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catena-Poly[zinc(II)-bis{μ-(*N*-carbamoylglycinato)}-*O*:*O*″;*O*″:*O*], [Zn($C_3H_5N_2O_3$)$_2$]

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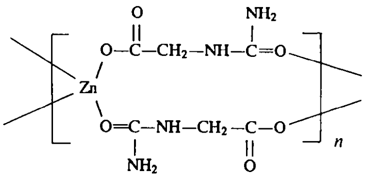
Abstract

The structure of [Zn(hyda)$_2$] (hydaH = *N*-carbamoylglycine or hydantoic acid) consists of polymeric linear chains in which pairs of Zn^{II} ions are connected by pairs of hydantoate anions coordinated through their carboxylic and amidic O atoms. The coordination around the metal atom is tetrahedral.

Comment

It is well known that for the neutral amide group both protonation and metal-ion coordination occur at the amide O atom, whereas metal coordination at the amide N atom takes place only by substitution of an amide H atom (Sigel & Martin, 1982). The additional presence of a carboxylic group in the molecule can, in principle, lead to chelate-ring formation involving either the amide O or N atoms. Nevertheless, it has been observed that *N*-acetyl amino acids usually coordinate only through the carboxylic O atom (Battaglia, Bonamartini Corradi, Marcotrigiano & Pellacani, 1977); only one case of coordination of an amidic O atom to a metal atom is known (Menabue & Saladini, 1988). In order to verify the coordination capability of the amidic group toward metal ions we report here the crystal and molecular structure of the title compound, (I).



(I)

A drawing showing the labelling scheme is presented in Fig. 1 and bond distances and angles are reported in Table 2.

The Zn^{II} atom coordinates to two carboxylic O atoms from two crystallographically independent anionic ligands and to two amidic O atoms from two symmetry-generated anions in a weakly distorted tetrahedral geometry. Each anion bridges two Zn atoms through its amidic and carboxylate O atoms, giving rise to one-dimensional polymeric chains.

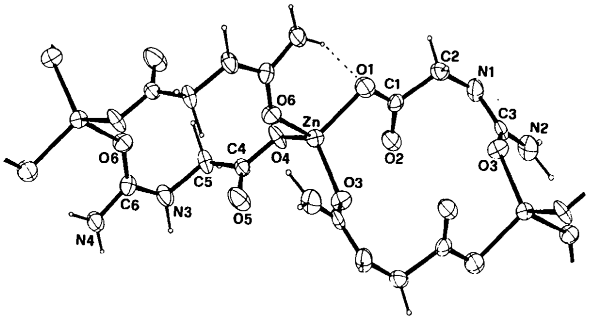


Fig. 1. *ORTEP* (Johnson, 1965) view of the [Zn(hyda)$_2$] moiety showing the atom numbering and the displacement ellipsoids (40%) for non-H atoms. The H atoms are represented as spheres of arbitrary radii.

The Zn—O distances are similar to each other in spite of the different nature of the O atoms and fall in the range found for other tetragonal Zn^{II} carboxylates (Clegg, Little & Straughan, 1986; Rodier, Ceolin, Plat & Zumbihl, 1990), although, in the present case, the carboxylic groups are monodentate. The distances Zn—O(2) = 2.662 (5) and Zn—O(5) = 2.783 (5) Å are significantly greater than the sum of the corresponding covalent radii (2.14 Å) (Pauling, 1960), *i.e.* the carboxyl group does not form a chelate ring as observed in the dithiobenzoate and acetate complexes of Zn^{II} (Bonamico, Dessy, Fares & Scaramuzza, 1972; Niekerk, Schoening & Talbot, 1953). The involvement of O(2) and O(5) in strong hydrogen bonds prevents their coordination to the Zn atom, favouring tetrahedral geometry that is uncommon for zinc(II) carboxylate complexes. The bond angles at the Zn atom lie in a narrow range (103.4–121.4°).

