Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# *catena*-Poly[[[tetraaquazinc(**II**)]-$\mu$-4,4′-bipyridine-$\kappa^2N$:$N'$] 3-carboxylatophenoxyacetate monohydrate]

**Jing-Gui Zhao, Chang-Sheng Gu, Li-Hua Huo, Ji-Wei Liu and Shan Gao***

School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China

Correspondence e-mail:
shangao67@yahoo.com

Received 10 November 2004
Accepted 29 November 2004
Online 11 December 2004

**Key indicators**

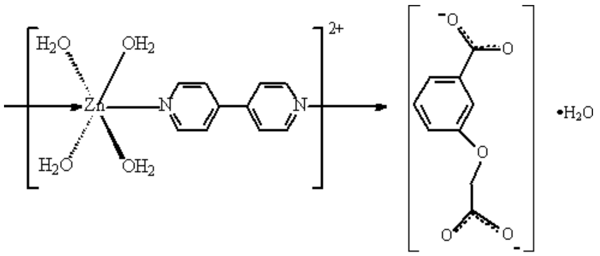
Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.040
$wR$ factor = 0.089
Data-to-parameter ratio = 15.2

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

The crystal structure of the title complex, $\{[Zn(C_{10}H_8N_2)(H_2O)_4](C_9H_6O_5)\cdot H_2O\}_n$, is built of infinite polymeric cationic $\{[Zn(4,4'\text{-bipy})(H_2O)_4]^{2+}\}_n$ chains (4,4′-bipy = 4,4′-bipyridine), 3-carboxylatophenoxyacetate dianions (3-CPOA$^{2-}$) and solvent water molecules. Both symmetry-independent Zn atoms and 4,4′-bipy ligands occupy special positions on crystallographic inversion centres and form two symmetry-independent cationic chains stretching along the $c$ axis of the crystal. Each of the two Zn atoms has an octahedral coordination environment formed by the O atoms of four water molecules and the N atoms of two 4,4′-bipy ligands in *trans* positions with respect to each other. The 4,4′-bipy ligands perform a bridging function, linking together two adjacent Zn atoms in the chain. The shortest Zn$\cdots$Zn separation within the chains is equal to the $c$ translation [11.425 (2) Å]. The chains are further linked into a three-dimensional supramolecular network *via* hydrogen-bonding and $\pi$–$\pi$ stacking interactions, involving the dianion and the coordinated and uncoordinated water molecules.

## Comment

The two main strategies currently used in crystal engineering are based on either coordination bonds or weaker intermolecular interactions (Iglesias *et al.*, 2003; Burrows *et al.*, 1997). In the latter methodology, hydrogen bonds and $\pi$–$\pi$ stacking interactions have attracted most interest, due to their relative strength and directionality, as well as their low dependence on the properties of metal ions. In this respect, 3-carboxyphenoxyacetic acid (3-CPOAH$_2$), with its multiple coordination sites and the capability of participating in hydrogen bonds as both a donor and an acceptor, represents an excellent candidate for the construction of supramolecular complexes (Gu *et al.*, 2004). Previously, we have reported the structures of mononuclear Ni$^{II}$ and Co$^{II}$ complexes based on



(I)

this ligand (Gao *et al.*, 2004; Li *et al.*, 2004), in which intermolecular hydrogen bonds form regular three-dimensional supramolecular networks. Furthermore, 4,4′-bipyridine (4,4′-bipy) is recognized as a good rigid rod-type building block for the construction of transition metal complexes with extended networks (Lu *et al.*, 1999), and there have been several reports on complexes containing the [Zn(4,4′-bipy)($H_2O$)$_n$] ($n$ = 2–4) fragment (Zhou & Yu, 2001; Carlucci *et al.*, 1997; Tong *et al.*, 1998). The above considerations led us to the design and synthesis of a metal–organic framework containing both [Zn(4,4′-bipy)($H_2O$)$_n$] and 3-CPOA$^{2-}$ fragments. The title complex, [Zn(4,4′-bipy)($H_2O$)$_4$](3-CPOA)·$H_2O$, (I), was prepared under hydrothermal conditions and its crystal structure is reported here.

