Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tetraaqua(2,2′-bipyridine)zinc(II) terephthalate

Hongbin Xu,[a] Yucang Liang,[b] Zhongmin Su,[a]* Yahui Zhao,[a] Kuizhan Shao,[a] Hengjun Zhang[a] and Shumei Yue[a]

[a]Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, Jilin 130024, People's Republic of China, and [b]Anorganisch-Chemisches Institut, Technische Universität Muenchen, Lichtenbergstraße 4, D-85747 Garching, Germany

Correspondence e-mail: zmsu@nenu.edu.cn

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.060
wR factor = 0.201
Data-to-parameter ratio = 15.7

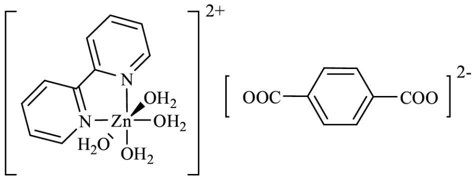
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 18 November 2003
Accepted 18 December 2003
Online 10 January 2004

A discrete zinc(II) coordination complex, [Zn(bpy)-(H_2O)$_4$](tp) [bpy = 2,2′-bipyridine ($C_{10}H_8N_2$) and tp = terephthalate ($C_8H_4O_4$)], has been prepared from the hydrothermal reaction of Zn(CH_3COO)$_2$·2H_2O, bpy and terephthalic acid in water. The zinc ion has a distorted octahedral coordination environment, with two N atoms from bpy and four water molecules. The terephthalate anion does not coordinate to the Zn^{II} metal center. Hydrogen bonds and π–π stacking interactions play important roles in the production of a three-dimensional supramolecular structure.

Comment

The design and synthesis of coordination polymers has attracted much attention in recent years, owing to their fascinating molecular structures (Moulton & Zaworotko, 2001; Eddaoudi *et al.*, 2001). Appropriate bridging ligands are very important in the construction of coordination polymers with two- or three-dimensional networks. These include polypyridyl, pyrazine and carboxylate ligands. Terephthalates (tp, also called 1,4-benzenedicarboxylate) have been used in many synthetic systems because they can form short bridges *via* one carboxylate end or long bridges *via* the benzene ring, leading to a great variety of structures (Sun *et al.*, 2001). A porous polymer [{Zn_4O(bdc)$_3$}(dmf)$_8$–(C_6H_5Cl)]$_n$ (bdc = 1,4-benzenedicarboxylate) has been reported, which can absorb and desorb nitrogen gas (Li *et al.*, 1999). Several infinite two- and three-dimensional coordination polymers with 1,4-benzene-dicarboxylate bridging ligands have been prepared (Hagrman *et al.*, 1999; Li *et al.*, 1998; Groenman *et al.*, 1999). However, structural reports on terephthalate acting as counter-anions are not common, although one example of an Ni^{II} complex has been reported very recently (Xiao *et al.*, 2003). Here we report a zinc(II) discrete coordination complex, [Zn(bpy)(H_2O)$_4$](tp), (I), prepared from the hydrothermal reaction of Zn(CH_3COO)$_2$·2H_2O, bpy and terephthalic acid in H_2O.



(I)

The crystallographic analysis reveals that the compound is composed of two discrete ions. The zinc ion has a distorted octahedral coordination environment, with two N atoms from the bpy ligand, which is present in typical chelating coord-

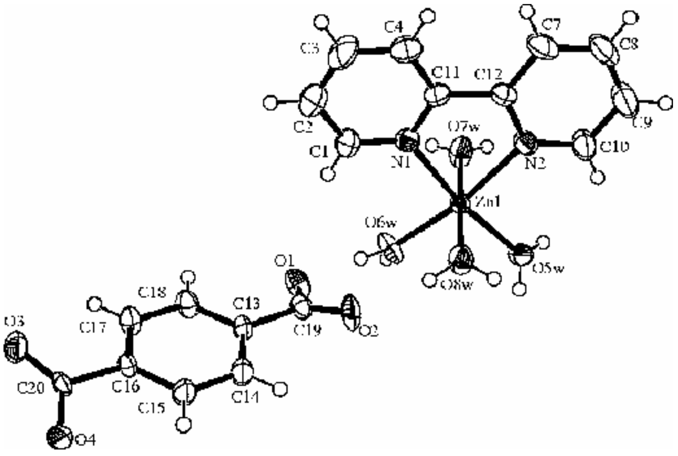


Figure 1
ORTEP-3 (Farrugia, 1997) plot of the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

