molecules, have symmetry 1 and are significantly non-planar according to standard statistical tests (Tazzoli & Domeneghetti, 1980; Deganello & Piro, 1981). It would thus appear that the hydrogen bond, in the absence of strong intramolecular vibrational coupling, may affect the balance between the repulsion of the carboxyl O atoms and the electronic configuration along the C—C bond.

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The Structure of Diaqua(*N*-salicylidene-L-threoninato)copper(II)

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Abstract

The structure of the Schiff-base-type complex diaqua(*N*-salicylidene-L-threoninato)copper(II) {[Cu($C_{11}H_{11}NO_4$)(H_2O)$_2$], a = 6·681 (4), b = 13·640 (8), c = 14·646 (8) Å, β = 90·88 (4)°, Z = 4, V = 1335 Å^3, monoclinic, space group $P2_1$} has been solved by three-dimensional Fourier methods and refined by the block-diagonal least-squares technique, H atoms excluded, to an R value of 0·070 for 2324 reflections. The asymmetric unit consists of two complex units situated at a hydrogen-bond distance from each other. The coordination sphere around the Cu^{II} central atoms is slightly distorted square pyramidal (4 + 1). The basal planes consist of the tridentate *N*-salicylidene-L-threonine group and an O atom of a water molecule [in one complex unit Cu(1)—O(1) = 1·95 (1), Cu(1)—N(1) = 1·95 (1), Cu(1)—O(3) = 1·92 (1), Cu(1)—O(4) = 1·96 (1) Å; in the other, Cu(2)—O(7) = 1·98 (1), Cu(2)—N(2) = 1·93 (1), Cu(2)—O(9) = 1·92 (1), Cu(2)—O(10) = 1·97 (1) Å]. The axial positions are occupied by O atoms of the second water molecules [Cu(1)—O(5) = 2·42 (1) and Cu(2)—O(11) = 2·34 (1) Å]. The orientation of the 1-hydroxyethyl group of the threoninato residue is different in the two complex units. In one complex unit the hydroxyl O atom of this group points towards the axial water molecule and in the other it points away.

Introduction

Earlier, three structures of the transition-metal complexes derived from salicylaldehyde and amino acids were solved in this laboratory: *catena*-μ-(*N*-salicylidene-L-tyrosinato-*O,O'*)-copper(II) (Hämäläinen,

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Ahlgrén, Turpeinen & Rantala, 1978), aqua(*N*-salicylidene-L-phenylalaninato)copper(II) dimer (Hämäläinen, Turpeinen, Ahlgrén & Rantala, 1978) and diaqua-μ-(*N*-salicylidene-L-valinato-*O*)-(*N*-salicylidene-L-valinato)dicopper(II) (Korhonen & Hämäläinen, 1979). Continuing the structural studies of these Schiff-base complexes we now present the structure of mononuclear diaqua(*N*-salicylidene-L-threoninato)-copper(II).

Experimental

Crystal preparation and analyses

To 100 ml ethanol–water mixture (1:4) was added 60 ml warm (323 K) water containing 0·01 mol (1·12 g) of L-threonine (E. Merck AG, for Biochemische Zwecke) and 0·01 mol (1·22 g) of salicylaldehyde (Eastman Kodak Co.). The yellow mixture was stirred at this temperature for a few minutes and then 0·01 mol (2·00 g) of solid copper(II) acetate monohydrate was gradually added. Stirring was continued until all the copper(II) acetate was dissolved, and the dark-green solution was left in an open vessel to evaporate at room temperature (298 K). After about one week the crude product was precipitated as fine needles, which were dissolved in warm (323 K) water. The filtered solution was left to evaporate at 323 K. After three to four days green prisms were obtained.

The electrolytical copper analysis gave Cu 19·76%, which is in good agreement with the calculated value of 19·81% for the formula $C_{11}H_{15}CuNO_6$ ($M_r = 320{\cdot}81$).

