 (11)	29 (2)	294 (27)	25 (7)	88 (25)	−64 (11)
O(3)	6584 (10)	595 (4)	4400 (20)	131 (13)	39 (3)	533 (43)	−21 (9)	215 (37)	77 (16)

Fourier synthesis was calculated and the water oxygen atoms were located. Structure factors calculated at this stage had a reliability index, R, of 0·22; $R=\sum||F_o|-|F_c||/\sum|F_o|$. Three cycles of full-matrix least-squares refinement reduced R to 0·132. Anisotropic temperature factors and individual scale factors for the five layers further reduced R to 0·084. Through another difference Fourier synthesis the hydrogen atoms were located. Their peak electron densities ranged from 0·8 to 1·2 e $Å^{-3}$, except for the hydrogen atom H(13) which had a peak density of 0·5 e $Å^{-3}$. When the refinement was continued, now including the hydrogen atoms with isotropic temperature factors, R dropped to 0·072.

During the final refinement, the calculated structure factors were corrected for the anomalous dispersion of copper, $\Delta f'=-2{\cdot}15$ and $\Delta f''=0{\cdot}75$ (Cromer, 1965). The least-squares refinement was terminated when the shifts of the parameters were less than 0·02 of the calculated standard deviations. The final R is 0·066. An additional difference Fourier synthesis was calculated; the peaks, positive and negative, were all below 0·5 e $Å^{-3}$.

The final parameters of the atoms are listed in Tables 2 and 3. The table of observed and calculated structure factors is available.*

The scattering factors used for C, N, O, and Cu^+ were those described by Doyle & Turner (1968), and those for the hydrogen atoms were obtained from Stewart, Davidson & Simpson (1965). In the final cycles of refinement, weights were used according to the formula described by Cruickshank (1965):

$$w=(45{\cdot}0+F_o+0{\cdot}015F_o^2+0{\cdot}0002F_o^3)^{-1}.$$

* The table has been deposited with the National Lending Library, England, as Supplementary Publication No. 30071. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Positional parameters and isotropic temperature factors for the hydrogen atoms*

	Bonded to	x	y	z	B
H(1)	O(3)	0·588 (15)	0·058 (7)	0·337 (25)	5·3 (4·1)
H(2)	O(3)	0·657 (11)	0·035 (5)	0·584 (20)	4·6 (2·3)
H(3)	N	1·001 (12)	0·071 (5)	0·390 (20)	4·8 (2·4)
H(4)	N	0·856 (12)	0·068 (4)	0·277 (18)	4·1 (2·1)
H(5)	C(1)	1·062 (14)	0·157 (5)	0·134 (20)	5·7 (2·5)
H(6)	C(1)	0·870 (14)	0·149 (6)	−0·068 (23)	7·2 (3·1)
H(7)	C(2)	0·772 (11)	0·185 (4)	0·296 (15)	3·6 (1·8)
H(8)	C(2)	0·946 (9)	0·184 (4)	0·476 (17)	3·2 (1·8)
H(9)	C(3)	1·021 (13)	0·281 (5)	0·231 (19)	5·0 (2·3)
H(10)	C(3)	0·862 (11)	0·274 (4)	0·047 (19)	3·6 (2·1)
H(11)	C(4)	0·712 (12)	0·307 (5)	0·403 (18)	5·3 (2·2)
H(12)	C(4)	0·893 (14)	0·316 (6)	0·560 (24)	7·2 (3·1)
H(13)	C(5)	0·958 (18)	0·406 (7)	0·348 (27)	8·7 (3·9)
H(14)	C(5)	0·832 (13)	0·389 (5)	0·121 (24)	5·8 (2·9)