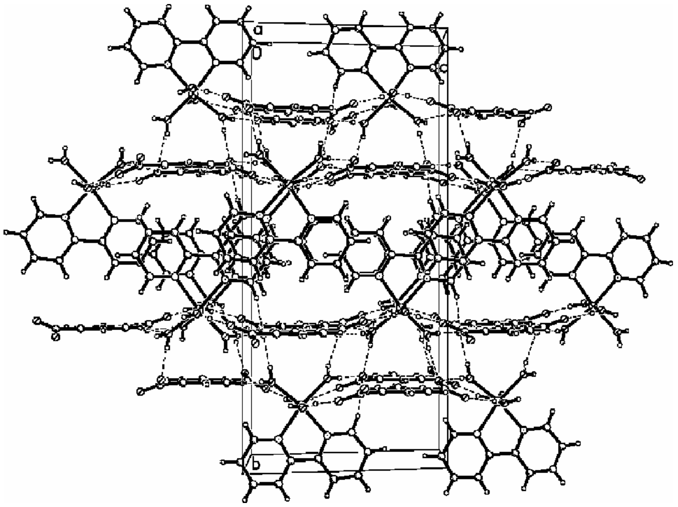


Figure 2
A packing diagram of the title compound, with hydrogen bonds shown as dashed lines.

ination mode, and four water molecules; the terephthalate acts as a counter-anion and does not coordinate directly to the Zn^{II} ion, as shown in Fig. 1. The plane of bpy and the plane of the tp benzene ring are almost perpendicular [82.7 (1)°]. The molecules are connected by three types of hydrogen-bonding interactions. One is the interaction of the carboxylate groups and coordinated water molecules; another is the interaction of C—H of the tp and coordinated water molecules; the third is the interaction of C—H of bpy and the O atom of the carboxylate group, as shown in Fig. 2. Moreover, π–π stacking interactions are observed between adjacent bpy moieties. Hydrogen-bonding interactions and π–π stacking result in the formation of a three-dimensional supramolecular structure.

Experimental

A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.133 g), terephthalic acid (0.084 g), bpy (0.078 g) and H_2O (16 ml) in the molar ratio 1:1:1:2:1778 was sealed in a 25 ml Teflon-lined stainless-steel autoclave and heated for 7 d at 453 K. After the mixture had been allowed to cool to room temperature, colorless block-shaped crystals of (I) were obtained; these were washed with distilled water and dried at room temperature.

Crystal data

$[Zn(C_{10}H_8N_2)(H_2O)_4](C_8H_4O_4)$
$M_r = 457.73$
Monoclinic, $P2_1/c$
$a = 7.641$ (2) Å
$b = 23.508$ (5) Å
$c = 11.134$ (2) Å
$\beta = 102.40$ (3)°
$V = 1953.5$ (7) Å^3
$Z = 4$

$D_x = 1.556$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13997 reflections
$\theta = 1.7$–27.5°
$\mu = 1.31$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.41 × 0.38 × 0.23 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.540$, $T_{max} = 0.737$
4476 measured reflections

