

Bis(isoquinoline-1-carboxylato- κ^2O,N)(1,10-phenanthroline- κ^2N,N')-zinc(II) dimethylformamide sesquisolvate

Jean-Claude Daran,^a Pascale Lemoine^{b*} and Bernard Viossat^{b,c}

^aLaboratoire de Chimie de Coordination, UPR 8241 CNRS, 205 route de Narbonne, 31077 Toulouse CEDEX 04, France, ^bLaboratoire de Cristallographie et RMN biologiques, UMR 8015 CNRS, Faculté des Sciences Pharmaceutiques et Biologiques de Paris V, 4 avenue de l'Observatoire, 75270 Paris CEDEX 06, France, and ^cLaboratoire de Chimie Générale, Faculté de Médecine et de Pharmacie, 34 rue du Jardin des Plantes, BP199, 86005 Poitiers CEDEX, France
Correspondence e-mail: lemoine@pharmacie.univ-paris5.fr

Received 22 October 2001

Accepted 30 January 2002

Online 12 March 2002

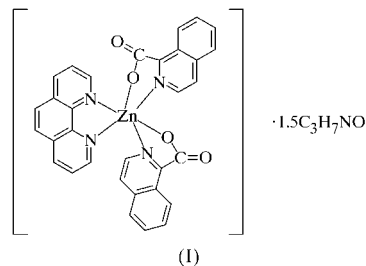
The asymmetric unit of the title compound, $[\text{Zn}(\text{C}_{10}\text{H}_6\text{NO}_2)_2 \cdot (\text{C}_{12}\text{H}_8\text{N}_2)] \cdot 1.5\text{C}_3\text{H}_7\text{NO}$, contains one monomeric zinc complex and 1.5 disordered dimethylformamide solvate molecules. The Zn atom is coordinated to one 1,10-phenanthroline ligand and to two isoquinolinecarboxylate anions (IQC^-) *via* their N and O atoms. The complex exhibits a distorted octahedral geometry around the Zn^{II} atom, with the apical positions occupied by the O atoms of the IQC^- ligands. The Zn atom lies 0.049 (1) Å out of the basal plane. The crystal packing is characterized by several hydrogen bonds.

Comment

Complexes of Cu^{II} , Fe^{III} , Co^{II} , Ni^{II} , Ti^{IV} and Zn^{II} with 3,5-disubstituted salicylates (non-steroidal anti-inflammatory drugs, NSAIDs), and ternary complexes of Cu^{II} with added phenanthrolines, have been prepared and characterized by Ranford *et al.* (1993). Following this work, we have recently synthesized and characterized a ternary complex of Cu^{II} with *N,O*-isoquinoline-1-carboxylic acid (HIQC) and the heteroaromatic nitrogen base 2,9-dimethyl-1,10-phenanthroline (Lemoine & Viossat, 2001). In the present work, we describe the synthesis and crystal structure of bis(isoquinoline-1-carboxylato- κ^2O,N)(1,10-phenanthroline- κ^2N,N')zinc(II) dimethylformamide sesquisolvate, (I).

In monomeric (I), the Zn atom is surrounded by one bidentate 1,10-phenanthroline ligand, coordinated *via* atoms N21 and N30, and two anionic bidentate isoquinolinecarboxylate (IQC^-) ligands, coordinated *via* atoms N1, O1, N11 and O11. The complex exhibits a distorted octahedral geometry around the Zn^{II} atom, with the apical positions occupied by atoms O1 and O11. The Zn atom lies 0.049 (1) Å

out of the basal plane (N1/N11/N21/N30). The degree of deviation from an ideal octahedron is appreciable, with the angles of the octahedron ranging from 76.04 (6) to 101.16 (6)°.



The Zn–N21 and Zn–N30 distances in (I) are in agreement with those observed in *cis*-diaquabis(1,10-phenanthroline)zinc sulfate hexahydrate [2.136 (3)–2.192 (4) Å; Hu & Liu, 1991] and in the $[\text{Zn}(1,10\text{-phenanthroline})_3]^{2+}$ complex (mean 2.17 Å; Bencini *et al.*, 1989), but are clearly longer than those in $[\text{Zn}(1,10\text{-phenanthroline})\text{Cl}_2]$ (mean 2.06 Å; Khan & Tuck, 1984), due to the change in coordination number from six to four. The chelation of Zn^{II} by the IQC^- ligands in (I) leads to planar N/C/C/O/Zn rings, *P*1 (N1/C2/C1/O1/Zn) and *P*2 (N11/C12/C11/O11/Zn); the maximum deviation is 0.067 (2) Å for atom N11, with a dihedral angle between planes *P*1 and *P*2 of 83.18 (4)°.

