Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Aquabis(2-nitrobenzoato-κ*O*)(1,10-phenanthroline-κ^2*N*,*N*′)zinc(II)

Kou-Lin Zhang,[a]* Jian-Guo Lin,[a] Ya-Qiong Wang,[a] Wen-Lin Xu[a]* and Jiu-Tong Chen[b]

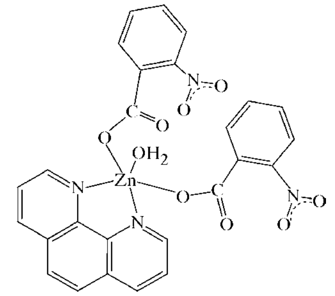
[a]Chemistry and Chemical Engineering College, Yangzhou University, Yangzhou 225002, People's Republic of China, and [b]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China
Correspondence e-mail: koulinzhang2002@yahoo.com

Received 14 June 2004
Accepted 23 July 2004
Online 21 August 2004

The title compound, $[Zn(C_7H_4NO_4)_2(C_{12}H_8N_2)(H_2O)]$, has been synthesized. X-Ray analysis reveals that it is a neutral zinc(II) mononuclear carboxylate complex based on mixed N- and O-donor ligands. The Zn atom is five-coordinate in a distorted trigonal–bipyramidal coordination environment involving two O atoms of two monodentate 2-nitrobenzoate molecules, two N atoms of a 1,10-phenanthroline molecule and one O atom of a water molecule. The axial positions are occupied by a carboxylate O atom from the 2-nitrobenzoate ligand and an N atom from the 1,10-phenanthroline ligand [N—Zn—O = 167.66 (9)°].

Comment

Aromatic carboxylic acids have been used extensively in medicine as non-steroidal anti-inflammatory drugs (Stuhlmeier *et al.*, 1999; Emery *et al.*, 2002). The carboxylate ligand can coordinate with metal ions that can have synergetic or antagonistic effects on biological activity. The anti-inflammatory and antibacterial activities of some metal complexes have been found to be higher than in the parent carboxylic acids (Dendrinou-Samara *et al.*, 1998). Furthermore, the antibacterial effect of some drugs is enhanced when they coordinate with metal ions (Chohan & Sherazi, 1997). It is therefore very important to study the structure and bonding relationships of such complexes, in order to synthesize highly effective antimicrobial species. Recently, we have paid special attention to studying the interactions of aromatic carboxylic acids with zinc, which is a very important element to human beings. Zinc has been known to regulate biological activity in more than 300 metalloenzymes, and zinc and its complexes have antibacterial and antiviral activities (Korant *et al.*, 1974; Simo *et al.*, 2000; Clercq, 1997). Zinc may also act as an antisickling agent and play a very important role in the prevention of pain crisis in sickle-cell disease. To date, zinc has been used successfully in the treatment of several diseases (Cunnane, 1988); a complex of zinc(II) acetate with erythromycin has been used successfully in clinical medicine for acne therapy (Hoogdalem, 1998), and some aliphatic carboxylic acid zinc(II) complexes containing additional N-donor ligands have been found to exhibit some biological activity (Zelenak *et al.*, 2002). In the present study, we report the synthesis and crystal structure of the title complex, (I). The biological activity of (I) against common bacterial strains is to be investigated.



(I)

To the best of our knowledge, (I) is the only reported zinc complex containing 2-nitrobenzoate as a ligand. Selected geometric parameters are listed in Table 1. As shown in Fig. 1, (I) is a mononuclear neutral zinc(II) complex in which the carboxylate group exhibits a monodentate coordination mode. By contrast, in the mononuclear zinc complex of diaquabis(4-nitrobenzoato)zinc(II), each carboxylate ligand forms a primary and a secondary Zn—O bond (Necefoglu *et al.*, 2001). The Zn ion in (I) is coordinated by two O atoms from two monodentate 2-nitrobenzoate ligands (O1 and O5), two N atoms from the 1,10-phenanthroline ligand (N1 and N2) and one O atom from the water molecule (O9), and exhibits distorted trigonal–bipyramidal coordination. The trigonal base plane is defined by atoms N2, O5 and O9, and atoms O1 and N1 occupy the axial positions [O1—Zn—N1 =

