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Crystal and Molecular Structure of Bis(N-benzoylglycinato)triaquozinc(II) Dihydrate

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The crystal structure of bis(N-benzoylglycinato)-triaquozinc(II) dihydrate was determined from three-dimensional X-ray data collected by counter methods. The colourless crystals are triclinic with the space group P1. The unit cell parameters are $a = 5.157(2)$, $b = 5.192(2)$, $c = 20.092(9)$ Å, $\alpha = 83.60(4)°$, $\beta = 86.19(4)°$, $\gamma = 83.42(3)°$, $V = 530.3$ Å^3 *and* $Z = 1$. *The structure was solved from 2332 reflections and was refined to an R index of 0.043.*

The zinc atom in the molecule is coordinated by an oxygen atom of the carboxyl group of each N-benzoylglycinate anion and by three water molecules, resulting in a 5-coordinated, slightly distorted trigonal bipyramidal geometry with two water molecules occupying the apical positions. The mean Zn–O (basal) and Zn–O(apical) distances are 1.988 and 2.165 Å, respectively. All metal-bonded and all free water molecules are engaged in a network of intermolecular and intramolecular hydrogen-bonding.

Introduction

N-benzoylglycine, commonly known as hippuric acid, is a simple amino acid derivative containing a peptide group. The interactions of the carboxylate group with metal ions of interest may give information regarding the bonding characteristics of protein-like donor molecules towards metals. The requirement of charge compensation and sterical saturation favours additional water coordination to the metal ion in the neighbourhood of a peptide bond, the nitrogen of which is not able to bind to a metal ion without crystal field stabilisation energy [1]. The crystal structure of copper(II) hippurate [2, 3] has revealed that there exists a unique type of carboxylate bonding such that a single carboxyl oxygen atom binds to the copper atom. Recently Udupa and Krebs [4, 5] have investigated the crystal structure of copper(II) N-acetylglycinates, and we report in this paper the results of the crystal structure of zinc N-benzoylglycinate pentahydrate.

Experimental

Zinc N-benzoylglycinate pentahydrate, $Zn(C_6H_5\text{-}CONHCH_2COO)_2 \cdot 5H_2O$, was prepared by interacting a hot aqueous solution of N-benzoylglycine with a slight excess of zinc carbonate [6]. The mixture was kept on a water bath till the reaction was complete. The unreacted zinc carbonate was filtered off, and the filtrate produced colourless crystals. *Anal.*: found C 42.0, H 5.0, N 5.5, Zn 12.5%; calcd. for $[ZnC_{18}H_{26}N_2O_{11}]$, C, 42.2, H 5.1, N 5.5, Zn 12.8%. The crystals were found to be very thin plates, and it was very difficult to get satisfactory single crystals even by slow evaporation. The unit cell dimensions were determined by preliminary Weissenberg and precession photographs, and were refined by least-squares from diffractometer coordinates of 15 high-order reflections.

The crystals are triclinic with (at -115 °C) $a = 5.157(2)$, $b = 5.192(2)$, $c = 20.092(9)$ Å, $\alpha = 83.60(4)$, $\beta = 86.19(4)$, $\gamma = 84.42(3)°$, $V = 530.3$ Å^3. The calculated density is $d_x = 1.60$ g cm^{-3} for one formula unit, $Z = 1$. A statistical intensity test did not reveal a center of symmetry of the compound, thus suggesting the space group $P1-C_1^1$ (No. 1).

The X-ray intensity data were collected at -115 °C on a single crystal with dimensions $0.05 \times 0.10 \times 0.12$ mm^3, using a Syntex $P2_1$ four-circle diffractometer with graphite monochromated MoKα radiation ($\lambda K\alpha_1$ 0.70926 Å, $\lambda K\alpha_2$ 0.71354 Å, θ–2θ scan, scintillation counter, take-off angle 6°). The sampling interval (in 2θ) for each reflection was from 1.0° below the calculated MoKα_1 maximum to 1.0° above the MoKα_2 maximum. The scan rate was varied from 2° per min to 15° per min (in 2θ) depending on the intensity of the reflection. Background measurements with the total time for back-

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ground counts being equal to the scan time were made at the start and end of each scan, keeping the counter stationary. A standard reflection was measured for every 50 reflections.

A complete set of 2368 unique reflections was measured up to $(\sin\theta)/\lambda = 0.64$ Å^{-1}. A set of 2332 reflections were accepted as statistically above background on the basis that $I \geqq 1.96\ \sigma(I)$. The linear absorption coefficient is $\mu = 12.6$ cm^{-1}, and an empirical absorption correction was applied. Data reduction was done using Lorentz and polarization corrections, including a Wilson plot.