As illustrated in Fig. 1, the asymmetric unit of (I) consists of two half-cations [Zn(4,4′-bipy)($H_2O$)$_4$]$_2$, one 3-carboxylatophenoxyacetate dianion and one water molecule of crystallization. Each of the two symmetry-independent Zn$^{II}$ atoms occupies a special position on a crystallographic inversion centre and has an octahedral coordination environment, formed by the N atoms of two 4,4′-bipy ligands [Zn1—N1 2.1582 (18) Å and Zn2—N2 2.1610 (19) Å] and the O atoms of four coordinated water molecules [Zn—O 2.093–2.141 Å]. Each of the two independent 4,4′-bipy ligands also lies on an inversion centre.

The two C—O bond distances in each of the carboxylate groups in the dianion are almost identical (Table 1), as one would expect for deprotonated carboxylate groups. The O1—C11—O2 carboxylate group is not perfectly coplanar with the benzene ring, the dihedral angle being 14.3 (4)°. The oxyacetate group is a little closer to the benzene plane, the C13—O3—C12—C11 and O3—C12—C11—O1 torsion angles being −174.0 (2) and 169.7 (2)°, respectively. The benzene ring of the dianion is almost parallel to the 4,4′-bipy planes of both independent cations, forming dihedral angles of 0.1 (3) and 12.4 (3)° with each of the two 4,4′-bipy ligands. The planes of the two independent 4,4′-bipy ligands form a dihedral angle of 12.4 (4)°.

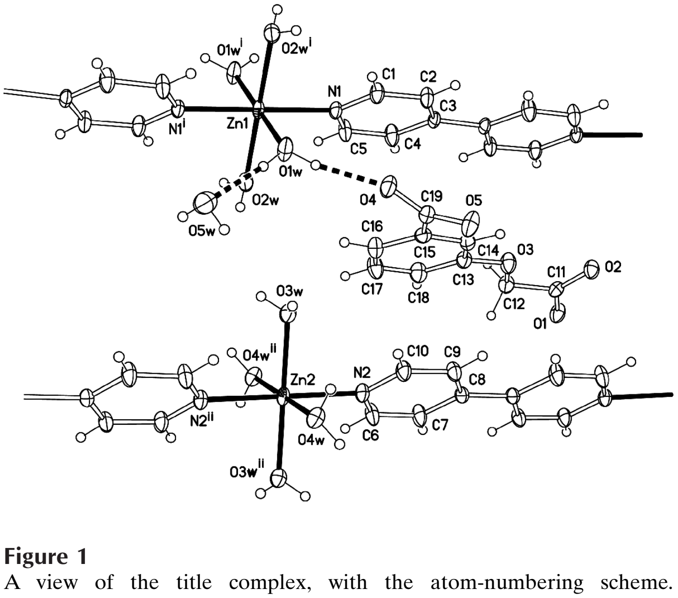


**Figure 1**
A view of the title complex, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines (see Table 1 for symmetry codes).

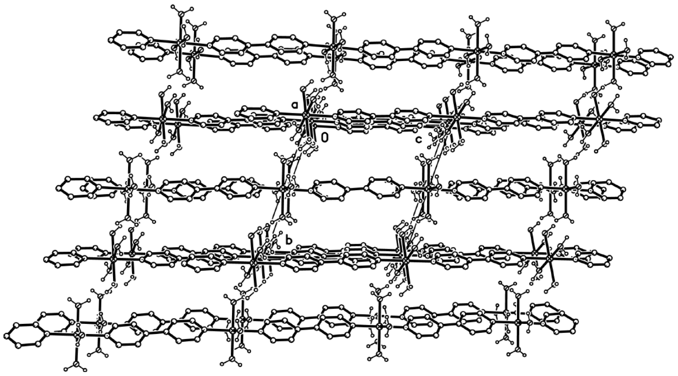


**Figure 2**
Infinite [Zn(4,4′-bipy)($H_2O$)$_4$]$_n$ chains in the structure of (I). H atoms bonded to C atoms, the uncoordinated water molecules and the 3-carboxylatophenoxyacetate dianions have been omitted.

