metal-organic compounds

Bis(2-aminopyridine-N)bis(benzo-ato-O)zinc

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The crystal structure of the title compound, [Zn-$(C_7H_5O_2)_2(C_5H_6N_2)_2$], is built of monomeric [Zn(2-apy)$_2$-(OBz)$_2$] molecules (apy is aminopyridine and OBz is benzoate). The Zn atom lies on a twofold symmetry axis and adopts a slightly distorted tetrahedral coordination. The Zn$\cdots$O distances to the non-coordinated O atoms are long at 2.872 (3) Å. Each non-ligating carbonyl O atom of the benzoate anion accepts one intramolecular and one inter-molecular hydrogen bond from the amino group. The molecules form a chain along the c axis through intermolecular N—H$\cdots$O hydrogen bonds between the amino and carboxyl groups.

Comment

Zinc is a relatively abundant element in biological organisms and plays an essential role in a large number of enzymatic reactions (Liljas *et al.*, 1972). Zinc(II), being a d^{10} ion, gives a UV–visible spectrum which does not provide information on its structure. The structure of the zinc binding site could be elucidated by X-ray crystallography. The number of reports on

(I)
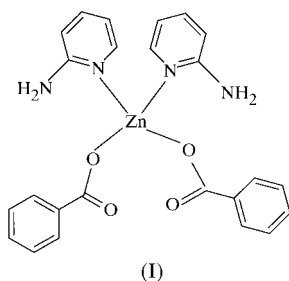
monomeric zinc complexes containing carboxylate and basic ligands are quite limited. In this paper, we report the crystal structure of the title compound, bis(2-aminopyridine-N)bis-(benzoato-O)zinc, (I), which has been determined in an attempt to understand the structural behaviour of nitrogen-containing ligands when coordinating to zinc carboxylates.

The Zn atom of the central ZnO$_2$N$_2$ system is in a slightly deformed tetrahedral coordination formed by two benzoate anions and two 2-aminopyridine molecules. The bond lengths in the coordination polyhedron are normal. The Zn—N bond distance of 2.052 (4) Å is in accord with similar distances reported previously, *e.g.* 2.039 (8) Å in [ZnCl$_2$(C$_{17}$H$_{19}$N$_3$)$_2$] (Parvez & Rusiewicz, 1995) and 2.056 (4) Å in [Zn(C$_5$H$_7$-NO$_2$)$_2$] (Ng *et al.*, 1995), and the Zn—O distance of 1.930 (3) Å is a little shorter than similar reported distances, *e.g.* 1.959 (3) Å in [Zn(C$_3$H$_5$O$_2$)$_2$(CH$_4$N$_2$S)$_2$] (Smolander *et al.*, 1994) and 1.963 (2) Å in [Zn(C$_7$H$_5$O$_2$)$_2$(CH$_4$N$_2$S)$_2$] (Cernak *et al.*, 1995). Two additional Zn$\cdots$O interactions to the non-coordinated O atoms of the carboxylate groups are long [2.872 (3) Å].

The deformation of the coordination polyhedron, which is centred on a twofold axis, mainly involves the two angles bisected by that axis, *i.e.* O1—Zn—O1^i, which is widened to 127.9 (2)°, and N2—Zn—N2^i, which is narrowed to 100.6 (2)° [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. This appears to be due to steric effects, as shown by the two non-bonded contacts C12$\cdots$N2^i = 3.422 (6) and O2$\cdots$O1^i = 3.393 (7) Å. Some influence is also exerted by the intramolecular N1—H$\cdots$O1 hydrogen bond on the N2$\cdots$O1 [3.128 (5) Å] contact. This N$\cdots$O distance is different from the corresponding value found in similar complexes containing the ZnO$_2$N$_2$ unit, which exhibit one short and one long additional interaction, *e.g.* 2.645 (2) and 3.034 (2) Å [angle 118.5 (1)°] in [Zn(CH$_3$-COO)$_2$(im)$_2$] (im is imidazole), and 2.692 (2) and 3.151 (2) Å [angle 116.3 (1)°] in [Zn(CH$_3$CH$_2$COO)$_2$(im)$_2$] (Horrocks *et al.*, 1982).