The structure was solved [7] by fixing the coordinates of the zinc atom at 0.5, 0.5, 0.5. After isotropic refinement of the zinc atom, all the other 31 non-hydrogen atoms were located from difference Fourier maps. The atomic scattering factors for Zn, O, N, C and H were taken from the International Tables [8]. The H atoms in the water molecules were located from subsequent difference Fourier maps. Their coordinates were refined. The positions of the H atoms in the organic groups were calculated assuming C–H distances of 0.95 Å. They were not refined, but were included in the structure factor calculations. Full matrix least-squares refinement with anisotropic temperature factors for all the non-hydrogen atoms and fixed isotropic temperature factors of 3.0 for all H atoms converged to residuals $R_1 = 0.043$ and $R_2 = 0.054$, where $R_1 = \Sigma(\|F_o|-|F_c\|)/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$. The weighting scheme was based on the counting statistics of the intensities.

The final coordinates and thermal parameters of the atoms are given in Tables I and II. Tables of the H atom coordinates of the organic ligands and of the calculated and observed structure factors are available from the Editor.

TABLE I. Coordinates of the Non-Hydrogen Atoms in the Structure of Bis(N-benzoylglycinato)triaquozinc(II) Dihydrate.

	x	y	z
Zn	0.5	0.5	0.5
O(1)	0.5531(7)	0.7999(7)	0.4320(2)
O(2)	0.2067(8)	0.6812(8)	0.3887(2)
O(3)	0.4678(10)	0.6912(9)	0.2388(3)
O(4)*	0.7699(9)	0.2548(9)	0.4413(2)
O(5)*	0.2126(9)	0.7357(9)	0.5579(3)
O(6)	0.5191(10)	0.3179(10)	0.7592(3)
O(7)	0.6146(8)	0.1346(8)	0.6107(2)
O(8)	0,7542(7)	0.5113(7)	0.5684(2)
O(9)*	0.2390(8)	0.2414(7)	0.5000(2)
O(10)*	0.3534(8)	0.7683(8)	0.6846(2)
O(11)*	0.8741(8)	0.4765(8)	0.3147(2)
N(1)	0.2505(10)	0.0495(10)	0.2767(2)
N(2)	0.9054(10)	0.1133(10)	0.7238(3)
C(1)	0.3848(15)	0.8222(12)	0.3870(4)
C(2)	0.4164(11)	0.0455(11)	0.3315(3)
C(3)	0.2870(15)	0.8712(14)	0.2336(4)
C(4)	0.1080(12)	0.8950(12)	0.1768(3)
C(5)	−0.0915(13)	0.0991(12)	0.1671(3)
C(6)	−0.2480(15)	0.1060(14)	0.1135(4)
C(7)	−0.2099(14)	0.9172(14)	0.0695(3)
C(8)	−0.0129(14)	0.7166(14)	0.0794(3)
C(9)	0.1425(14)	0.7047(13)	0.1331(3)
C(10)	0.4559(14)	−0.0519(15)	0.8669(4)
C(11)	0.4207(16)	−0.2336(18)	0.9215(4)
C(12)	0.6041(17)	−0.4490(14)	0.9325(4)
C(13)	0.8233(17)	−0.4743(14)	0.8893(4)
C(14)	0.8590(14)	−0.2896(14)	0.8347(3)
C(15)	0.6734(12)	−0.0767(12)	0.8234(3)
C(16)	0.6926(14)	0.1340(15)	0.7662(4)
C(17)	0.9390(11)	0.3119(12)	0.6686(3)
C(18)	0.7514(14)	0.3103(14)	0.6128(4)

*O(4), O(5), O(9), O(10), and O(11) are water oxygens.

Results and Discussion

The crystal structure consists of bis(N-benzoylglycinato)triaquozinc(II) $[Zn(C_6H_5CONHCH_2COO)_2(OH_2)_3]$ units which are linked through the three coordinated water molecules and two additional ones by hydrogen bonding to the neighbouring molecules. Within the unit, the zinc atom is surrounded by five oxygen atoms. An ellipsoid plot of the molecule with atomic labelling is given in Fig. 1. A stereo-view of the unit cell is given in Fig. 2. The interatomic bond distances and bond angles are given in Table III.