Space group and unit cell

Oscillation and equi-inclination Weissenberg photographs taken around the three crystal axes revealed a monoclinic crystal system. Systematic absences indicated the monoclinic space group $P2_1$ (No. 4) (*International Tables for X-ray Crystallography*, 1969).

The cell dimensions and orientation matrix were determined and refined, with an automatic Syntex $P2_1$ diffractometer using the least-squares method, from the angular values of 24 reflections. Lattice parameters are given in the *Abstract*. The calculated density of 1·596 Mg m^{-3} for four molecules per unit cell agrees with the experimental density of 1·60 Mg m^{-3} measured by the flotation method in a mixture of carbon tetrachloride and methyl iodide.

Intensity measurements

The intensities of 3524 reflections from a crystal of dimensions 0·15 × 0·45 × 0·70 mm were collected on a Syntex $P2_1$ diffractometer using the ω-scan technique with a variable scan speed (2·0 to 15·0° min^{-1}) and graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·71069 Å). One selected reflection was monitored after every 60 reflections to check for possible variations. The data were corrected for Lorentz and polarization effects but not for absorption [μ(Mo $K\alpha$) = 1·86 mm^{-1}].

Structure determination

MULTAN 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and the XRAY 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) were used in solving and refining the structure. From

Table 1. *Fractional atomic coordinates* (×10^4) *with their standard deviations in parentheses and equivalent values of the anisotropic temperature factor coefficients* (Å^2 × 10^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Complex molecule *A*				
Cu(1)	−223 (2)	2415 (2)	1512 (1)	3·3
O(1)	−2897 (14)	2069 (8)	1915 (8)	4·2
O(2)	−5228 (14)	891 (8)	1842 (8)	4·2
O(3)	2013 (15)	2885 (8)	833 (7)	4·2
O(4)	−507 (15)	3687 (8)	2123 (7)	4·0
O(5)	1645 (15)	1689 (9)	2765 (7)	4·2
O(6)	−922 (15)	90 (9)	2674 (7)	4·4
N(1)	−393 (17)	1153 (9)	886 (7)	3·3
C(1)	−3551 (21)	1208 (12)	1665 (11)	3·8
C(2)	−2111 (19)	548 (11)	1151 (10)	3·4
C(3)	−1535 (21)	−302 (11)	1822 (10)	3·8
C(4)	106 (28)	−1003 (14)	1464 (16)	6·3
C(5)	753 (21)	867 (11)	236 (9)	3·4
C(6)	2526 (19)	1419 (11)	−76 (8)	3·1
C(7)	3719 (21)	894 (12)	−690 (9)	3·8
C(8)	5555 (26)	1317 (16)	−1028 (11)	5·3
C(9)	5929 (26)	2277 (15)	−757 (14)	6·0
C(10)	4748 (25)	2801 (15)	−150 (12)	5·3
C(11)	3031 (17)	2366 (12)	236 (8)	3·2
Complex molecule *B*				
Cu(2)	4460 (2)	4394 (2)	3194 (1)	3·2
O(7)	7161 (15)	3990 (8)	3616 (7)	4·2
O(8)	9445 (14)	4271 (9)	4708 (7)	4·3
O(9)	2172 (15)	5049 (8)	2664 (7)	3·8
O(10)	4712 (15)	3632 (8)	2063 (7)	4·1
O(11)	2589 (16)	3194 (9)	3944 (8)	4·9
O(12)	3236 (16)	4586 (10)	5859 (7)	5·4
N(2)	4604 (15)	5240 (8)	4248 (8)	3·2
C(12)	7742 (20)	4357 (12)	4374 (9)	3·6
C(13)	6136 (20)	4935 (10)	4898 (9)	3·1
C(14)	5168 (18)	4217 (8)	5599 (8)	2·5
C(15)	6447 (26)	4102 (16)	6455 (13)	5·9
C(16)	3471 (21)	5954 (13)	4427 (10)	4·2
C(17)	1729 (23)	6254 (11)	3883 (11)	4·0
C(18)	515 (29)	6994 (13)	4226 (14)	6·0
C(19)	−1249 (31)	7274 (17)	3803 (16)	7·2
C(20)	−1729 (31)	6839 (15)	2969 (16)	6·6
C(21)	−631 (26)	6120 (12)	2576 (11)	4·5
C(22)	1191 (22)	5798 (12)	3051 (11)	4·2