The salient structural feature of (I) is the presence of linear —Zn—4,4′-bipy—Zn—4,4′-bipy— chains running along the *c* axis of the crystal structure. The shortest Zn···Zn separation within each of the chains is equal to the *c* translation [11.425 (2) Å]. The array of infinite parallel chains gives rise to a square grid-like structure, as shown in Fig. 2, and the 3-carboxylatophenoxyacetate groups and water molecules occupy the spaces within the cells of the grid. They are further interlinked through hydrogen bonds involving water molecules and the O atoms of 3-carboxylatophenoxyacetate groups, with O···O distances in the range 2.664–2.949 Å and O—H···O angles in the range 133–175° (Table 2). In addition, there are $\pi$–$\pi$ stacking interactions between the 4,4′-bipy ligands and the benzene rings of the dianions, with centroid–centroid distances of 3.789 (3) Å (for the N1 ring) and 3.726 (3) Å (for the N2 ring). As a result, a three-dimensional supramolecular network is constructed *via* hydrogen-bonding and $\pi$–$\pi$ stacking interactions (Fig. 3).

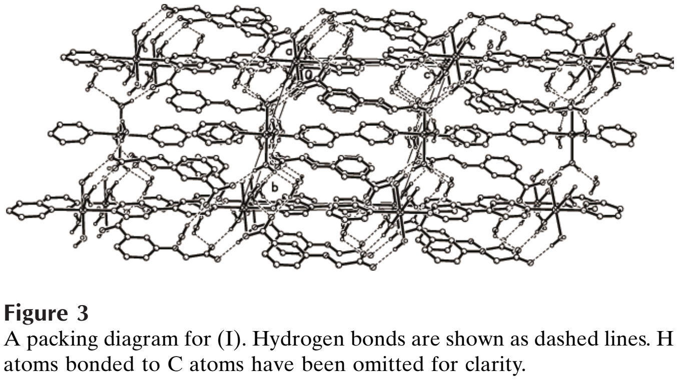


**Figure 3**
A packing diagram for (I). Hydrogen bonds are shown as dashed lines. H atoms bonded to C atoms have been omitted for clarity.

*Acta Cryst.* (2005). E**61**, m76–m78 Jing-Gui Zhao *et al.* • [Zn($C_{10}H_8N_2$)($H_2O$)$_4$]($C_9H_6O_5$)·$H_2O$ **m77**

## Experimental

Zinc diacetate dihydrate (2.20 g, 10 mmol), 4,4′-bipyridine (1.56 g, 10 mmol) and 3-CPOAH$_2$ (1.96 g, 10 mmol) were dissolved in water (20 ml) and the pH was adjusted to 7 with 0.1 *M* NaOH. The mixture was sealed in a 25 ml Teflon-lined stainless steel bomb and held at 393 K for 5 d. The bomb was cooled naturally to room temperature, and colourless prismatic crystals of (I) were obtained after several days. CHN analysis, calculated for $C_{38}H_{48}N_4O_{20}Zn_2$: C 45.12, H 4.78, N 5.54%; found: C 45.33, H 4.84, N 5.49%.

*Crystal data*

$[Zn(C_{10}H_8N_2)(H_2O)_4](C_9H_6O_5)\cdot H_2O$
$M_r = 505.79$
Triclinic, $P\overline{1}$
$a = 9.3049$ (8) Å
$b = 11.1595$ (15) Å
$c = 11.4248$ (18) Å
$\alpha = 108.526$ (5)°
$\beta = 106.493$ (8)°
$\gamma = 90.737$ (6)°
$V = 1071.6$ (2) Å$^3$
$Z = 2$
$D_x = 1.568$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 10 081 reflections
$\theta = 3.9$–27.5°
$\mu = 1.20$ mm$^{-1}$
$T = 293$ (2) K
Prism, colourless
0.36 × 0.25 × 0.19 mm

*Data collection*

Rigaku RAXIS-RAPID diffractometer
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.671$, $T_{max} = 0.803$
10 614 measured reflections
4885 independent reflections
3517 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 12$
$k = -14 \rightarrow 13$
$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.089$
$S = 1.02$
4885 reflections
322 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.2994P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn1—N1 | 2.1582 (18) | Zn2—O4*W* | 2.1408 (17) |
| Zn1—O1*W* | 2.0935 (18) | O1—C11 | 1.259 (3) |
| Zn1—O2*W* | 2.1294 (17) | O2—C11 | 1.246 (3) |
| Zn2—N2 | 2.1610 (19) | O4—C19 | 1.252 (3) |
| Zn2—O3*W* | 2.0955 (17) | O5—C19 | 1.251 (3) |