4476 independent reflections
3222 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -30 \rightarrow 30$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.202$
$S = 1.10$
4476 reflections
286 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1219P)^2 + 0.4398P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.25$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O5*W*	2.034 (3)	Zn1—N1	2.143 (4)
Zn1—O6*W*	2.040 (3)	Zn1—O8*W*	2.147 (4)
Zn1—O7*W*	2.126 (4)	Zn1—N2	2.164 (4)
O5*W*—Zn1—O6*W*	96.22 (15)	O7*W*—Zn1—O8*W*	179.07 (14)
O5*W*—Zn1—O7*W*	88.71 (14)	N1—Zn1—O8*W*	88.21 (15)
O6*W*—Zn1—O7*W*	91.41 (15)	O5*W*—Zn1—N2	93.67 (14)
O5*W*—Zn1—N1	169.56 (15)	O6*W*—Zn1—N2	169.89 (15)
O6*W*—Zn1—N1	94.11 (15)	O7*W*—Zn1—N2	86.70 (16)
O7*W*—Zn1—N1	92.60 (15)	N1—Zn1—N2	76.08 (15)
O5*W*—Zn1—O8*W*	90.41 (14)	O8*W*—Zn1—N2	93.06 (15)
O6*W*—Zn1—O8*W*	88.98 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7*W*—H7···O2^{i}	0.84 (2)	1.95 (4)	2.749 (5)	159 (8)
O6*W*—H6···O1	0.85 (2)	1.78 (2)	2.638 (5)	178 (9)
O5*W*—H5···O4^{ii}	0.85 (2)	1.80 (3)	2.643 (4)	167 (8)
O8*W*—H4···O3^{iii}	0.84 (2)	2.09 (6)	2.803 (5)	142 (8)
O7*W*—H3···O3^{ii}	0.85 (2)	1.90 (3)	2.732 (5)	166 (8)
O8*W*—H2···O2	0.85 (2)	1.90 (2)	2.745 (5)	170 (8)
O6*W*—H1···O4^{iv}	0.84 (2)	1.90 (3)	2.706 (5)	160 (8)
O5*W*—H11···O1^{v}	0.84 (2)	1.87 (2)	2.710 (5)	171 (8)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 + x, y, z - 1$; (iii) $x, y, z - 1$; (iv) $1 + x, \frac{3}{2} - y, z - \frac{1}{2}$; (v) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

Acta Cryst. (2004). E**60**, m142–m144 Hongbin Xu *et al.* • $[Zn(C_{10}H_8N_2)(H_2O)_4](C_8H_4O_4)$ **m143**

The positions of the H atoms were positioned geometrically (C—H = 0.93 Å), assigned a fixed isotropic displacement parameter of 0.08 $Å^2$, and allowed to ride on their respective parent C atoms. The H atoms of the coordinated water molecules were located in a difference Fourier map and were refined with restrained O—H distances and unrestrained H—O—H angles. The highest electron-density peak is 1.91 Å from atom O1 and 1.62 Å from atom C1.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *RAPID-AUTO* (Rigaku, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL/PC* (Sheldrick, 1997).

The authors thank the National Natural Science Foundation of China (project Nos. 20160025 and 20243003) and the Trans-Century Training Programme Foundation for Talents of the State Education Commission of China.

References

Eddaoudi, M., Moler, D. B., Li, H. L., Chen, B. L., Reineke, T. M., O'Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.

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

Groenman, R. H., MacGillivery, L. R. & Atwood, J. L. (1999). *Inorg. Chem.* **38**, 208–209.

Hagrman, D., Hagrman, P. J. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 3165–3168.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Li, H., Davis, C. E., Groy, T. L., Kelley, D. G. & Yaghi, O. M. (1998). *J. Am. Chem. Soc.* **120**, 2186–2187.

Li, H., Eddaoudi, M., O'Keeffe, M. & Yaghi, O. M. (1999). *Nature (London)*, **402**, 276–279.

Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.

Rigaku (1998). *PROCESS-AUTO* and *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

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

Sun, D. F., Cao, R., Liang, Y. C., Shi, Q., Su, W. P. & Hong, M. C. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2335–2340.

Xiao, H. P., Shi, Z., Zhu, L. G., Xu, R. R. & Pang, W. Q. (2003). *Acta Cryst.* C**59**, m82–m83.

m144 Hongbin Xu *et al.* • $[Zn(C_{10}H_8N_2)(H_2O)_4](C_8H_4O_4)$ *Acta Cryst.* (2004). E**60**, m142–m144