

A two-dimensional Zn^{II} coordination polymer constructed by benzotriazole-5-carboxylate and 1,4,8,9-tetraazatriphenylene

Rui-Yun Lu,^a Guo-You Luan^b and Zheng-Bo Han^{a*}

^aCollege of Chemistry, Liaoning University, 110036 Shenyang, People's Republic of China, and ^bCollege of Resource and Environment, Jilin Agricultural University, 110036 Changchun, People's Republic of China
Correspondence e-mail: ceshzb@lnu.edu.cn

Received 30 May 2010

Accepted 23 August 2010

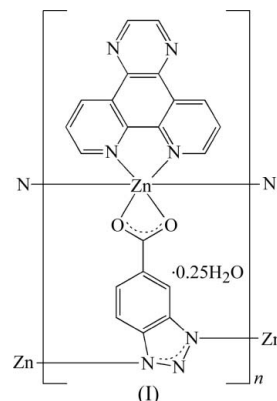
Online 10 September 2010

Poly[[$(\mu_3$ -benzotriazole-5-carboxylato- $\kappa^4 N^1:N^3:O,O')$ (1,4,8,9-tetraazatriphenylene- $\kappa^2 N^8,N^9$)zinc(II)] 0.25-hydrate], $\{[\text{Zn}(\text{C}_7\text{H}_3\text{N}_3\text{O}_2)(\text{C}_{14}\text{H}_8\text{N}_4)] \cdot 0.25\text{H}_2\text{O}\}_n$, exhibits a two-dimensional layer structure in which the asymmetric unit contains one Zn^{II} centre, one 1,4,8,9-tetraazatriphenylene (TATP) ligand, one benzotriazole-5-carboxylate (btca) ligand and 0.25 solvent water molecules. Each Zn^{II} ion is six-coordinated and surrounded by four N atoms from two different btca ligands and one chelating TATP ligand, and by two O atoms from a third btca ligand, to furnish a distorted octahedral geometry. The infinite connection of the metal ions and ligands forms a two-dimensional wave-like (6,3) layer structure. Adjacent layers are connected by C—H \cdots N hydrogen bonds. The solvent water molecules are located in partially occupied sites between parallel pairs of inversion-related TATP ligands that belong to two separate layers.

Comment

Considerable attention has been paid recently to the construction of inorganic–organic coordination polymers (Han *et al.*, 2006, 2010; Han, Deng & Goddard, 2007; Han, He *et al.*, 2007; Kaye *et al.*, 2007; Kaye & Long, 2005; Lin *et al.*, 2006; Ma, Han *et al.*, 2007; Ma, Sun *et al.*, 2007; Rosi *et al.*, 2003; Wong-Foy *et al.*, 2006) due to their interesting topological structures and potential applications as functional materials in molecular recognition, gas absorption, luminescence and magnetism (Ockwig *et al.*, 2005; Rao *et al.*, 2004; Bradshaw *et al.*, 2005; Pan *et al.*, 2004; Min & Suh, 2000; Deiters *et al.*, 2005; Ishikawa *et al.*, 2005; Lukin *et al.*, 2003; Tezuka & Oike, 2001). The rational design and synthesis of predictable coordination polymers have been significantly influenced by choosing appropriate metal ions and organic linkers. Among the various ligands, 1,2,3-triazole and its derivatives have attracted much attention for the construction of coordination polymers (Bai *et al.*, 2008;

Jones *et al.*, 2002; Lu *et al.*, 2005; Yang *et al.*, 2007; Tabernor *et al.*, 2004). Meanwhile, carboxylate derivatives of the 1,2,3-triazole ligand, particularly benzotriazole-5-carboxylic acid (H₂btca), have been used to produce homometallic porous metal–organic frameworks (MOFs) because of their diverse coordination modes and high structural stability (Zhang *et al.*, 2007).



With the intention of preparing btca-coordinated complexes and studying the influence of the size of the aromatic chelate ligand on the framework structure, we chose the bidentate-coordinating 1,4,8,9-tetraazatriphenylene (TATP) ligand as a second reagent (Han *et al.*, 2009; Ma *et al.*, 2008), and a new coordination polymer, the title compound, $[\text{Zn}(\text{btca})(\text{TATP})] \cdot 0.25\text{H}_2\text{O}$, (I), was successfully synthesized.

Single-crystal X-ray diffraction analysis reveals that (I) exhibits a two-dimensional layer structure in which the asymmetric unit consists of one Zn^{II} centre, one btca ligand, one TATP ligand and 0.25 solvent water molecules (Fig. 1). Each Zn^{II} centre is six-coordinated, with a significantly distorted ZnN_4O_2 octahedral coordination geometry consisting of two carboxylate O atoms (O1 and O2) from one btca ligand, two N atoms (N4 and N5) from one chelating TATP ligand and two N atoms [N3ⁱ and N1ⁱⁱ; symmetry codes: (i) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$] from two different btca ligands. Two of the N atoms (N1ⁱⁱ and N4) occupy the axial positions, with an N1ⁱⁱ—Zn—N4 angle of 168.56 (6)°. The other axial angles are both less than 160°.