The zinc atom in the molecule is strongly bonded to the oxygen atoms O(1) and O(8) of the carboxylate groups at distances of 1.985 and 1.971 Å respectively, and in addition to the water oxygen O(9) at 2.007 Å. These three oxygen atoms form the basal plane of a trigonal bipyramid with the zinc atom in the center. The average bond distance in the plane is 1.988 Å, the bond angles going from 105.7° to 127.3°. The additional water molecules O(4) and O(5) approach the zinc atom in axial positions at 2.158 and 2.172 Å and make an angle of 177.1° with the zinc atom. In O-bonded zinc(II) complexes the Zn–O distances are found in the range 1.96–2.20 Å [9, 10]. The observed bond lengths in the present complex are in good agreement with those of similar complexes. Zinc is known to form linear, tetrahedral, square pyramidal, trigonal bipyramidal, octahedral and dodecahedral geometries [11]. It forms a variety of five-coordinate complexes [12–18], among which the trigonal bipyramid TBP is more common than the square pyramid SP (many of the structures are intermediates, but with an obvious tendency towards the TBP or the SP). Generally, the five-coordinate geometries are experienced either by preference of the metal atom or by the

TABLE II. Anisotropic Temperature Factors of the Non-Hydrogen Atoms in Bis(N-benzoylglycinato)triaquozinc(II) Dihydrate.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	0.58(2)	0.73(2)	1.69(2)	0.19(1)	−0.04(1)	−0.09(1)
O(1)	1.1(1)	1.0(1)	1.7(1)	0.3(1)	−0.2(1)	0.0(1)
O(2)	1.7(2)	1.7(2)	2.5(2)	−0.8(1)	−0.4(1)	0.0(1)
O(3)	1.9(2)	1.4(2)	2.1(2)	0.7(2)	−0.4(2)	−0.6(2)
O(4)	0.8(2)	1.0(2)	1.7(2)	0.1(1)	0.2(1)	−0.4(1)
O(5)	1.0(2)	1.1(2)	1.8(2)	0.0(1)	−0.1(2)	0.1(1)
O(6)	1.3(2)	2.1(2)	2.1(2)	0.3(2)	0.2(2)	0.5(2)
O(7)	1.5(2)	1.5(2)	2.7(2)	−0.5(1)	−0.2(1)	0.1(1)
O(8)	1.0(1)	1.1(1)	1.6(1)	0.3(1)	−0.1(1)	0.0(1)
O(9)	0.9(1)	0.5(1)	3.0(2)	0.1(1)	−0.2(1)	0.0(1)
O(10)	1.3(2)	1.3(1)	2.1(2)	0.2(1)	−0.1(1)	0.2(1)
O(11)	1.2(2)	1.3(1)	2.1(2)	0.1(1)	−0.3(1)	−0.2(1)
N(1)	1.7(2)	1.3(2)	1.6(2)	0.2(2)	−0.4(2)	−0.2(1)
N(2)	1.1(2)	1.6(2)	1.8(2)	0.3(1)	−0.1(1)	0.3(2)
C(1)	1.5(3)	0.5(2)	1.2(2)	0.4(2)	0.1(2)	−0.2(2)
C(2)	1.2(2)	0.9(2)	2.0(2)	0.0(2)	−0.2(2)	0.1(2)
C(3)	1.4(3)	1.2(3)	1.8(3)	−0.1(2)	−0.1(2)	0.2(2)
C(4)	1.4(2)	1.7(2)	1.3(2)	−0.2(2)	−0.1(2)	0.1(2)
C(5)	2.1(3)	1.6(2)	2.1(2)	0.2(2)	−0.4(2)	−0.3(2)
C(6)	2.4(3)	2.5(3)	2.7(3)	0.5(2)	−0.8(2)	0.1(2)
C(7)	2.4(3)	2.8(3)	1.9(2)	−0.4(2)	−0.9(2)	0.3(2)
C(8)	2.7(3)	2.6(3)	1.7(2)	−0.4(2)	−0.2(2)	−0.5(2)
C(9)	2.2(3)	2.1(3)	2.1(2)	0.3(2)	0.1(2)	−0.3(2)
C(10)	2.1(3)	3.1(3)	2.6(3)	0.1(2)	0.2(2)	0.2(2)
C(11)	3.0(3)	4.6(4)	2.4(3)	−0.7(3)	0.3(2)	0.9(3)
C(12)	3.9(4)	2.5(3)	2.0(3)	−1.2(3)	−0.6(2)	0.9(2)
C(13)	4.1(4)	2.0(3)	2.7(3)	0.1(3)	−0.8(3)	0.6(2)
C(14)	2.4(3)	2.0(3)	2.1(2)	0.2(2)	0.0(2)	0.0(2)
C(15)	1.7(2)	1.9(2)	1.6(2)	−0.3(2)	−0.4(2)	0.1(2)
C(16)	1.0(3)	1.7(3)	1.4(3)	0.1(2)	−0.1(2)	0.2(2)
C(17)	1.0(2)	1.5(2)	1.9(2)	−0.1(2)	−0.1(2)	0.3(2)
C(18)	0.9(2)	1.3(2)	1.2(2)	0.6(2)	0.2(2)	−0.1(2)