In the anion, the amidic carbonyl oxygen–metal coordination causes a slight lengthening of the C—O distances with respect to the free peptide, increasing the multiple character of the C—N bonds (Battaglia, Bonamartini Corradi, Marotrigiano & Pellacani, 1977). The resulting near planarity of the NCON units leads to low basicity of the NH groups, preventing their complexation to the metal.

Crystal packing is determined by hydrogen bonds which join the polymeric chains through N atoms and carboxylic and amidic O atoms. A strong intrachain hydrogen bond is also present, linking N(4) and O(1).

Experimental

Hydantoic acid was purchased from Sigma and used as received. A methanolic solution (0.05 dm^3) of zinc(II) acetate (0.02 mol dm^{-1}) was added to a methanolic solution (0.02 dm^3) of the amino acid (0.1 mol dm^{-1}). After some hours crystals of [Zn(hyda)$_2$] separated (yield 80%). Analysis: found C 23.90, H 3.55, N 18.90%; calculated for $[Zn(C_3H_5N_2O_3)_2]$ C 24.05, H 3.35, N 18.70%.

Crystal data

$[Zn(C_3H_5N_2O_3)_2]$
$M_r = 299.55$
Monoclinic
$P2_1/n$
$a = 7.871$ (7) Å
$b = 10.233$ (4) Å
$c = 13.318$ (2) Å
$\beta = 102.40$ (9)°
$V = 1048$ (1) Å^3
$Z = 4$

$D_x = 1.90$ Mg m^{-3}
$D_m = 1.88$ Mg m^{-3}
D_m measured by flotation in $CHBr_3 + CHCl_2\text{-}CCl_3$
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6\text{-}15°$
$\mu = 2.42$ mm^{-1}
$T = 298$ K
0.15 × 0.12 × 0.12 mm
White

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical (Ugozzoli, 1983)
$T_{min} = 0.98$, $T_{max} = 1.02$
2042 measured reflections
1961 independent reflections

1366 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.033$
$\theta_{max} = 25°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 15$
2 standard reflections
frequency: 4 min
intensity variation: <0.1%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.048$
1366 reflections
154 parameters
H-atom parameters not refined
Unit weights applied

$(\Delta/\sigma)_{max} = 0.35$
$\Delta\rho_{max} = 0.5$ e Å^{-3}
$\Delta\rho_{min} = -0.6$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn	0.2535 (1)	0.23153 (7)	0.02855 (6)	0.0241 (2)
O(1)	0.2765 (6)	0.0841 (5)	0.1282 (4)	0.0358 (18)
O(2)	0.5495 (7)	0.1205 (5)	0.1251 (4)	0.0355 (17)
O(3)	0.6650 (6)	−0.1749 (5)	0.0932 (3)	0.0273 (14)
O(4)	0.3329 (7)	0.3949 (4)	0.0983 (4)	0.0315 (16)
O(5)	0.2617 (8)	0.4786 (5)	−0.0576 (4)	0.0446 (20)
O(6)	0.0018 (6)	0.7418 (5)	0.0187 (4)	0.0303 (15)
N(1)	0.6636 (8)	−0.0926 (6)	0.2484 (4)	0.0346 (23)
N(2)	0.9181 (8)	−0.1527 (6)	0.2072 (4)	0.0364 (20)
N(3)	0.2851 (7)	0.7328 (6)	0.0133 (5)	0.0313 (20)
N(4)	0.1036 (8)	0.8680 (6)	−0.0957 (5)	0.0392 (23)
C(1)	0.4352 (9)	0.0573 (6)	0.1526 (5)	0.0237 (21)
C(2)	0.483 (1)	−0.0616 (7)	0.2224 (5)	0.0319 (24)
C(3)	0.7505 (9)	−0.1422 (6)	0.1807 (5)	0.0259 (21)
C(4)	0.3017 (8)	0.4920 (6)	0.0355 (5)	0.0224 (21)
C(5)	0.3248 (9)	0.6244 (6)	0.0863 (5)	0.0288 (22)
C(6)	0.1256 (8)	0.7782 (6)	−0.0201 (5)	0.0249 (19)