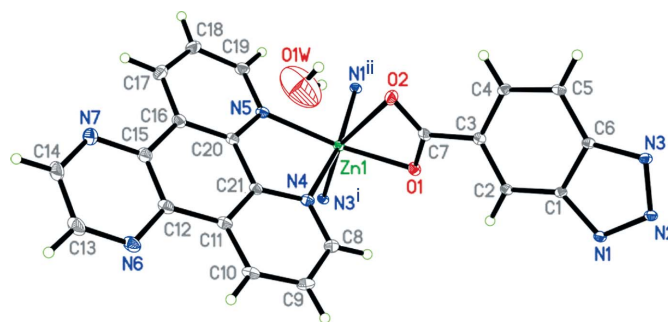


Figure 1
A view of the components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.]

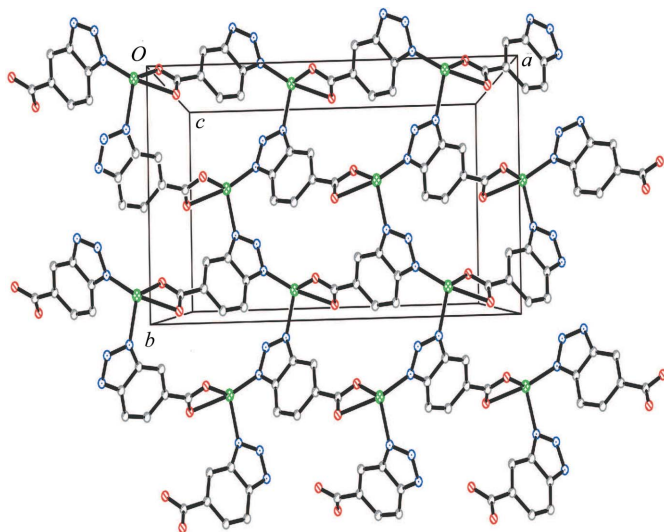


Figure 2
A view of a single (6,3) layer of (I) along the *ab* plane. H atoms and TATP ligands have been omitted for clarity.

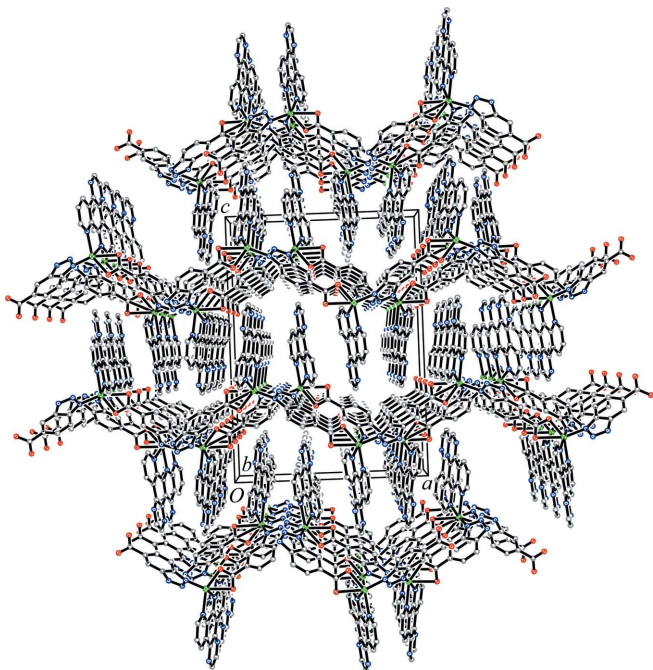


Figure 3
The three-dimensional structure of (I), viewed along the *b* axis. The water molecules have been omitted for clarity.

The btca ligand of (I) coordinates to three different Zn atoms *via* *O,O'*-bidentate chelation and monodentate bridging coordination modes through two of the triazole N atoms. The latter link two adjacent Zn^{II} centres to form a one-dimensional zigzag chain (Fig. 2). These chains are then crosslinked by the *O,O'*-bidentate coordination from the btca ligand to a Zn atom in a neighbouring chain to give an extended wave-like (6,3) network layer structure. Adjacent layers are connected together through C—H···N hydrogen-bonding interactions between btca and TATP ligands to help form the three-dimensional supramolecular structure (Fig. 3). The 0.25-

occupancy water molecules are located between the TATP ligands of adjacent layers, where, on account of the O1W···O2 distance of 2.804 (14) Å, they probably form O—H···O hydrogen bonds with one of the carboxylate O atoms of a btca ligand.

