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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JA1002). Services for accessing these data are described at the back of the journal.

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Hexaaquazinc(II) bis[*N*-(4-amino-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidin-2-yl)glycinate] dihydrate

PALOMA ARRANZ-MASCARÓS,^a M. LUZ GODINO,^a RAFAEL LÓPEZ,^a RAFAEL CUESTA,^b CRISTÓBAL VALENZUELA-CALAHORRO^c AND DANIEL MARTÍN-RAMOS^d

^aDepartamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, ^bDepartamento de Química Inorgánica y Orgánica, EUP de Linares, Universidad de Jaén, 23700 Linares (Jaén), Spain, ^cDepartamento de Química Inorgánica, Universidad de Granada, 18071 Granada, Spain, and ^dDepartamento de Mineralogía y Petrología, Universidad de Granada, 18071 Granada, Spain. E-mail: parranz@ujaen.es

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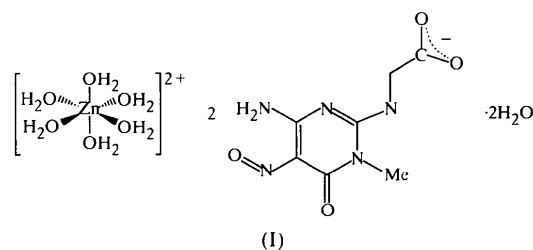
Abstract

In the title compound, $[\text{Zn}(\text{H}_2\text{O})_6](\text{C}_7\text{H}_8\text{N}_5\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, the crystal structure consists of a stacking along the *b*

axis of hexaaquazinc(II) cations which lie on inversion centres, glycinate anions and water molecules.

Comment

The title compound, (I), was obtained during our continuing research on the reactivity of metal ions with *N*-protected amino acids. The introduction of a substituent at the amino group in an α -amino acid gives rise to *N*-protected amino acids, which are of interest for the following reasons: (i) the *N*-substituent (4-amino-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidine) is an analogue of the potent antitumour agent 2,4-diamino-6-benzyloxy-5-nitrosopyrimidine (Pegg *et al.*, 1995; Loktinova & Pegg, 1996; Roy *et al.*, 1996); (ii) they are especially useful in directing peptide synthesis (Haurowitz, 1963) with markedly reduced racemization (Goldberg & Dice, 1974; Photaki, 1974); (iii) the involvement of these compounds in biological processes has been proved in many cases (Bonamartini Corradi, 1992); (iv) the possibility of modifying the chelating behaviour of the amino acid depending on the nature of the substituent (Arranz Mascarós *et al.*, 1999). We have found in previous studies that in the case of glycine with 4-amino-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidine as the *N*-substituent, the amino acid residue acts as a monodentate ligand towards metal ions (Mn^{II} , Cu^{II} , Zn^{II} and Cd^{II}) through the carboxylate group in mono- or bidentate mode (Arranz Mascarós, 1997). These compounds have tremendous versatility in the formation of hydrogen-bonded complexes because of the presence of numerous hydrogen-bond donor and acceptor groups, and it is well known that in the case of nucleic acid bases, these interactions determine the specificity of recognition between nucleic acid bases and DNA.



The crystal structure of the title complex consists of a stack along the *b* axis consisting of hexaaquazinc(II) cations, glycinate anions and water molecules (Fig. 1). The Zn^{II} atom is positioned on a centre of inversion and is hexacoordinated by water molecules with D_{2h} geometry.

The Zn—O bond lengths vary between 2.048 (1) and 2.143 (1) Å, and the O—Zn—O angles are close to 90 or 180°. These results are in agreement with usual values (Mak & Huang, 1987).

On the other hand, certain bond lengths differ from those found (values in brackets) in neutral *N*-(4-amino-