TABLE III. Interatomic Distances and Bond Angles in the Crystal Structure of Bis(N-benzoylglycinato)triaquozinc(II) Dihydrate.

Distances (A)		Angles (°)	
Zn Coordination			
Zn–O(1)	1.985(4)	O(1)–Zn–O(4)	89.2(2)
Zn–O(4)	2.158(5)	O(1)–Zn–O(5)	91.9(2)
Zn–O(5)	2.172(5)	O(1)–Zn–O(8)	105.7(2)
Zn–O(8)	1.971(4)	O(1)–Zn–O(9)	127.3(2)
Zn–O(9)	2.007(4)	O(4)–Zn–O(5)	177.1(2)
		O(4)–Zn–O(8)	93.1(2)
		O(4)–Zn–O(9)	88.7(2)
		O(5)–Zn–O(8)	89.2(2)
		O(5)–Zn–O(9)	88.5(2)
		O(8)–Zn–O(9)	127.1(2)
N-Benzoylglycinate			
C(1)–O(1)	1.282(8)	Zn–O(1)–C(1)	111.1(4)

(continued overleaf)

TABLE III. *(continued)*

C(1)–O(2)	1.235(9)	O(1)–C(1)–O(2)	123.4(7)
C(1)–C(2)	1.531(9)	O(1)–C(1)–C(2)	114.4(6)
C(2)–N(1)	1.437(8)	O(2)–C(1)–C(2)	122.2(6)
N(1)–C(3)	1.326(9)	C(1)–C(2)–N(1)	114.3(5)
C(3)–O(3)	1.243(9)	C(2)–N(1)–C(3)	122.1(6)
C(3)–C(4)	1.500(10)	N(1)–C(3)–O(3)	121.4(7)
C(4)–C(9)	1.383(9)	N(1)–C(3)–C(4)	118.3(6)
C(4)–C(5)	1.396(9)	O(3)–C(3)–C(4)	120.3(7)
C(5)–C(6)	1.383(10)	C(3)–C(4)–C(5)	122.6(6)
C(6)–C(7)	1.382(10)	C(3)–C(4)–C(9)	118.1(6)
C(7)–C(8)	1.376(10)	C(5)–C(4)–C(9)	119.3(6)
C(8)–C(9)	1.378(10)	C(4)–C(5)–C(6)	118.9(6)
C(18)–O(8)	1.296(8)	C(5)–C(6)–C(7)	121.5(7)
C(18)–O(7)	1.221(9)	C(6)–C(7)–C(8)	119.3(7)
C(18)–C(17)	1.532(9)	C(7)–C(8)–C(9)	120.0(6)
C(17)–N(2)	1.443(8)	C(8)–C(9)–C(4)	121.1(6)
N(2)–C(16)	1.346(9)	Zn–O(8)–C(18)	110.9(4)
C(16)–O(6)	1.234(9)	O(8)–C(18)–O(7)	123.9(7)
C(16)–C(15)	1.502(10)	O(8)–C(18)–C(17)	113.4(6)
C(15)–C(10)	1.378(10)	O(7)–C(18)–C(17)	122.6(6)
C(15)–C(14)	1.386(9)	C(18)–C(17)–N(2)	113.5(5)
C(14)–C(13)	1.391(10)	C(17)–N(2)–C(16)	120.2(5)
C(13)–C(12)	1.381(11)	N(2)–C(16)–O(6)	122.0(7)
C(12)–C(11)	1.387(12)	N(2)–C(16)–C(15)	117.3(6)
C(11)–C(10)	1.381(11)	O(6)–C(16)–C(15)	120.6(7)
		C(16)–C(15)–C(14)	124.2(6)
		C(16)–C(15)–C(10)	116.8(6)
		C(14)–C(15)–C(10)	119.0(6)
		C(15)–C(14)–C(13)	119.8(7)
		C(14)–C(13)–C(12)	120.8(7)
		C(13)–C(12)–C(11)	119.1(7)
		C(12)–C(11)–C(10)	119.8(8)
		C(11)–C(10)–C(15)	121.4(7)