the first Fourier summation based on Cu^{II} atoms from the *MULTAN* calculations the coordination spheres around both central atoms were determined. The remaining nonhydrogen atoms were located by successive Fourier syntheses. After every step the positional and isotropic thermal parameters were refined. The final refinement of parameters for all 38 nonhydrogen atoms of the asymmetric unit was carried out by the block-diagonal least-squares technique with isotropic thermal parameters and unit weights to the R value 0·100 ($R = \sum||F_o| - |F_c||/\sum|F_o|$). The refinement was continued by the block-diagonal least-squares method with anisotropic thermal parameters to the R value 0·070.* The 2324 reflections having $I > 2\sigma(I)$ were included in the refinement. The weighting scheme used was $w = 1/(50{\cdot}0 + |F_o| + 0{\cdot}005|F_o|^2)$ and the function minimized was of the form $\sum w(|F_o| - |F_c|)^2$. Attempts were made to locate the H atoms from a difference Fourier map, but not all could be located unambiguously and H atoms were therefore excluded from the calculations. The scattering factors for nonhydrogen atoms were from Cromer & Mann (1968). Anomalous-dispersion corrections were applied for the Cu atoms, using the values of f' and f'' given by Cromer & Liberman (1970). Calculations were carried out on a Univac 1108 computer.

Results and discussion

The atomic fractional coordinates with their standard deviations and U_{eq} values (Hamilton, 1959) are given in Table 1. The structure and numbering scheme of the title compound are shown in Fig. 1.

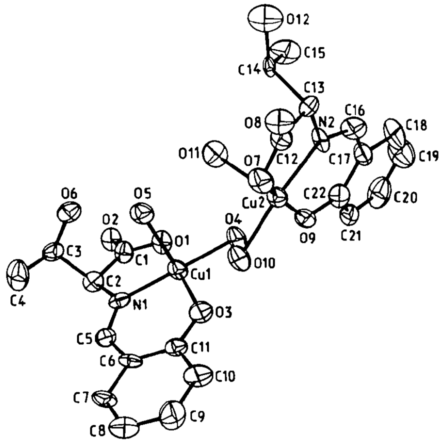

Fig. 1. The structure and numbering scheme of the asymmetric unit. Thermal ellipsoids are scaled to enclose 50% probability.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with standard deviations in parentheses*

The labelling of the atoms is in accordance with Fig. 1.