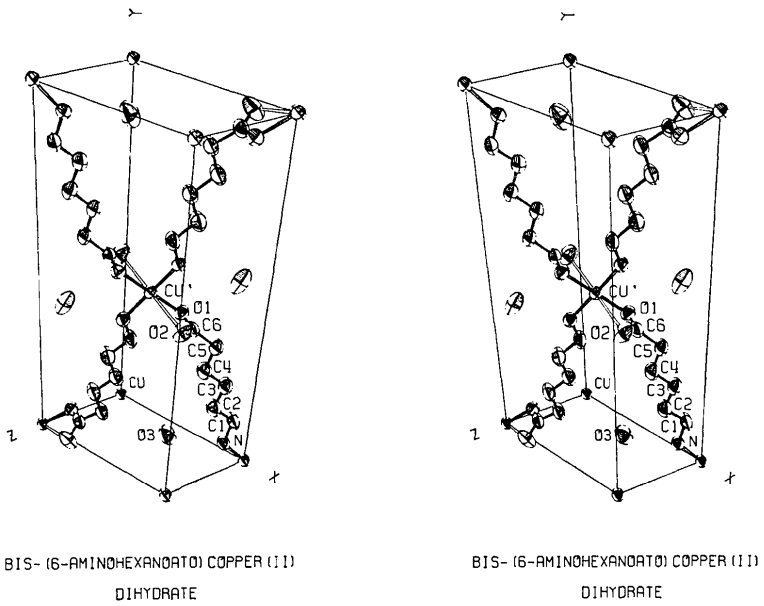

Fig. 1. A stereoscopic drawing of bis-(6-aminohexanoato)copper(II) dihydrate, showing the unit cell and its contents. The thermal ellipsoids are scaled to include a probability of 80%.

Preliminary calculations were performed on a SAAB D21 computer using the program system described by Abrahamsson, Aleby, Larsson, Nilsson, Selin & Westerdahl (1965). The calculations were completed on an IBM 360/65 computer using the program library of the Department of Inorganic Chemistry, University of Göteborg: *LALS*, least-squares full-matrix refinement, originally written by P. K. Gantzel, R. A. Sparks & K. N. Trueblood, University of California, Los Angeles; *BLOCK*, least-squares block-diagonal refinement, originally written by O. Lindgren, University of Göteborg; *DRF*, Fourier summations, and *DISTAN*, angles and distances and their standard deviations, originally written by A. Zalkin, University of California, Berkeley. The drawings were produced by *ORTEP*, written by Johnson (1965).

Table 4. *Bond distances and angles*

Symmetry-related atoms are denoted as follows:

	x, y, z;	v	$1+x, y, z$
′	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$;	vi	$x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$
″	$1-x, 1-y, 1-z$;	vii	$1\frac{1}{2}-x, y-\frac{1}{2}, 1\frac{1}{2}-z$
‴	$1\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$;	viii	$1-x, -y, 1-z$
iv	$x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$;		

(*a*) In the coordination polyhedron

Cu′–O(1)	1·967 (5) Å	O(1)–Cu′–N‴	86·8 (2)°
Cu′–O(2)	2·768 (6)	O(1)–Cu′–O(2)	51·8 (2)
Cu′–N‴	1·994 (6)	O(2)–Cu′–N‴	88·9 (2)

(*b*) In the 6-aminohexanoato molecule

N—C(1)	1·472 (10) Å	Cu^{v}–N—C(1)	122·1 (5)°
C(1)–C(2)	1·502 (12)	N—C(1)–C(2)	114·4 (7)
C(2)–C(3)	1·510 (11)	C(1)–C(2)–C(3)	113·5 (8)
C(3)–C(4)	1·508 (12)	C(2)–C(3)–C(4)	113·5 (8)
C(4)–C(5)	1·515 (11)	C(3)–C(4)–C(5)	114·2 (8)
C(5)–C(6)	1·517 (12)	C(4)–C(5)–C(6)	110·7 (8)
C(6)–O(1)	1·278 (9)	C(5)–C(6)–O(1)	116·9 (7)
C(6)–O(2)	1·232 (9)	C(5)–C(6)–O(2)	121·5 (8)
		O(1)–C(6)–O(2)	121·5 (7)
		C(6)–O(1)–Cu′	112·0 (4)
		C(6)–O(2)–Cu′	74·7 (5)

(*c*) Involving hydrogen atoms

H(1)–O(3)	0·68 (13) Å	H(8)—C(2)	0·97 (8) Å
H(2)–O(3)	0·90 (10)	H(9)—C(3)	0·98 (11)
H(3)–N	0·95 (10)	H(10)–C(3)	0·85 (9)
H(4)–N	0·92 (10)	H(11)–C(4)	1·18 (10)
H(5)–C(1)	1·00 (11)	H(12)–C(4)	0·93 (12)
H(6)–C(1)	1·00 (12)	H(13)–C(5)	0·89 (14)
H(7)–C(2)	1·03 (9)	H(14)–C(5)	0·87 (12)

Description of the structure

The atomic arrangement in the unit cell of bis-(6-aminohexanoato)copper(II) dihydrate is shown in Fig. 1. The interatomic distances and angles, as well as their standard deviations, are given in Table 4.