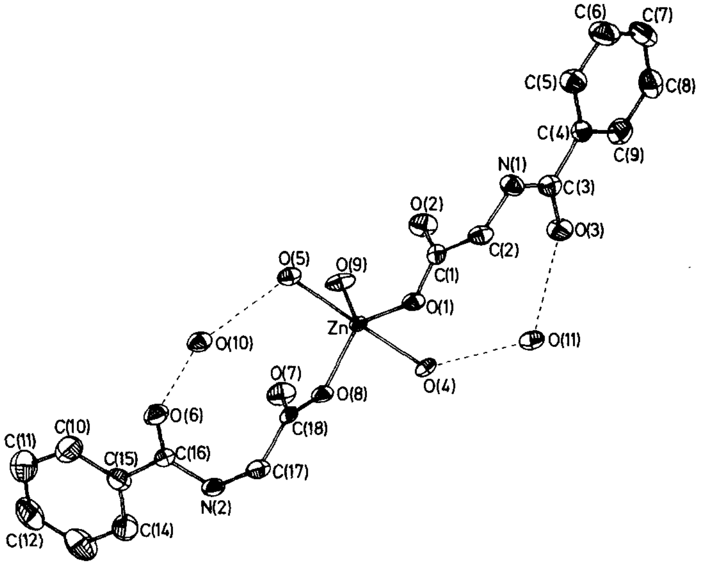

Fig. 1. $[Zn(C_6H_5CONHCH_2COO)_2(OH_2)_3]\cdot 2H_2O$: Ellipsoid plot of the complex with atomic designations. The hydrogen bridges to the two neighbouring non-coordinated water molecules are indicated.

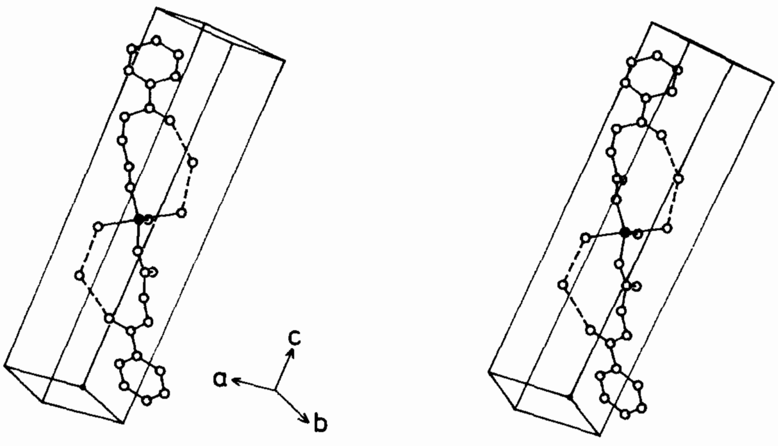

Fig. 2. Stereo plot of the unit cell of $[Zn(C_6H_5CONHCH_2COO)_2(OH_2)_3]\cdot 2H_2O$.

TABLE IV. Positions of Hydrogen Atoms Involved in Hydrogen Bonding in $[Zn(C_6H_5CONHCH_2COO)_2(OH_2)_3]\cdot 2H_2O$.

	x	y	z
H(1)	0.788(11)	0.324(12)	0.399(4)
H(2)	0.711(13)	0.137(14)	0.440(3)
H(3)	0.258(12)	0.724(11)	0.599(4)
H(4)	0.115(13)	0.626(14)	0.565(4)
H(5)	0.207(11)	0.105(11)	0.533(3)
H(6)	0.075(12)	0.341(12)	0.493(4)
H(7)	0.471(11)	0.884(11)	0.670(3)
H(8)	0.392(13)	0.687(13)	0.710(3)
H(9)	0.967(11)	0.586(12)	0.332(3)
H(10)	0.791(13)	0.508(12)	0.291(3)
H(11)	0.113(11)	0.183(12)	0.274(3)
H(12)	0.035(11)	−0.033(12)	0.728(3)

structure of the ligand. As no sterical strain is imposed by the two unidentate N-benzoylglycine ligands and the three water molecules, the observed coordination indicates a strong preference of the zinc center towards five-coordination.