Complex molecule *A*		Complex molecule *B*	
Cu(1)–O(1)	1·95 (1)	Cu(2)–O(7)	1·98 (1)
Cu(1)–N(1)	1·95 (1)	Cu(2)–N(2)	1·93 (1)
Cu(1)–O(3)	1·92 (1)	Cu(2)–O(9)	1·92 (1)
Cu(1)–O(4)	1·96 (1)	Cu(2)–O(10)	1·97 (1)
Cu(1)–O(5)	2·42 (1)	Cu(2)–O(11)	2·34 (1)
O(1)–C(1)	1·30 (2)	O(7)–C(12)	1·27 (2)
O(2)–C(1)	1·23 (2)	O(8)–C(12)	1·24 (2)
O(3)–C(11)	1·32 (2)	O(9)–C(22)	1·34 (2)
O(6)–C(3)	1·41 (2)	O(12)–C(14)	1·44 (2)
N(1)–C(2)	1·47 (2)	N(2)–C(13)	1·45 (2)
N(1)–C(5)	1·29 (2)	N(2)–C(16)	1·26 (2)
C(1)–C(2)	1·53 (2)	C(12)–C(13)	1·54 (2)
C(2)–C(3)	1·56 (2)	C(13)–C(14)	1·57 (2)
C(3)–C(4)	1·55 (2)	C(14)–C(15)	1·52 (2)
C(5)–C(6)	1·48 (2)	C(16)–C(17)	1·46 (2)
C(6)–C(7)	1·41 (2)	C(17)–C(18)	1·39 (2)
C(7)–C(8)	1·45 (2)	C(18)–C(19)	1·38 (3)
C(8)–C(9)	1·39 (3)	C(19)–C(20)	1·39 (3)
C(9)–C(10)	1·39 (3)	C(20)–C(21)	1·36 (3)
C(10)–C(11)	1·42 (2)	C(21)–C(22)	1·46 (2)
C(11)–C(6)	1·41 (2)	C(22)–C(17)	1·41 (2)
O(1)–Cu(1)–N(1)	83·2 (5)	O(7)–Cu(2)–N(2)	83·2 (5)
O(1)–Cu(1)–O(3)	164·4 (5)	O(7)–Cu(2)–O(9)	166·3 (5)
O(1)–Cu(1)–O(4)	88·8 (4)	O(7)–Cu(2)–O(10)	91·5 (4)
N(1)–Cu(1)–O(3)	95·3 (5)	N(2)–Cu(2)–O(9)	94·3 (4)
N(1)–Cu(1)–O(4)	171·1 (4)	N(2)–Cu(2)–O(10)	170·9 (4)
O(3)–Cu(1)–O(4)	91·3 (5)	O(9)–Cu(2)–O(10)	89·1 (4)
O(1)–Cu(1)–O(5)	97·8 (4)	O(7)–Cu(2)–O(11)	98·6 (4)
N(1)–Cu(1)–O(5)	91·2 (4)	N(2)–Cu(2)–O(11)	93·6 (4)
O(3)–Cu(1)–O(5)	97·7 (4)	O(9)–Cu(2)–O(11)	95·0 (4)
O(4)–Cu(1)–O(5)	93·9 (4)	O(10)–Cu(2)–O(11)	94·5 (4)
O(1)–C(1)–O(2)	124·0 (14)	O(7)–C(12)–O(8)	125·0 (14)
O(1)–C(1)–C(2)	117·3 (12)	O(7)–C(12)–C(13)	115·4 (11)
O(2)–C(1)–C(2)	118·6 (14)	O(8)–C(12)–C(13)	119·6 (12)
C(1)–C(2)–N(1)	107·5 (12)	C(12)–C(13)–N(2)	108·0 (11)
N(1)–C(2)–C(3)	113·4 (11)	N(2)–C(13)–C(14)	108·4 (10)
C(1)–C(2)–C(3)	106·2 (12)	C(12)–C(13)–C(14)	107·6 (11)
C(2)–C(3)–O(6)	109·8 (12)	C(13)–C(14)–O(12)	109·6 (10)
C(2)–C(3)–C(4)	114·4 (13)	C(13)–C(14)–C(15)	111·9 (11)
C(2)–N(1)–C(5)	120·0 (13)	C(13)–N(2)–C(16)	120·3 (12)
N(1)–C(5)–C(6)	124·0 (13)	N(2)–C(16)–C(17)	125·3 (14)
C(5)–C(6)–C(7)	113·7 (13)	C(16)–C(17)–C(18)	118·0 (15)
C(5)–C(6)–C(11)	123·7 (12)	C(16)–C(17)–C(22)	122·6 (14)
C(6)–C(7)–C(8)	120·5 (15)	C(17)–C(18)–C(19)	122·5 (19)
C(7)–C(8)–C(9)	115·3 (16)	C(18)–C(19)–C(20)	117·4 (20)
C(8)–C(9)–C(10)	124·3 (17)	C(19)–C(20)–C(21)	124·1 (19)
C(9)–C(10)–C(11)	120·7 (17)	C(20)–C(21)–C(22)	117·8 (16)
C(10)–C(11)–C(6)	116·4 (13)	C(21)–C(22)–C(17)	118·6 (14)
O(3)–C(11)–C(6)	125·6 (12)	O(9)–C(22)–C(17)	125·5 (14)
O(3)–C(11)–C(10)	117·9 (15)	O(9)–C(22)–C(21)	115·8 (13)
C(11)–C(6)–C(7)	122·6 (12)	C(22)–C(17)–C(18)	119·3 (15)