The Zn–O [mean 2.069 (1) Å] and Zn–N(IQC^-) [mean 2.141 (2) Å] distances compare with the corresponding values in a similar environment in diaquabis[2,2,5,5-tetramethyl-1-oxo-3-imidazoline-4-carboxylato]zinc(II) [2.07 Å for mean Zn–O and 2.09 Å for mean Zn–N; Kozhemyak *et al.*, 1980]. The isoquinoline mean planes, *P*3 (N1/C2–C10) and *P*4 (N11/C12–C20), make dihedral angles of 3.66 (4) and 7.85 (4)° with planes *P*1 and *P*2, respectively. The Zn^{II} atom is displaced from the 1,10-phenanthroline least-squares plane *P*5 (N21/C22–C29/N30/C31–C34) by 0.221 (1) Å. The dihedral angles between planes *P*1 and *P*5, and *P*2 and *P*5 are 89.60 (4) and 73.00 (4)°, respectively.

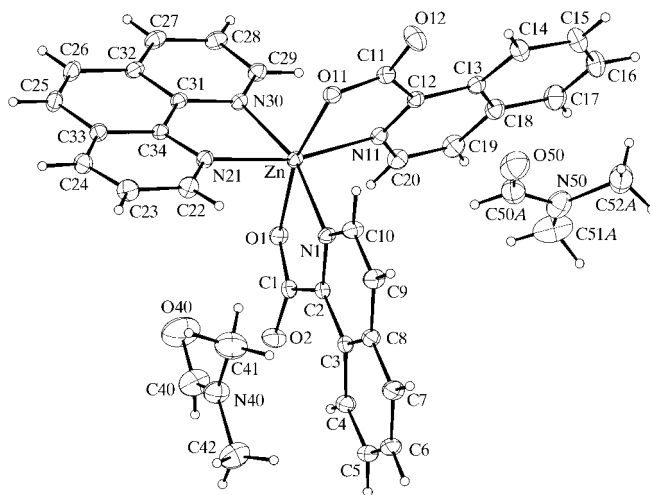


Figure 1

A perspective view of the asymmetric unit of (I) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The N40 solvent molecule has an occupancy of 0.5.

The crystal structure of (I) is completed by disordered dimethylformamide (DMF) solvate molecules. In the first DMF molecule, the three C atoms (C50, C51 and C52) and their corresponding H atoms are disordered over two sites, denoted by the suffix *A* (occupancy 0.73) or *B* (occupancy 0.27). The N atom (N40) in the second DMF solvent molecule lies on an inversion centre, leading to a statistical disorder.

As shown in Fig. 2, the packing in (I) is governed by π - π -stacking interactions, which occur between phenanthroline ligands related through inversion centres at $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, thus creating self-assembling dimers, with an average spacing of 3.358 (1) Å. Moreover, two contacts, C4—H4...O2 [2.867 (2) Å and 123°] and C14—H14...O12 [2.848 (3) Å and 125°], may be considered as weak hydrogen bonds. Weak van der Waals contacts [the shortest being 3.140 (6) Å for C22...O40] contribute to the cohesion of the crystal structure of (I).

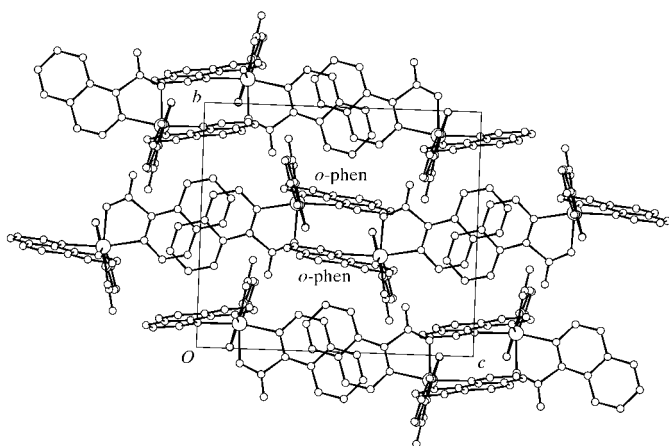


Figure 2
The molecular packing in (I) viewed along [100], showing the π -stacking interactions between phenanthroline ligands.

Experimental

Bis(isoquinolinecarboxylato)zinc(II) was prepared by mixing aqueous solutions of the sodium salt of isoquinolinecarboxylic acid (1.95 g, 10 mmol) and zinc chloride (1.36 g, 10 mmol) in excess for a better yield. The resulting precipitate was collected by filtration, washed with water and dried overnight. The title complex was obtained in a dimethylformamide medium by reaction of this zinc(II) complex with 1,10-phenanthroline (Phen/Zn 1:1). The reaction mixture was stirred for 30 min. Colourless parallelepiped crystals of (I) were obtained by slow evaporation.