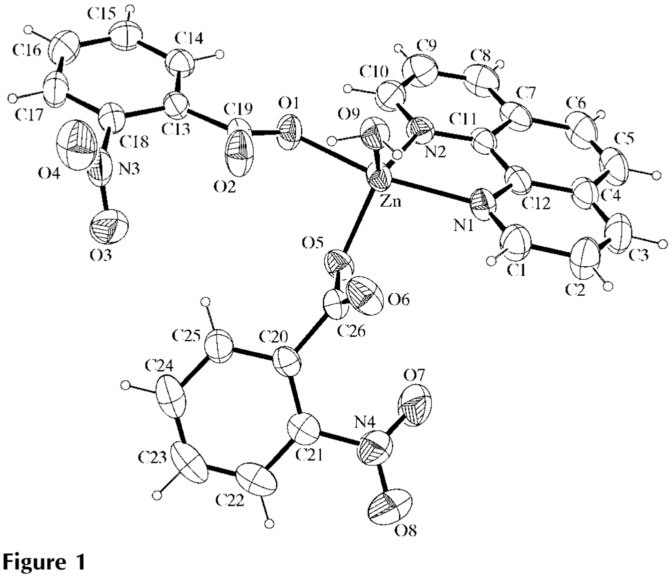


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are shown at the 50% probability level.

DOI: 10.1107/S0108270104018165

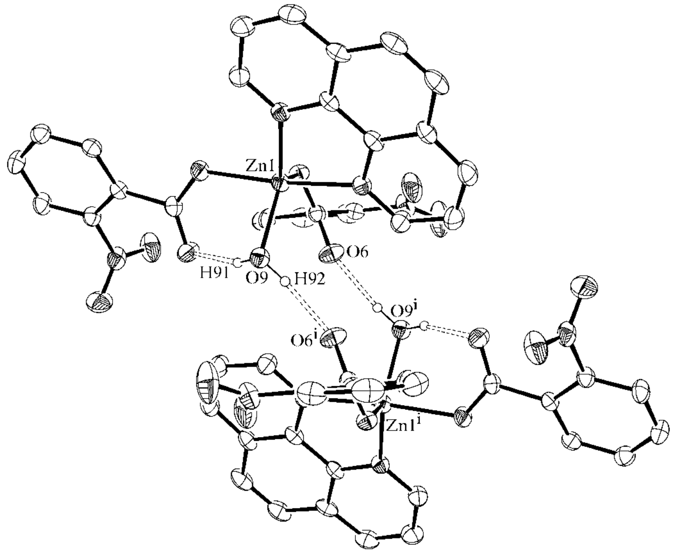


Figure 2
A view of the dimer built from intermolecular O—H···O hydrogen bonding (dashed lines). Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

167.66 (9)°]. The Zn—O5 distance [1.996 (2) Å] is shorter than the Zn—O1 distance [2.081 (2) Å], and the Zn—O1 and Zn—O5 distances are both shorter than those observed in some benzoic acid zinc complexes containing N-donor ligands (Zelenak *et al.*, 2004). The Zn—O9 distance is 2.043 (2) Å, which is in agreement with the distance (2.053 Å) in the related complex *catena*-[bis[aqua(μ-terephthalato)(1,10-phenanthroline)zinc]] (Sun *et al.*, 2001). Many hydrolytic enzymes contain a zinc(II) ion in the active site because zinc-bound water or hydroxide is an excellent nucleophilic agent (Jiang & Guo, 2004). The mean Zn—N distance in (I) (2.132 Å) is similar to that in the zinc complex $[Zn(SO_4)(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$ (2.135 Å; Harvey *et al.*, 2000), but shorter than that in $[Zn(C_{12}H_8N_2)_2(H_2O)_2]$-$SO_4\cdot 6H_2O$ (2.171 Å; Hu & Liu, 1991). The five-membered chelate ring is nearly planar, with, however, a slight bending (2.2°) between the phenanthroline and N2/Zn/N1 planes.

A strong intermolecular hydrogen bond exists, involving uncoordinated atom O6 of the carboxylate group as an acceptor and atom O9 as a donor (Table 2), resulting in the formation of a dimer (Fig. 2). There is also an intramolecular hydrogen bond between the other H atom of the water molecule and uncoordinated atom O2 of the other carboxylate group (Table 2).

Experimental

A water–methanol (1:1 *v*/*v*) solution (3 ml) of $Zn(MeCOO)_2\cdot 2H_2O$ (0.0657 g, 0.3 mmol) was added to a water–methanol (1:1 *v*/*v*) solution (3 ml) of 2-nitrobenzoic acid (0.1000 g, 0.6 mmol), NaOH (0.0238 g, 0.6 mmol) and 1,10-phenanthroline (0.593 g, 0.3 mmol). A white powder was obtained after several days and was recrystallized from a mixed solvent composed of dimethylformamide, methanol and water (1:1:1 *v*/*v*/*v*); white block-shaped crystals were obtained after several days (yield 48%). Analysis calculated for $C_{26}H_{18}N_4O_9Zn$: C 52.41, H 3.05, N 9.40%; found: C 52.52, H 2.97, N 9.49%.