The coordination geometry around both central Cu^{II} atoms of the asymmetric unit is square pyramidal (4 + 1). Three of the square-planar coordination sites are occupied by a carboxylate O atom, a N atom and an aldehyde O atom of the tridentate *N*-salicylidene-L-threonine group. The fourth site of the square plane is occupied by an O atom of a water molecule at a distance of 1·96–1·97 Å from Cu^{II}. The fifth coordinated atom, an O atom of a second water molecule at a distance of 2·34–2·42 Å, lies at the apex of the pyramid. The coordination distances and angles around the Cu^{II} atoms are given in Table 2.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35874 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Atoms C(9) and C(10) of the benzene ring of the adjacent complex, at distances of 4·17 and 4·15 Å respectively, hinder the formation of octahedral coordination around Cu(1). The octahedral coordination around Cu(2) is hindered by the benzene atoms C(7) and C(8) of the adjacent complex at distances of 4·39 and 4·12 Å respectively. The Cu(1)···Cu(2) distance between the monomers is 4·79 Å, which is longer, for instance, than the 4·07 Å in the related valinato complex (Korhonen & Hämäläinen, 1979) and the 4·36 Å in *catena-μ-*(*N*-salicylidene-L-tyrosinato-*O,O'*)-copper(II) (Hämäläinen, Ahlgrén, Turpeinen & Rantala, 1978).

The orientation of the 1-hydroxyethyl group of the threoninato residue is different in the two monomers of the asymmetric unit. In one monomer the hydroxyl O(6) points towards the axial water molecule O(5), while in the second the hydroxyl O(12) points away from the corresponding axial water molecule O(7).

The square-pyramidal (4 + 1) coordination is found also in other related Schiff-base Cu^{II} complexes, but the origin of the coordinated atoms can vary. In the tyrosinato complex the coordination plane consists of the tridentate ligand and an O atom of an adjacent carboxylate group. In other corresponding compounds the plane is formed by the tridentate ligand group and an O atom of a water molecule (Ueki, Ashida, Sasada & Kakudo, 1967, 1969; Hämäläinen, Turpeinen, Ahlgrén & Rantala, 1978; Korhonen & Hämäläinen, 1979).

The axial atom of the square pyramid can also be different in origin. In the title compound and in aqua(*N*-salicylideneglycinato)copper(II) tetrahydrate (Ueki *et al.*, 1969) the axial atom is an O atom of a water molecule at a longer distance from the Cu atom than the atoms forming the basal plane. In aqua-(*N*-salicylideneglycinato)copper(II) hemihydrate (Ueki *et al.*, 1967) and in the α-aminoisobutyrato complex (Fujimaki, Oonishi, Muto, Nakahara & Konijama, 1971) and in the tyrosinato complex the corresponding axial atom is an O atom of the adjacent carboxylate group. In the phenylalaninato complex the apex of the square pyramid is occupied by a phenolic O atom from an adjacent salicylidene group.

The bond lengths and angles around the bonded atoms (Table 2) are in fairly good agreement with the values found in the related complexes mentioned above.

Each monomeric complex consists of three approximately planar groups: the coordination-plane atoms, the carboxylate group, and the ring of the salicylidene residue. The displacements of selected atoms from the least-squares planes and angles between the planes are presented in Table 3. The displacement of Cu(1) from its coordination plane is 0·17 Å, which is nearly the same as the displacement of Cu(2) (0·18 Å) from its coordination plane. Comparison with the values found in related complexes shows the displacements to be greater than the 0·14 Å in the glycinato complex, but similar to the 0·18–0·20 Å in the phenylalaninato complex. In the tyrosinato complex the deviation of the Cu atom is only 0·06 Å and in the valinato complex the displacement of Cu(1) in one complex molecule of the

Table 3. *Equations of the least-squares planes, deviations* (Å) *of atoms from these planes and angles* (°) *between the planes, with e.s.d.'s in parentheses*

Atoms indicated with an asterisk were omitted from the calculation of the planes.