Crystal data

$[\text{Zn}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)] \cdot 1.5\text{C}_3\text{H}_7\text{NO}$	$D_m = 1.47 \text{ Mg m}^{-3}$
$M_r = 699.55$	D_m measured by flotation in $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 17.077(2) \text{ \AA}$	Cell parameters from 8000 reflections
$b = 12.747(1) \text{ \AA}$	$\theta = 2.1\text{--}26.1^\circ$
$c = 14.422(1) \text{ \AA}$	$\mu = 0.84 \text{ mm}^{-1}$
$\beta = 93.22(1)^\circ$	$T = 170(2) \text{ K}$
$V = 3134.2(5) \text{ \AA}^3$	Parallelepiped, colourless
$Z = 4$	$0.40 \times 0.25 \times 0.20 \text{ mm}$
$D_x = 1.482 \text{ Mg m}^{-3}$	

Table 1

Selected geometric parameters (Å, °).

Zn1—O11	2.0531 (14)	C1—C2	1.540 (3)
Zn1—O1	2.0851 (14)	O11—C11	1.273 (2)
Zn1—N11	2.1285 (16)	N11—C12	1.321 (3)
Zn1—N1	2.1537 (15)	C11—O12	1.229 (3)
Zn1—N21	2.1845 (15)	C11—C12	1.535 (3)
Zn1—N30	2.1873 (15)	N21—C34	1.354 (2)
O1—C1	1.270 (2)	N30—C31	1.355 (2)
N1—C2	1.323 (2)	C31—C34	1.439 (3)
C1—O2	1.232 (2)		
O11—Zn1—O1	165.63 (5)	O2—C1—O1	125.25 (18)
O11—Zn1—N11	77.50 (6)	O2—C1—C2	119.13 (17)
O1—Zn1—N11	93.82 (6)	O1—C1—C2	115.61 (16)
O11—Zn1—N1	93.51 (6)	C10—N1—Zn1	124.17 (13)
O1—Zn1—N1	76.35 (6)	C11—O11—Zn1	118.08 (12)
N11—Zn1—N1	98.85 (6)	N11—C12—C11	113.91 (16)
O11—Zn1—N21	94.45 (6)	O11—C11—C12	115.43 (17)
O1—Zn1—N21	96.23 (6)	C12—N11—Zn1	114.41 (12)
N11—Zn1—N21	165.91 (6)	C20—N11—Zn1	124.62 (13)
N1—Zn1—N21	93.12 (6)	O12—C11—O11	124.92 (18)
O11—Zn1—N30	101.16 (6)	O12—C11—C12	119.64 (17)
O1—Zn1—N30	90.74 (5)	N21—C34—C31	117.61 (16)
N11—Zn1—N30	94.00 (6)	C22—N21—Zn1	127.62 (13)
N1—Zn1—N30	162.29 (6)	C34—N21—Zn1	114.09 (12)
N21—Zn1—N30	76.04 (6)	C29—N30—Zn1	127.53 (13)
N1—C2—C1	113.32 (15)	C31—N30—Zn1	114.03 (12)
C1—O1—Zn1	118.48 (12)	N30—C31—C34	117.54 (16)
C2—N1—Zn1	115.50 (12)		

Data collection

Stoe IPDS diffractometer
 φ scans
 24 106 measured reflections
 6128 independent reflections
 5303 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

$\theta_{\text{max}} = 26.1^\circ$
 $h = -20 \rightarrow 21$
 $k = -15 \rightarrow 15$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2

$R(F) = 0.033$
 $wR(F^2) = 0.082$
 $S = 1.03$
 6128 reflections
 490 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 1.7050P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$

H atoms were treated as riding, with C—H distances in the range 0.93–0.96 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$, and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Data collection: *IPDS Software* (Stoe & Cie, 1996); cell refinement: *IPDS Software*; data reduction: *XRED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1009). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

- Bencini, A., Midollini, S. & Zanchini, C. (1989). *Inorg. Chem.* **28**, 1963–1969.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Hu, N.-H. & Liu, Y.-S. (1991). *Acta Cryst.* **C47**, 2324–2326.
- Khan, M. A. & Tuck, D. G. (1984). *Acta Cryst.* **C40**, 60–62.
- Kozhemyak, N. V., Podberezskaya, N. V. & Bakakin, V. V. (1980). *Zh. Strukt. Khim.* **21**, 124–128.
- Lemoine, P. & Viossat, B. (2001). *Acta Cryst.* **C57**, 1248–1250.
- Ranford, J. D., Sadler, P. J. & Tocher, D. A. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3393–3399.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (1996). *IPDS Manual* (Version 2.75) and *XRED* (Revision 1.08). Stoe & Cie, Darmstadt, Germany.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.