Crystal data

$[Zn(C_7H_4NO_4)_2(C_{12}H_8N_2)(H_2O)]$
$M_r = 595.81$
Triclinic, $P\overline{1}$
$a = 10.1418$ (5) Å
$b = 11.3396$ (6) Å
$c = 11.9874$ (6) Å
$\alpha = 97.422$ (1)°
$\beta = 104.139$ (1)°
$\gamma = 108.644$ (1)°
$V = 1234.03$ (11) Å^3
$Z = 2$
$D_x = 1.603$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4336 reflections
$\theta = 1.8$–25.1°
$\mu = 1.06$ mm^{-1}
$T = 293$ (2) K
Block, white
0.76 × 0.32 × 0.12 mm

Data collection

Siemens SMART CCD diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.669$, $T_{max} = 0.891$
6301 measured reflections
4261 independent reflections
3775 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.1$°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 11$
$l = -12 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.105$
$S = 1.13$
4261 reflections
367 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 1.5531P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—O5	1.996 (2)	Zn—N2	2.089 (3)
Zn—O9	2.043 (2)	Zn—N1	2.174 (3)
Zn—O1	2.081 (2)		
O5—Zn—O9	119.42 (9)	O1—Zn—N2	90.91 (10)
O5—Zn—O1	90.25 (9)	O5—Zn—N1	99.73 (10)
O9—Zn—O1	87.88 (10)	O9—Zn—N1	93.45 (10)
O5—Zn—N2	117.54 (10)	O1—Zn—N1	167.66 (9)
O9—Zn—N2	123.02 (10)	N2—Zn—N1	78.07 (10)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H91···O2	0.85 (2)	1.85 (3)	2.678 (3)	163 (4)
O9—H92···O6^{ii}	0.85 (2)	1.83 (4)	2.671 (3)	174 (4)

Symmetry code: (ii) $1 - x, 1 - y, 1 - z$.

All H atoms attached to C atoms were positioned geometrically, with C—H distances of 0.93 Å and U_{iso}(H) values of $1.2U_{eq}$(C). The H atoms of the water molecules were found in a difference Fourier synthesis and their coordinates were refined using restraints [O—H = 0.85 (2) Å and H···H = 1.39 (2) Å] and with a U_{iso}(H) value of $1.5U_{eq}$(O9).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

We thank the Natural Science Foundation of Yangzhou University and the National Natural Science Foundation of China for financial support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1058). Services for accessing these data are described at the back of the journal.

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Chohan, Z. H. & Sherazi, S. K. A. (1997). *Met. Based Drugs*, **4**, 327–332.

Clercq, E. D. (1997). *Met. Based Drugs*, **4**, 173–192.

Cunnane, S. C. (1988). *Zinc: Clinical and Biochemical Significance*. Boca Raton, Florida, USA: CRC Press.

Dendrinou-Samara, C., Tsotsou, G., Ekateriniadou, L. V., Kortsaris, A. H., Raptopoulou, C. P., Terzis, A., Kyriakidis, D. A. & Kessissoglou, D. P. (1998). *J. Inorg. Biochem.* **71**, 171–179.

Emery, P., Kong, S. X., Ehrich, E. W., Watson, D. J. & Towheed, T. E. (2002). *Clin. Ther.* **24**, 1225–1291.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Harvey, M., Baggio, S., Mombru, A. & Baggio, R. (2000). *Acta Cryst.* C**56**, 771–774.

Hu, N.-H. & Liu, Y.-S. (1991). *Acta Cryst.* C**47**, 2324–2326.

Jiang, P. & Guo, Z. (2004). *Coord. Chem. Rev.* **248**, 205–229.

Korant, B. D., Kauer, J. C. & Butterworth, B. F. (1974). *Nature* (*London*), **248**, 588–590.

Necefoglu, H., Clegg, W. & Scott, A. J. (2001). *Acta Cryst.* E**57**, m472–m474.

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

Siemens (1994). *SAINT* and *SHELXTL* (Version 5). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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

Simo, B., Perello, L., Ortiz, R., Castineiras, A., Latorre, J. & Canton, E. (2000). *J. Inorg. Biochem.* **81**, 275–283.

Stuhlmeier, K. M., Li, H. & Kao, J. J. (1999). *Biochem. Pharmacol.* **57**, 313–320.

Sun, D., Cao, R., Liang, Y., Shi, Q., Su, W. & Hong, M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2335–2341.

Van Hoogdalem, E. J. (1998). *J. Eur. Acad. Dermatol. Venereol.* **11**, S13–19.

Zelenak, V., Gyoryoryov, K. & Mlynarcik, D. (2002). *Met. Based Drugs*, **8**, 269–277.

Zelenak, V., Sabo, M., Massa, W. & Llewellyn, P. (2004). *Inorg. Chim. Acta*, **357**, 2049–2059.