Plane (1)

$$3\cdot36595x - 5\cdot31323y + 11\cdot17741z = 0\cdot15760$$

O(1)	−0·092 (9)	Cu(1)*	0·174 (2)
N(1)	0·088 (11)	O(2)*	−0·332 (9)
O(3)	−0·082 (10)	C(1)*	−0·133 (14)
O(4)	0·086 (10)	C(2)*	0·128 (12)

Plane (2)

$$2\cdot21662x - 5\cdot16254y + 12\cdot57950z = 0\cdot69467$$

O(1)	0·004 (9)	Cu(1)*	−0·089 (2)
O(2)	0·004 (9)	N(1)*	−0·262 (11)
C(1)	−0·010 (14)	O(3)*	−0·690 (10)
C(2)	0·003 (12)	O(4)*	−0·039 (10)

Plane (3)

$$3\cdot49071x - 5\cdot03304y + 11\cdot13912z = 0\cdot09756$$

C(6)	−0·015 (12)	Cu(1)*	0·294 (2)
C(7)	−0·018 (14)	O(1)*	−0·017 (9)
C(8)	0·034 (18)	N(1)*	0·172 (11)
C(9)	−0·017 (17)	O(3)*	0·081 (10)
C(10)	−0·016 (17)	O(4)*	0·235 (10)
C(11)	0·033 (11)	C(5)*	−0·009 (14)

Plane (4)

$$3\cdot42340x + 9\cdot77652y - 7\cdot04157z = 3\cdot75732$$

O(7)	0·049 (10)	Cu(2)*	−0·184 (2)
N(2)	−0·049 (10)	O(8)*	0·336 (9)
O(9)	0·046 (10)	C(12)*	0·072 (10)
O(10)	−0·046 (10)	C(13)*	−0·281 (13)

Plane (5)

$$1\cdot89593x + 11\cdot42277y - 6\cdot90369z = 3\cdot42048$$

O(7)	−0·001 (10)	Cu(2)*	0·239 (2)
O(8)	−0·002 (9)	N(2)*	0·506 (10)
C(12)	0·004 (13)	O(9)*	0·919 (10)
C(13)	−0·001 (13)	O(10)*	0·197 (10)

Plane (6)

$$3\cdot50578x + 9\cdot45129y - 7\cdot35956z = 3\cdot66156$$

C(17)	−0·002 (16)	Cu(2)*	−0·296 (2)
C(18)	0·019 (19)	O(7)*	−0·041 (10)
C(19)	−0·023 (21)	N(2)*	−0·221 (10)
C(20)	0·011 (20)	O(9)*	−0·089 (10)
C(21)	0·006 (18)	O(10)*	−0·096 (10)
C(22)	−0·010 (15)	C(16)*	−0·076 (14)

Angles (°) between planes (e.s.d.'s are 0·6–1·7°)

(1) and (2)	11·2	(3) and (6)	68·8
(1) and (3)	1·6	(4) and (5)	14·9
(1) and (4)	67·3	(4) and (6)	2·0
(2) and (3)	12·3	(5) and (6)	16·2
(2) and (5)	51·2		

dimeric asymmetric unit is 0·07 Å and in the other just 0·02 Å.

In the carboxylate groups of complex molecules *A* and *B* the bond lengths are the same, within error limits. In both groups, too, the distance from the C atom to the coordinated O atom is greater [C(1)—O(1) = 1·30 and C(12)—O(7) = 1·27 Å] than the distance to the uncoordinated O atom [C(1)—O(2) = 1·23 and C(12)—O(8) = 1·24 Å].

The angles between the least-squares coordination plane and the benzene ring in the complex units *A* and *B* are 1·6 and 2·0° respectively. In related complexes, for instance the valinato and phenylalaninato complexes, the corresponding values are 12·8 and 8·8° and 23·4 to 24·2° respectively.