| | | | |
|---|---|---|---|
| O1*W*—Zn1—N1 | 90.92 (7) | O3*W*—Zn2—N2 | 89.68 (7) |
| O1*W*—Zn1—O2*W* | 90.21 (8) | O3*W*—Zn2—O4*W* | 90.62 (7) |
| O2*W*—Zn1—N1 | 88.97 (7) | O4*W*—Zn2—N2 | 90.17 (7) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*W*1···O4 | 0.84 (3) | 1.88 (3) | 2.696 (2) | 164 (3) |
| O1*W*—H1*W*2···O5*W* | 0.84 (3) | 1.96 (3) | 2.797 (3) | 175 (3) |
| O2*W*—H2*W*1···O1$^{i}$ | 0.85 (3) | 1.87 (3) | 2.719 (2) | 172 (2) |
| O2*W*—H2*W*2···O2$^{ii}$ | 0.84 (2) | 2.03 (3) | 2.832 (3) | 157 (3) |
| O3*W*—H3*W*1···O2$^{ii}$ | 0.85 (2) | 1.91 (3) | 2.746 (2) | 170 (3) |
| O3*W*—H3*W*2···O5$^{iii}$ | 0.85 (2) | 1.83 (3) | 2.664 (3) | 165 (3) |
| O4*W*—H4*W*1···O4$^{iii}$ | 0.85 (3) | 1.94 (3) | 2.781 (3) | 174 (3) |
| O4*W*—H4*W*2···O1$^{iv}$ | 0.84 (3) | 1.91 (3) | 2.746 (3) | 171 (2) |
| O5*W*—H5*W*1···O2$^{ii}$ | 0.85 (3) | 2.31 (3) | 2.949 (3) | 133 (3) |
| O5*W*—H5*W*2···O5$^{iii}$ | 0.85 (3) | 1.94 (3) | 2.766 (3) | 164 (4) |

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

Water H atoms were located in difference Fourier maps and refined with O—H distances restrained to 0.85 (1) Å and with $U_{iso}(H) = 1.5U_{eq}(O)$. All other H atoms were placed in calculated positions, with C—H = 0.93 (aromatic) or 0.97 Å (aliphatic), and refined in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

The authors thank the National Natural Science Foundation of China (grant No. 20101003), Heilongjiang Province Natural Science Foundation (grant No. B0007), the Scientific Fund of Remarkable Teachers of Heilongjiang Province (grant No. 1054G036) and Heilongjiang University for supporting this study.

## References

Burrows, A. D., Menzer, S., Mingos, D. M. P., White, A. J. P. & Williams, D. J. (1997). *J. Chem. Soc. Dalton Trans.* pp. 4237–4240.
Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1801–1804.
Gao, S., Li, J.-R., Liu, J.-W., Gu, C.-S. & Huo, L.-H. (2004). *Acta Cryst.* E**60**, m22–m23.
Gu, C.-S., Liu, J.-W., Huo, L.-H., Zhao, H., Zhao, J.-G. & Gao, S. (2004). *Acta Cryst.* E**60**, o760–o761.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Iglesias, S., Castillo, O., Luque, A. & Romaán, P. (2003). *Inorg. Chim. Acta*, **349**, 273–278.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Li, S. J., Gu, C. S, Gao, S., Zhao, H., Zhao, J. G. & Huo, L. H. (2004). *Chin. J. Struct. Chem.* **20**, 835–838.
Lu, J. K., Lawandy, M. A. & Li, J. (1999). *Inorg. Chem.* **38**, 2695–2704.
Rigaku Corporation (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Tong, M. L., Cai, J. W., Yu, X. L., Chen, X. M., Ng, S. W. & Mak, T. C. W. (1998). *Aust. J. Chem.* **51**, 637–640.
Zhou, C. H. & Yu, K. B. (2001). *Chin. J. Inorg. Chem.* **17**, 699–703.

**m78** Jing-Gui Zhao *et al.* • $[Zn(C_{10}H_8N_2)(H_2O)_4](C_9H_6O_5)\cdot H_2O$ *Acta Cryst.* (2005). E**61**, m76–m78