Four aminohexanoate molecules are coordinated to each copper atom, two of them *via* a carboxylate oxygen atom and the other two *via* a nitrogen atom. In the cell, each copper atom is centrosymmetrically surrounded by these four ligands (Fig. 1). Each ligand coordinates two copper atoms forming two-dimensional, four-connected networks. These are parallel to the (101) plane.

The coordination about the copper atom is planar for the four closest, centrosymmetrical ligands which nearly form a square (Fig. 2). These two oxygen and nitrogen atoms are *trans* with respect to each other. The distances Cu–O(1) = 1·967 (5) and Cu–N = 1·994 (6) Å are in close agreement with those determined previously for similar copper(II) structures (Freeman, 1967; Cingi, Guastini, Musatti & Nardelli, 1970). The second oxygen atoms, O(2) and O(2″), of the two carboxylate groups bound, one above and one below the 'square' plane, complete a distorted octahedron at 2·768 (5) Å from the copper; thus, the coordination number of the copper atom is six. The distortion is clearly indicated by the fact that the angles of O(1)–Cu′–O(2) and O(1″)–Cu′–O(2″) are equal to 51·8 (2)°, and thus both of these Cu–O bonds are bent in the direction of their neighbouring oxygen atoms, O(1), (Fig. 2).

Table 5. *Least-squares planes*

(*a*) Coefficients

The equations of the planes are expressed in the form

$$AX+BY+CZ=D$$

where X, Y, and Z are Cartesian coordinates obtained from the fractional coordinates x, y, and z by the transformation:

$$X=8{\cdot}5500x-1{\cdot}4914z, \quad Y=20{\cdot}0\text{Є}8y, \quad \text{and} \quad Z=4{\cdot}9241z\,.$$

Plane		A	B	C	D
1	O(1)O(2)C(6)C(5)	0·39518	0·79050	−0·46791	8·2042
2	NC(1)C(2)C(3)C(4)C(5)C(6)	−0·68147	−0·04565	−0·73043	−6·0654

(*b*) Deviations from planes (Å)

(The figures within the parentheses were not included in the calculation of the plane.)

Δ (1)

O(1)	O(2)	C(5)	C(6)	Cu′
−0·004	−0·005	+0·012	−0·003	(−0·030)

Δ (2)

N	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Cu′	Cu^{v}	O(1)	O(2)
−0·012	+0·113	−0·035	−0·033	−0·099	−0·062	+0·128	(+1·404)	(+0·239)	(+1·329)	(−0·833)

The following three planes formed by the centrosymmetric ligand atoms all pass through the central copper atom by symmetry (Fig. 2): O(1)N'''O(1'')N^{iv}, (plane *A*); O(1)O(2)O(1'')O(2''), (plane *B*); O(2)N'''O(2'')N^{iv}, (plane *C*). The angle between the 'square' plane (plane *A*) and plane *B* is 91·2°, that between plane *B* and plane *C* is 93·3°, and that between plane *B* and the plane of the carboxylate group (plane 1 of Table 5) is equal to 0·7°.

Bond lengths and angles for the ligand molecule are listed in Table 4. The C–C and C–N bond lengths, and the corresponding angles, agree with the average values obtained from previously determined structures. The difference between the C(6)–O(1) and the C(6)–O(2) bond lengths reflects the difference in the strength of the coordinate bonds in which the oxygen atoms, O(1) and O(2), are involved. The carboxylate group, O(1)O(2)C(6)C(5), is planar; its least-squares plane forms an 87·9° angle with the plane defined by the chain NC(1)C(2)C(3)C(4)C(5)C(6) (plane 1 and plane 2 in Table 5).