The angles between the coordination, carboxylate and benzene-ring least-squares planes of the two complex molecules of the asymmetric unit are 67·3, 51·2 and 68·8°, respectively, and are considerably smaller than the corresponding angles of 87·1, 89·3 and 89·1° in the valinato complex.

There are no significant differences in corresponding bond lengths and angles in the two complexes of the asymmetric unit (Table 2). The mean values of the C—C bond distances of the benzene rings in the complex molecules *A* and *B* are 1·41 and 1·40 Å respectively.

In Cu^{II} complexes formed between salicylaldehyde and glycine, L-tyrosine or L-phenylalanine, the bond between the N and C atoms of the amino acid part has been found to be shorter than the normal single bond (1·47–1·49 Å), and the bond between the N and C atoms of the aldehyde part has the usual N=C value (1·29–1·30 Å). A different situation prevails in the α-aminoisobutyrato complex, where the N—C single bonds have normal values and the N=C double bonds are shorter than the usual double-bond value. In the valinato complex the bond lengths in question cannot be classified as of either type since, within large error limits, the values of both the N—C single bonds (1·48–1·49 Å) and the N=C double bonds (1·29–1·30 Å) are normal. In the title compound the N—C single bonds are 1·47 and 1·45 Å and the N=C double bonds are 1·29 and 1·26 Å, respectively, in the two complex units *A* and *B*.

Table 4 presents selected intermolecular distances in the asymmetric unit and Table 5 selected intermolecular and contact distances between adjacent asymmetric units. As can be seen in Table 4, the water molecules O(4) and O(10) of the coordination square planes and also the axial water molecules O(5) and O(11) of the square pyramids are engaged in hydrogen bonding, which unites two formula units into an asymmetric unit. Table 5 and Fig. 2 show that the uncoordinated terminal hydroxyl oxygen atoms O(6) and O(12) are engaged in strong hydrogen-bond formation between adjacent asymmetric units, which may explain the different orientations of the terminal 1-hydroxyethyl groups.

Table 4. *Selected intermolecular distances* (Å) *in the asymmetric unit less than* 3·5 Å *with standard deviations in parentheses*

O(3)···O(10)	2·73 (1)	O(5)···O(6)	2·78 (2)
O(4)···O(9)	2·69 (1)	O(5)···O(11)	2·75 (2)
O(4)···O(10)	3·49 (1)	O(4)···C(21)	3·38 (2)
O(4)···O(11)	3·42 (2)	O(4)···C(22)	3·37 (2)

Table 5. *Intermolecular distances* (Å) *between adjacent asymmetric units less than* 3·5 Å *with standard deviations in parentheses*

$O(10)\cdots O(1^{i})$	2·67 (1)	$C(11)\cdots O(2^{i})$	3·29 (2)
$O(5)\cdots O(2^{i})$	2·73 (1)	$O(8)\cdots C(17^{i})$	3·34 (2)
$O(7)\cdots O(4^{i})$	2·74 (1)	$C(8)\cdots O(9^{iii})$	3·34 (2)
$O(6)\cdots O(12^{iv})$	2·75 (2)	$O(8)\cdots C(22^{i})$	3·42 (2)
$O(8)\cdots O(11^{i})$	2·81 (2)	$C(6)\cdots O(2^{i})$	3·45 (2)
$O(8)\cdots O(12^{i})$	3·05 (1)	$O(12)\cdots C(19^{iv})$	3·46 (3)
$O(10)\cdots O(4^{i})$	3·19 (1)	$O(8)\cdots C(18^{ii})$	3·48 (2)

Symmetry code

(i) $x+1, y, z$

(ii) $-x+1, y-\frac{1}{2}, -z+1$

(iii) $-x+1, y-\frac{1}{2}, -z$

(iv) $-x, y-\frac{1}{2}, -z+1$

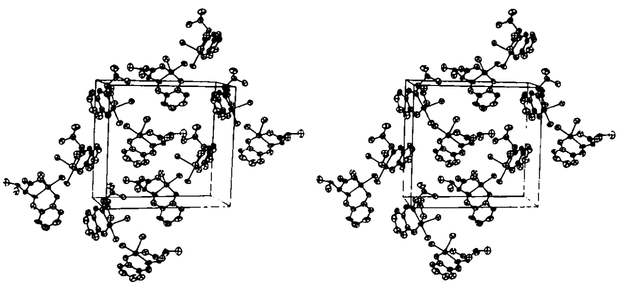

Fig. 2. Stereoscopic view of the unit cell. The view direction is approximately along the *a* axis; the *b* axis is horizontal and the *c* axis approximately vertical.