Craig and co-workers [19] have predicted from theoretical calculations that the axial bond lengths in the TBP are always longer than the basal length to the extent of 7–9%. In the present case the difference is near 8%. The degree of distortion of the ideal TBP is to be seen in the average deviation of the bond angles, which is 4.0° from the TBP but about 10.3° from the SP. These values indicate only a slight distortion compared to other known five-coordinated zinc moieties, including complexes with mixed nitrogen and oxygen ligand atoms.

TABLE V. Hydrogen Bonding in the Structure of Bis(N-benzoylglycinato)triaquozinc(II) Dihydrate. Distances in Å and Angles in deg.

H	H-Donor A	H-Acceptor B		Distances A–H	H···B	A···B	Angles A–H···B
H(1)	O(4)	O(11)	(000)*	0.88(6)	1.85(6)	2.719(6)	172(5)
H(2)	O(4)	O(1)	(0–10)	0.72(6)	2.04(6)	2.756(6)	178(5)
H(3)	O(5)	O(10)	(000)	0.88(5)	1.86(5)	2.721(7)	169(4)
H(4)	O(5)	O(8)	(–100)	0.80(6)	2.01(6)	2.739(6)	151(5)
H(5)	O(9)	O(5)	(0–10)	0.94(5)	1.93(5)	2.765(5)	148(5)
H(6)	O(9)	O(4)	(–100)	0.95(6)	2.06(5)	2.751(6)	128(5)
H(7)	O(10)	O(7)	(010)	0.92(5)	1.85(6)	2.707(6)	155(4)
H(8)	O(10)	O(6)	(000)	0.65(6)	2.11(6)	2.716(7)	155(5)
H(9)	O(11)	O(2)	(100)	0.90(5)	1.88(6)	2.717(6)	156(5)
H(10)	O(11)	O(3)	(000)	0.65(7)	2.11(6)	2.733(7)	161(5)
H(11)	N(1)	O(11)	(–100)	0.93(5)	2.06(5)	2.909(7)	151(4)
H(12)	N(2)	O(10)	(0–10)	0.95(5)	2.03(5)	2.879(7)	147(5)

*The numbers indicate the translations of the B atoms along *a*, *b*, and *c* to be applied to the coordinates of Table I.

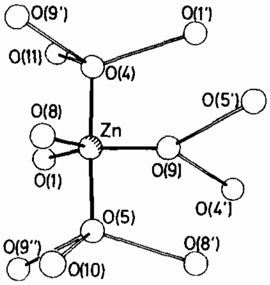

Fig. 3. Hydrogen bonding arrangement around the zinc–oxygen coordination.

Except for the carbonyl group, the bond distances and bond angles of N-benzoylglycinate are not significantly different from those of the free ligand [20]. The two unique N-benzoylglycinate anions have comparable bond distances and bond angles, within experimental error. The carboxyl oxygen atoms bonded to zinc have a mean C–O bond distance of 1.289 Å which is significantly longer than the adjacent C–O bond, 1.228 Å. The mean carbonyl double bond length of the peptide group, 1.239 Å, is slightly longer than the normal value of 1.20 Å [21] and the C–N bond length, 1.336 Å, is much shorter than the value of 1.47 Å for a single bond [22], which indicates an extensive delocalisation of the amide system [23] caused by involving the oxygen and the nitrogen atom of the peptide group in hydrogen bonding.

The water hydrogen positions and bond distances observed in the complex are given in Tables IV and V. Whereas the apical oxygens, O(4) and O(5), are tetrahedrally surrounded, each bonds to zinc and to three neighbouring oxygens through hydrogen bridges, the Zn-O···O and O···O···O interatomic angles going from 101.6° to 121.5° with an average of 109.5°. The basal oxygen, O(9), is located in a plane formed by the zinc and two hydrogen-bridged oxygen neighbours, O(4') and O(5'), with an average bond angle of 120.0°. In the line O(4), Zn, O(5) the additional bonds, inclusive of hydrogen bridges, show an eclipsed conformation, as shown in Fig. 3. The reason for this (apart from packing considerations) may be weak attraction between the bridging hydrogen atoms connected with the axial ligands O(4) and O(5) and the basal oxygen atoms. The space which is left in this conformation allows a rotation of the plane Zn, O(9), O(4'), O(5') around the axis Zn–O(9) by about 24°, relative to the basal plane of the complex.

This compound gives an interesting view into a typical network of hydrogen bridges stabilizing a trigonal bipyramidal complex of zinc.

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