The two-dimensional networks are linked together by hydrogen bonds (Fig. 3). The water molecule, H(1)O(3)H(2), has contacts with three different coordination spheres *via* the carboxylate oxygen atoms, O(2^{vi}) and O(2^{vii}), and the hydrogen atom H(4) of the amino group. The remaining hydrogen, H(3), of the amino group, is bonded to the carboxylate oxygen atom O(1'), (Fig. 3). The hydrogen bond parameters are listed in Table 6.

Table 6. *Hydrogen bond parameters*

Donor (*X*)	Acceptor (*Y*)	Hydrogen	*X*–H···*Y*	*X*–H	*X*···*Y*
O(3)	O(2^{vi})	H(1)	156°	0·68 Å	2·85 Å
O(3)	O(2^{vii})	H(2)	164	0·90	2·88
N	O(1')	H(3)	174	0·95	3·01
N	O(3)	H(4)	175	0·92	3·02

The shortest C–C distance between two different networks is 4·17 Å [C(2)–C(4')]. For the hydrogen atoms not involved in hydrogen bonds, there is only one contact involving a distance shorter than 3·0 Å, that is H(8)–H(11')=2·67 Å.

Discussion

The structural analysis of bis-(6-aminohexanoato)-copper(II) dihydrate clearly shows that four ligands coordinate unidentately to the central copper atom, two of them *via* a carboxylate atom and the other two *via* a nitrogen atom (Fig. 1). Thus, the formula reported by Velicko, Kuzmina & Ermalova (1965) is not correct; they claimed that copper is coordinated through a nine-membered chelate ring, formed by the amino nitrogen and the carboxylate oxygen atoms. Also, unidentate coordination formed by four ligands through their nitrogen atoms, as reported by Nakahara, Hidaka & Tsuchida (1956), does not agree with the present structure (Figs. 1 and 2). It does not seem probable that copper(II) can coordinate to the ε-amino nitrogen atom, in aqueous solution, unless the copper ions are first reduced and then slowly reoxidized. This is indicated from high precision e.m.f. measurements on the present system, which demonstrate that copper(II) ions only interact directly with carboxylate groups in aqueous solution (Österberg & Toftgård, 1972). This fact is further substantiated by another copper(II)–aminohexanoate structure, where the central copper atom is coordinated *via* eight oxygen atoms (Österberg, Sjöberg & Söderquist, 1970).

That the synthesis of the present crystals first requires the reduction and then the slow oxidation of copper(II) parallels the reconstitution of native Cu(II)–protein from apoprotein and copper ions. This re-

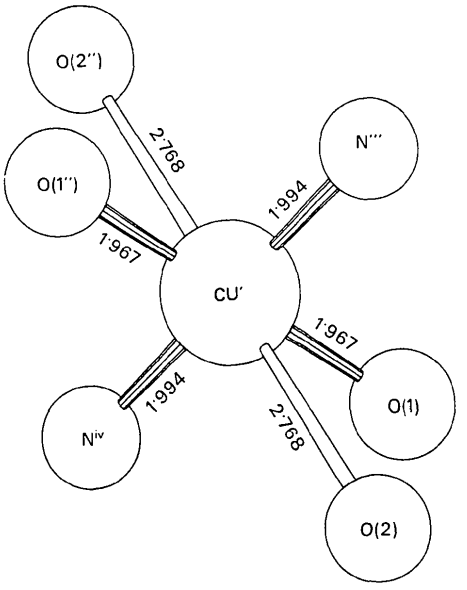

Fig. 2. Copper coordination with bond distances (in Å). The orientation is the same as in Fig. 1.

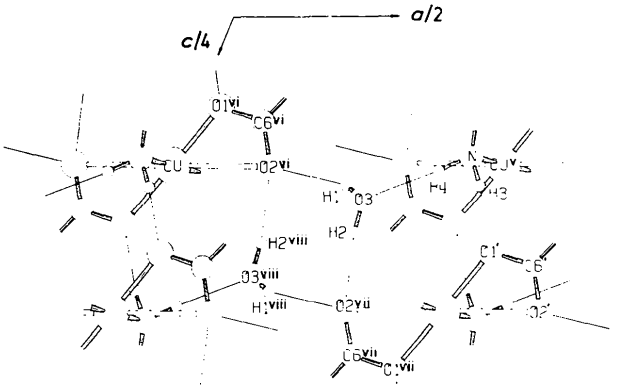

Fig. 3. Bis-(6-aminohexanoato)copper(II) dihydrate viewed down the *b* axis, showing the positions of the hydrogen bonds.