As expected, the C—O bond lengths [1.274 (5) Å] of the coordinated O atoms are somewhat longer than those of the non-ligating O atoms [1.213 (6) Å]. The latter suggests more double-bond character for the C—O bond (Davey & Stephens, 1971). The average C—C distance [1.375 (7) Å] in the phenyl ring agrees well with the value [1.380 (16) Å]
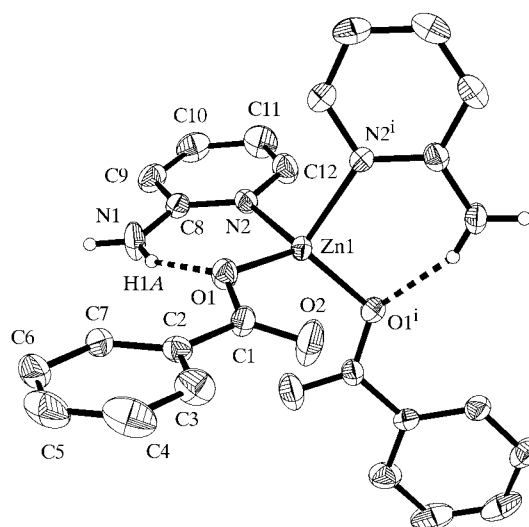

Figure 1
The molecular structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

reported by Allen *et al.* (1987). The 2-aminopyridine ligand is planar and coordinates so that the zinc ion lies near the plane. Thus, the carboxylate and its mode of coordination appear to be entirely normal. The molecules form a chain along the *c* axis through intermolecular N—H···O hydrogen bonds between the amino and carboxyl groups. The distance between the ring centroids (*Cg*) involve symmetry-related ligands, *i.e.* $Cg_{py}···Cg_{aryl}(1-x, 1-y, -z)$ is 3.821 (1) Å.

Experimental

The title compound was prepared by dissolving zinc dibenzoate (0.03 mmol) in EtOH (80 ml) followed by the addition of 2-amino-pyridine (0.06 mmol). The solution was heated to boiling until all the solid dissolved and was then filtered. The filtrate was allowed to stand at room temperature for two weeks over which time colourless prismatic crystals formed on slow evaporation of the solvent.

Crystal data

[Zn(C7H5O2)2(C5H6N2)2]	$D_x = 1.47$ Mg m^{-3}
$M_r = 495.83$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 6408
$a = 20.3597$ (7) Å	reflections
$b = 9.9400$ (3) Å	$\theta = 2.16–28.37°$
$c = 12.0064$ (4) Å	$\mu = 1.13$ mm^{-1}
$\beta = 112.336$ (1)°	$T = 293$ (2) K
$V = 2247.49$ (13) Å^3	Slab, colourless
$Z = 4$	$0.44 \times 0.22 \times 0.12$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	2785 independent reflections
	2151 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.072$
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 28.59°$
	$h = -25 \rightarrow 27$
$T_{min} = 0.636$, $T_{max} = 0.876$	$k = -13 \rightarrow 11$
7990 measured reflections	$l = -16 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1089P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.061$	$+ 3.7360P]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.108$	$(\Delta/\sigma)_{max} < 0.001$
2785 reflections	$\Delta\rho_{max} = 1.24$ e Å^{-3}
150 parameters	$\Delta\rho_{min} = -0.86$ e Å^{-3}
H-atom parameters constrained	

The maximum and minimum residual electron densities were located at 0.90 and 0.82 Å, respectively, from the Zn1 atom.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.930 (3)	N1—C8	1.342 (6)
Zn1—N2	2.052 (4)	N2—C8	1.345 (6)
O1—C1	1.274 (5)	N2—C12	1.344 (6)
O2—C1	1.213 (6)		
O1—Zn1—O1^i	127.9 (2)	C1—O1—Zn1	116.0 (3)
O1—Zn1—N2	103.5 (1)	C8—N2—Zn1	126.9 (3)
O1^i—Zn1—N2	109.1 (2)	C12—N2—Zn1	115.4 (3)

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.86	2.04	2.842 (6)	155
N1—H1B···O2^i	0.86	2.17	2.823 (8)	133

Symmetry code: (i) $x, 1-y, z-\frac{1}{2}$.

to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Cernak, J., Adzimova, I., Gerard, F. & Hardy, A. M. (1995). *Acta Cryst.* C51, 392–395.

Davey, G. & Stephens, F. S. (1971). *J. Chem. Soc. A*, pp. 1917–1920, 2577–2580.

Horrocks, W. D. Jr, Ishley, J. N. & Whittle, R. R. (1982). *Inorg. Chem.* 21, 3265–3269.

Liljas, A., Kannan, K. K., Bergsten, P. C., Waara, I., Fridborg, K., Strandberg, B., Caribom, V., Jarup, L., Lovgren, S. & Petef, M. (1972). *Nature New Biol.* 235, Part 57, pp. 131–137.

Nardelli, M. (1995). *J. Appl. Cryst.* 28, 659.

Ng, C. H., Fun, H.-K., Teo, S. B., Teoh, S. G. & Chinnakali, K. (1995). *Acta Cryst.* C51, 244–245.

Parvez, M. & Rusiewicz, M. (1995). *Acta Cryst.* C51, 2277–2279.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Smolander, K., Ahlgren, M., Melnik, M., Skorsepa, J. & Gyoryova, K. (1994). *Acta Cryst.* C50, 1900–1902.

Spek, A. L. (1990). *Acta Cryst.* A46, C-34.