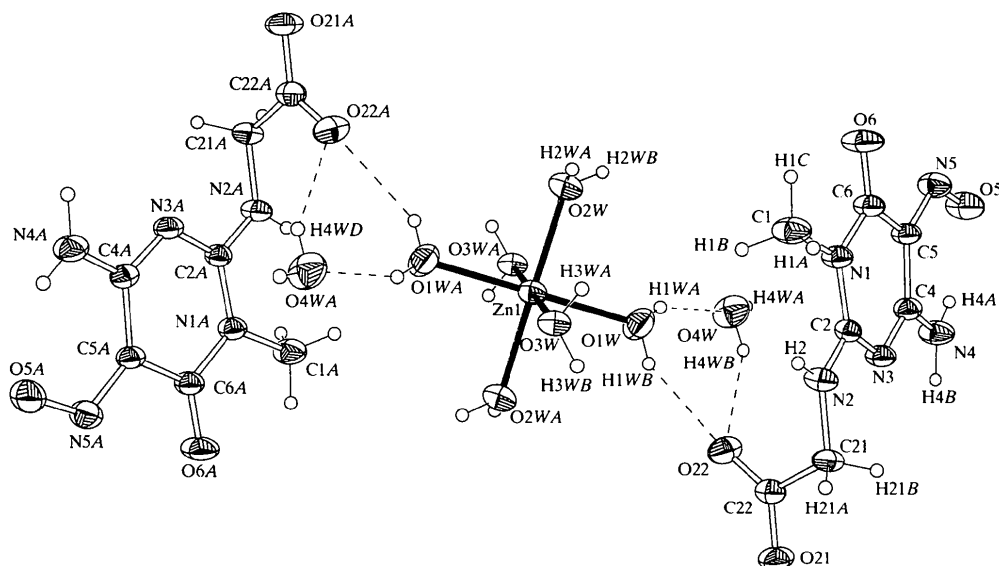


Fig. 1. A view of the title complex with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidin-2-yl)glycine (Low *et al.*, 1997), particularly C22—O21 1.257 (3) [1.292 (3) Å], C22—O22 1.243 (2) [1.207 (3) Å] and C21—C22 1.531 (2) Å [1.497 (3) Å]. These distances are consistent with deprotonation of the carboxyl group in (I). The N2—C21—C22—O22 torsion angle is similar for the two compounds.

The packing is stabilized by a large number of hydrogen bonds. All the H atoms of the coordinated water molecules are involved in hydrogen-bond formation. The nitroso O5 atom takes part as an acceptor in an intramolecular N4—H···O5 hydrogen bond with the adjacent 4-amino group to form a planar six-membered ring. Geometric details of the hydrogen bonding are given in Table 2.

Experimental

The ligand *N*-(4-amino-1-methyl-5-nitroso-6-oxo-1,6-dihydropyrimidin-2-yl)glycine was prepared according to the method of Arranz Mascarós *et al.* (1998). Complex (I) was obtained from aqueous solution at pH *ca.* 6.8. ZnCl₂ (0.75 mmol), dissolved in the minimum amount of water, was added to a solution of the potassium salt of the ligand (0.75 mmol, equimolar mixture) in the minimum amount of water (50 ml). A pink crystalline precipitate appeared and was filtered off, washed repeatedly with diethyl ether and dried over P₄O₁₀. Analysis, calculated for C₁₄H₃₂N₁₀O₁₆Zn: C 25.4, H 4.8, N 21.2%; found C 25.9, H 4.3, N 21.4%.

Crystal data

[Zn(H₂O)₆](C₇H₉N₅O₄)₂·2H₂O
M_r = 661.87
 Monoclinic
*P*2₁/*n*
 Mo Kα radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 15–45°

a = 6.9473 (6) Å
b = 7.4535 (6) Å
c = 25.0846 (17) Å
 β = 96.998 (6)°
V = 1289.25 (18) Å³
Z = 2
D_x = 1.705 Mg m⁻³
D_m not measured

μ = 1.048 mm⁻¹
T = 273 (2) K
 Block
 0.25 × 0.20 × 0.15 mm
 Pink

Data collection

Siemens P4 diffractometer
 2θ/ω scans
 Absorption correction:
 empirical (North *et al.*,
 1968)
T_{min} = 0.788, *T_{max}* = 0.855
 5178 measured reflections
 3715 independent reflections
 2746 reflections with
I > 2σ(*I*)

R_{int} = 0.031
 θ_{max} = 29.99°
h = -1 → 9
k = -1 → 10
l = -35 → 35
 4 standard reflections
 every 2.4 reflections
 frequency: 120 min
 intensity decay: 1.2%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.087
S = 0.985
 3715 reflections
 235 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0432*P*)²
 + 0.0019*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.385 e Å⁻³
 Δρ_{min} = -0.293 e Å⁻³
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Zn1—O2W	2.0485 (13)	C6—N1	1.397 (2)
Zn1—O3W ⁱ	2.0974 (13)	C6—C5	1.450 (2)
Zn1—O1W	2.1432 (14)	N1—C2	1.377 (2)
N2—C2	1.335 (2)	N1—C1	1.468 (2)
N2—C21	1.449 (2)	C5—C4	1.445 (2)