Table 2. *Selected geometric parameters* (Å, °)

Zn—O(1)	1.991 (5)	Zn—O(4)	1.950 (4)
Zn—O(3^{i})	1.955 (5)	Zn—O(6^{ii})	1.991 (5)
O(1)—C(1)	1.252 (8)	O(4)—C(4)	1.288 (8)
O(2)—C(1)	1.227 (9)	O(5)—C(4)	1.220 (8)
C(1)—C(2)	1.528 (9)	C(4)—C(5)	1.508 (8)
C(2)—N(1)	1.426 (10)	C(5)—N(3)	1.465 (9)
N(1)—C(3)	1.343 (10)	N(3)—C(6)	1.323 (8)
N(2)—C(3)	1.295 (9)	N(4)—C(6)	1.347 (9)
O(3)—C(3)	1.259 (7)	O(6)—C(6)	1.254 (8)
O(1)—Zn—O(3^{i})	109.2 (2)	O(4)—Zn—O(3^{i})	121.4 (2)
O(1)—Zn—O(4)	111.0 (2)	O(4)—Zn—O(6^{ii})	103.4 (2)
O(1)—Zn—O(6^{ii})	104.8 (2)	O(3^{i})—Zn—O(6^{ii})	105.5 (2)
O(1)—C(1)—O(2)	124.1 (6)	O(4)—C(4)—O(5)	123.0 (6)
O(1)—C(1)—C(2)	115.7 (6)	O(4)—C(4)—C(5)	114.4 (6)
O(2)—C(1)—C(2)	120.2 (7)	O(5)—C(4)—C(5)	122.5 (6)
C(1)—C(2)—N(1)	115.2 (6)	C(4)—C(5)—N(3)	113.2 (6)
C(2)—N(1)—C(3)	123.1 (6)	C(5)—N(3)—C(6)	122.7 (6)
N(1)—C(3)—N(2)	119.0 (6)	N(3)—C(6)—N(4)	116.8 (6)
N(1)—C(3)—O(3)	118.3 (6)	N(3)—C(6)—O(6)	121.6 (6)
N(2)—C(3)—O(3)	122.7 (6)	N(4)—C(6)—O(6)	121.6 (6)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $-x, 1 - y, -z$.

Intensity data were collected with a scan width of $(1.3 + 0.35\tan\theta)°$, a scan speed of 8.2° min^{-1} and a maximum time of 60 s per reflection. The structure was solved by conventional Patterson and Fourier techniques, and refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. H atoms were located on a difference Fourier map and were treated as fixed contributors with isotropic displacement parameters 1.0 Å higher than those of their parent atom. All calculations were carried out on a VAX 6310 computer using *SHELX*76 (Sheldrick, 1976), *PARST* (Nardelli, 1983) and *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71766 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1067]

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(Pyridine-2-thiolato-*N*,*S*)bis(triphenylphosphine)platinum(II) Hexafluorophosphate Chloroform Solvate

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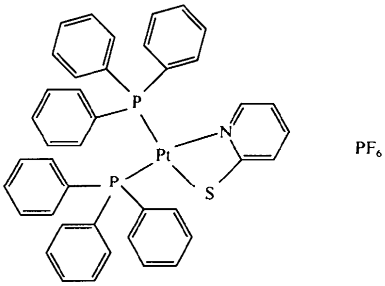
Abstract

The first structure determination of a monomeric platinum complex with a pyridine-2-thiolato ligand is reported. The Pt atom in (pyridine-2-thiolato-*N*,*S*)bis(triphenylphosphine)platinum(II) hexafluorophosphate chloroform solvate, $[Pt(C_5H_4NS)(PPh_3)_2]PF_6.CHCl_3$, is coordinated by two triphenylphosphine ligands and a pyridine-2-thiolato ligand through N and S atoms.