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The Structure of Monosodium Phosphoenolpyruvate

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Abstract

$C_3H_4O_6P^-.Na^+.H_2O$, $M_r = 208{\cdot}0$, is monoclinic, *Cc*, $a = 11{\cdot}423$ (2), $b = 23{\cdot}253$ (5), $c = 6{\cdot}604$ (1) Å, $\beta = 123{\cdot}63$ (1)°, $U = 1460{\cdot}6$ Å^3, $D_x = 1{\cdot}89$ Mg m^{-3}, $Z = 8$, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·44 mm^{-1}, $F(000) = 840$. Final $R = 0{\cdot}063$ for 1697 reflections. The two crystallographically independent molecules of phosphoenolpyruvate (PEP) (*A* and *B*) are almost mirror images of each other, the mirror being the planar enolpyruvate group. The torsion angle C(3)—C(2)—O(1)—P(1) is 122·6 in *A* and −112·0° in *B*, in contrast to −209·1° in PEP.K. The enolic C(2)—O(1) has a partial double-bond character [1·401 (*A*), 1·386 Å (*B*)]. The high-energy P∼O bond (1·595 and 1·610 Å) is comparable to that in PEP.K (1·612 Å). Na(1) has six nearest neighbours while Na(2) has only five. The Na^+ ions are involved in binding only the phosphates of different molecules, in contrast to the K^+ ion in PEP.K, which binds to both the phosphate and carboxyl ends of the same molecule. The planar carboxyl groups stack on each other at an average distance of 3·2 Å instead of forming hydrogen-bonded dimers usually found in carboxylate structures.

Introduction

Phosphoenolpyruvate (PEP) is known to play an important role in glycolysis as a substrate in the pyruvate kinase catalysed reaction, where adenosine 5′-triphosphate is synthesized by a phosphate-group transfer from PEP to adenosine 5′-diphosphate. For this phosphorylation reaction to proceed, the presence of divalent Mg^{2+} and monovalent K^+ cations is obligatory (Mahler & Cordes, 1969). Replacement of K^+ by Na^+ is known to inhibit the reaction. Hence it would be of interest to study the structure of PEP when bound to Na^+ and compare it with that of its K^+ complex. We report here the structure of monosodium phosphoenolpyruvate (PEP.Na) monohydrate as obtained from single-crystal X-ray analysis. The conformation of PEP in the present structure is found to be significantly different from that in its K^+ salt (Hosur & Viswamitra, 1981).

Experimental

Crystals of the monosodium salt of PEP (original sample from Boehringer Mannheim GmbH) were grown by slow diffusion of acetone into an aqueous solution of the compound. A single crystal 0·15 × 0·17 × 0·22 mm, with well developed prismatic faces, was used to determine the crystal data by rotation and Weissenberg photographs. The cell parameters were later refined on a CAD-4 diffractometer by least squares from 25 high-angle reflections. The density, measured by flotation in bromoform and acetone mixtures, indicated eight ($PEP.Na.H_2O$) units in the cell.

Systematic absences *hkl*: $h + k = 2n + 1$ and *h*0*l*: $l = 2n + 1$ indicated space groups *Cc* or *C*2/*c*.

Mo $K\alpha$ intensities to a 2θ limit of 56° (resolution = 0·76 Å) were collected on the diffractometer in the $\omega/2\theta$ scan mode. Background counts were measured at the two edges of the Bragg peak for $\frac{1}{6}$ of the total scan angle. There was no significant change in the intensities of the monitor reflections checked at regular intervals. The data consisted of 1697 unique reflections in the *hkl*

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