O22—C22	1.243 (2)	C2—N3	1.325 (2)
O21—C22	1.257 (2)	C22—C21	1.531 (2)
N5—O5	1.290 (2)	C4—N4	1.311 (2)
N5—C5	1.338 (2)	C4—N3	1.346 (2)
C6—O6	1.221 (2)		
O2W—Zn1—O3W	92.69 (5)	O5—N5—C5	117.75 (15)
O2W—Zn1—O1W	91.24 (6)	O22—C22—O21	125.21 (17)
O3W—Zn1—O1W	89.92 (6)		
N2—C21—C22—O21	−179.32 (15)	N2—C21—C22—O22	0.1 (2)

Symmetry code: (i) $-x, -y, -z$.

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WB...O22	0.81 (3)	2.22 (3)	2.903 (2)	142 (3)
O1W—H1WA...O4W	0.88 (3)	1.99 (3)	2.776 (2)	148 (3)
O2W—H2WA...O22 ⁱ	0.84 (3)	1.89 (3)	2.729 (2)	172 (3)
O2W—H2WB...O5 ⁱⁱ	0.88 (2)	1.79 (2)	2.6662 (19)	176 (2)
O3W—H3WA...O21 ⁱ	0.86 (2)	1.79 (2)	2.6415 (19)	170 (2)
O3W—H3WB...O21 ⁱⁱⁱ	0.86 (2)	1.88 (2)	2.728 (2)	172 (2)
O4W—H4WA...O6 ^{iv}	0.85 (3)	2.12 (3)	2.905 (2)	153 (3)
N2—H2...O3W ^v	0.86	2.27	3.086 (2)	159.3
N4—H4A...O5	0.85 (3)	1.94 (3)	2.613 (2)	135 (3)
N4—H4B...O6 ⁱ	0.93 (3)	1.92 (3)	2.749 (2)	147 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $1-x, 1-y, -z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $1-x, -y, -z$; (vi) $x, 1+y, z$.

H atoms were placed at their calculated positions (C—H 0.96 Å) and were refined at the final cycle, except for the H atoms on N2, C21 and C1.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b). Molecular graphics: PLUTON (Spek, 1995). Software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1042). Services for accessing these data are described at the back of the journal.

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Bis(2-ethyl-3-hydroxy-4-pyranonato)diiodotin(IV) acetonitrile solvate

ZHAISHENG LU,^a JOHN BURGESS,^b JOHN FAWCETT^b AND DAVID R. RUSSELL^b

^aDepartment of Chemistry, Xuzhou Normal University, Xuzhou 221009, Jiangsu, People's Republic of China, and ^bDepartment of Chemistry, University of Leicester, Leicester LE1 7RH, England. E-mail: jxf@leicester.ac.uk

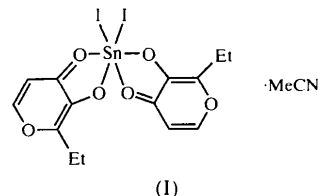
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Abstract

In the title compound, $[\text{SnI}_2(\text{C}_7\text{H}_7\text{O}_3)_2] \cdot \text{C}_2\text{H}_3\text{N}$, the ligand donor atoms are arranged around the Sn atom in a distorted octahedron, with the iodide ligands *cis* with respect to one another. The acetonitrile molecule of crystallization occupies interstitial positions in the structure.

Comment

The tin–ligand bond distances, some of the angles subtended by ligand donor atoms at tin, and carbon–oxygen and carbon–carbon bond distances in the chelate rings of the coordinated 2-ethyl-3-hydroxy-4-pyranonate (ethylmaltolate, etma) ligands in the title compound, bis(2-ethyl-3-hydroxy-4-pyranonato)diiodotin(IV) acetonitrile solvate, (I), are given in Table 1. The structure of



$\text{Sn}(\text{etma})_2\text{I}_2$ (Fig. 1) is, as expected, similar to that of its chloro analogue $\text{Sn}(\text{etma})_2\text{Cl}_2$ (Alsheri *et al.*, 1999). In both cases, the geometry around the Sn atom is approximately octahedral, with the halide ligands in *cis* positions. There is, however, a difference in the relative disposition of the two etma ligands. In $\text{Sn}(\text{etma})_2\text{I}_2$,