Comment

It has been demonstrated that the deprotonated 2-mercaptopyridine ligand C_5H_4NS functions either as a monodentate ligand, a bidentate chelating ligand or a bridging ligand when coordinated to metal centers (Deeming, Karim, Bates & Hursthouse, 1988). Recently, we have synthesized two mercury(II) complexes containing the pyridine-2-thiolato ligand, $Hg(C_5H_4NS)(O_2CCH_3)$ and $Hg(C_5H_4NS)_2$ (Wang & Fackler, 1989). Both compounds have one-dimensional structures in the solid phase. $Hg(C_5H_4NS)_2$ is especially interesting as the N atom on the C_5H_4NS ligand does not coordinate to the Hg center, thus enabling it to bind to a second metal center to form bimetallic compounds. We carried out the reaction of $Hg(C_5H_4NS)_2$ with $Pt(PPh_3)_2Cl_2$ in the presence of $TlPF_6$ hoping to obtain an HgPt bimetallic complex. Bimetallic platinum complexes have been reported in which the pyridine-2-thiolate ligand acts as a bridge between the metal centers (Umakoshi, Kinoshita, Fukui-Yasuba, Matsumoto, Ooi, Nakai & Shiro, 1989). The yellow product obtained from this reaction was analyzed by single-crystal X-ray diffraction, which showed the product to be $[Pt(C_5H_4NS)(PPh_3)_2]PF_6$, (1). Although this was not the bimetallic compound we expected, the synthesis and the structure of a monomeric platinum(II) complex containing pyridine-2-thiolate have not been reported previously.



(I)

The molecular structure of $[Pt(C_5H_4NS)(PPh_3)_2]PF_6$ is shown in Fig. 1. The Pt atom is coordinated by two triphenylphosphine ligands and one C_5H_4NS ligand through the N and S atoms with a distorted square-planar geometry [P(1)—Pt—S = 165.6 (1), P(2)—Pt—N = 163.8 (2)°]. Although the Pt—P distances are normal, the Pt—P(1) distance [2.295 (2) Å] is slightly longer than the Pt—P(2) distance [2.253 (2) Å], apparently as a result of the stronger *trans* effect of the S atom relative to N. The S—C(5) distance of 1.735 (7) Å is typical for an

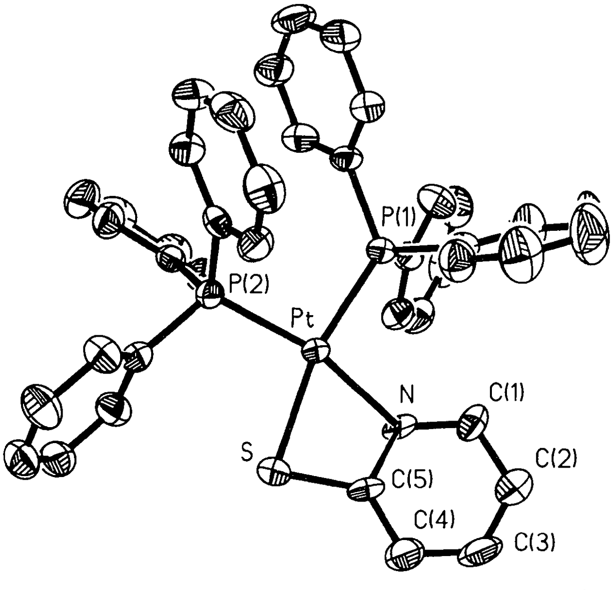


Fig. 1. A view of the $[Pt(C_5H_4NS)(C_{18}H_{15}P)_2]^+$ cation. Displacement ellipsoids have been drawn at the 50% probability level.