constitution is best achieved by the addition of Cu(I) to the apoprotein, and then subsequent oxidation (Omura, 1961). Thus, a complex involving some ε-amino groups may be considered as a potential structural model for those copper binding sites that readily undergo reduction and oxidation. Such a binding site having 'unidentate' ligands would allow the ligands to move independently, and thus the coordination sphere can be rearranged or changed without any serious damage to the protein. For instance, a linear copper(I) complex, kept in position by two ε-amino groups, situated in a somewhat hydrophobic environment, may be readily transformed into a copper(II) complex *via* oxidation and the simultaneous approach of two carboxylate groups.

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References

ABRAHAMSSON, S., ALEBY, S., LARSSON, K., NILSSON, B., SELIN, K. & WESTERDAHL, A. (1965). *Acta Chem. Scand.* **19**, 758–760.

CINGI, M. B., GUASTINI, C., MUSATTI, A. & NARDELLI, M. (1970). *Acta Cryst.* B**26**, 1836–1843.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.

CRUICKSHANK, D. W. (1965). Errors in least-squares methods; in *Computing Methods in Crystallography*. Edited by J. S. ROLLETT. Oxford: Pergamon Press.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

FREEMAN, H. C. (1967). *Advanc. Protein Chem.* **22**, 257–424.

INGRI, N. & SILLÉN, L. G. (1965). *Ark. Kem.* **23**, 97–121.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

MANAHAN, S. E. (1966). *Inorg. Chem.* **5**, 2063–2065.

NAKAHARA, A., HIDAKA, J. & TSUCHIDA, R. (1956). *Bull. Chem. Soc. Japan.* **29**, 925–928.

OMURA, T. (1961). *J. Biochem. Japan*, **50**, 389–393.

ÖSTERBERG, R. & SJÖBERG, B. (1972). *Contributions to Coordination Chemistry in Solution in Memory of Lars Gunnar Sillén*. Edited by E. HÖGFELDT. Stockholm: AB Allmänna Förlaget.

ÖSTERBERG, R., SJÖBERG, B. & SÖDERQUIST, R. (1970). *Chem. Commun.* pp. 1408–1410.

ÖSTERBERG, R. & TOFTGÅRD, B. (1972). *Bioinorg. Chem.* **1**, 295–308.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VELICKO, F. K., KUZMINA, N. A. & ERMALOVA, L. D. (1965). *Zh. prikl. khim.* **38**, 153–159.

Acta Cryst. (1973). B**29**, 1141

The Crystal Structure of *p*-Nitroacetophenone

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p-Nitroacetophenone, $C_8H_7NO_3$, forms monoclinic crystals in the space group $P2_1/c$ with four molecules in a unit cell of dimensions: $a=10{\cdot}069$ (8), $b=8{\cdot}552$ (8), $c=9{\cdot}094$ (8) Å and $\beta=93{\cdot}85$ (1)°. The structure was refined by a full-matrix least-squares analysis of three-dimensional X-ray diffraction counter data to a final R value of 0·053. The molecule can be described as planar; the molecular plane lies close to the crystallographic (202) plane. The functional groups are slightly twisted about an axis that coincides approximately with the bond from the ring to the central atom of the group.

Introduction

A crystal structure determination of *p*-nitroacetophenone, $C_8H_7NO_3$, is of chemical interest since the compound contains two electron-withdrawing groups attached in competing positions to the benzene ring. The absence of major steric interactions ensures that the aromatic bond distances and the planarities of the functional groups with respect to the benzene ring will reflect primarily the inductive and resonance effects present.

Film techniques were initially employed to determine and refine the structure. When an automatic single-crystal diffractometer became available, a new set of intensity data was collected and the final refinement was based solely on these data.

Experimental

The compound was prepared by Dr T. T. Galkowski of Providence College. Three recrystallizations from anhydrous diethyl ether produced single crystals which