Compound (I) is the first example of a coordination polymer constructed by btca and TATP as mixed ligands. To date, only one complex with the btca ligand, *viz.* [Co₃(OH)₂(btca)₂] (Zhang *et al.*, 2007), has been reported, which forms a homometallic porous metal–organic framework with ‘*sra*’ topology. The layered structure of (I) is quite different from that of [Co₃(OH)₂(btca)₂], in which the btca ligands in a μ_5 -mode link {Co₃(OH)₂} chains to yield a three-dimensional framework.

In (I), two N atoms from the TATP ligand occupy two coordination positions of the Zn^{II} atom, while the remaining coordination positions are available for btca ligands, allowing the formation of the layer structure. Clearly, the presence of secondary chelate ligands in transition metal carboxylate systems contributes to the formation of low-dimensional coordination polymers, especially one-dimensional chains and two-dimensional layers, with the metal ions acting as nodes and the carboxylate ligands as linkers. These results indicate that aromatic chelate ligands have a significant impact on the framework structures of coordination polymers.

Experimental

TATP was prepared according to the method of Dickeson & Summers (1970). A mixture of Zn(NO₃)₂ (0.148 g, 0.5 mmol), benzotriazole-5-carboxylic acid (0.049 g, 0.3 mmol), TATP (0.068 g, 0.3 mmol), dimethylformamide (5 ml) and water (5 ml) was placed in a 23 ml Teflon reactor and stirred for 20 min in air, then heated at 453 K for 5 d, followed by cooling to room temperature at a rate of 5 K h⁻¹. The resulting brown prismatic crystals of (I) were isolated in *ca* 42% yield based on Zn.

Crystal data

[Zn(C ₇ H ₃ N ₃ O ₂)(C ₁₄ H ₈ N ₄)]· 0.25H ₂ O	<i>V</i> = 3567.8 (3) Å ³
<i>M_r</i> = 463.24	<i>Z</i> = 8
Orthorhombic, <i>Pbca</i>	Mo <i>K</i> α radiation
<i>a</i> = 17.3649 (9) Å	μ = 1.42 mm ⁻¹
<i>b</i> = 8.6087 (4) Å	<i>T</i> = 173 K
<i>c</i> = 23.8669 (12) Å	0.37 × 0.32 × 0.23 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	27994 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	3509 independent reflections
<i>T</i> _{min} = 0.623, <i>T</i> _{max} = 0.732	2865 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.063

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C19—H19A···N2 ⁱ	0.95	2.38	3.103 (3)	132

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

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.027$$

$$wR(F^2) = 0.071$$

$$S = 0.97$$

3509 reflections

289 parameters

H atoms treated by a mixture of independent and constrained refinement

$$\Delta\rho_{\max} = 0.52 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.36 \text{ e } \text{Å}^{-3}$$

The aromatic H atoms were placed at calculated positions in the riding-model approximation, with C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the water molecule could not be located reliably and were omitted from the model. The presence of solvent water molecules was determined according to the IR spectrum and thermogravimetric analysis (TGA) results. The TGA results indicate that the title compound loses its lattice water molecules below 340 K and the weight loss of 0.92% was consistent with that calculated (0.97%); the occupancy was thus fixed at 0.25.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was granted financial support from the National Natural Science Foundation of China (grant No. 20871063) and the Programme for Liaoning Excellent Talents at Universities (grant No. RC-05-11).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3250). Services for accessing these data are described at the back of the journal.

References

- Bai, Y. L., Tao, J., Huang, R. B. & Zheng, L. S. (2008). *Angew. Chem. Int. Ed.* **47**, 5344–5347.
- Bradshaw, D., Claridge, J. B., Cussen, E. J., Prior, T. J. & Rosseinsky, M. J. (2005). *Acc. Chem. Res.* **38**, 273–282.
- Bruker (2001). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Deiters, E., Bulach, V. & Hosseini, M. W. (2005). *Chem. Commun.* pp. 3906–3908.
- Dickeson, J. E. & Summers, L. A. (1970). *Aust. J. Chem.* **23**, 1023–1027.
- Han, S. S., Deng, W. Q. & Goddard, W. A. (2007). *Angew. Chem. Int. Ed.* **46**, 6289–6292.
- Han, Z. B., He, Y. K., Ge, C. H., Ribas, J. & Xu, L. (2007). *Dalton Trans.* pp. 3020–3024.
- Han, Z. B., Ji, J. W., An, H. Y., Zhang, W., Han, G. X., Zhang, G. X. & Yang, L. G. (2009). *Dalton Trans.* pp. 9807–9811.
- Han, Z. B., Ma, Y., Sun, Z. G. & You, W. S. (2006). *Inorg. Chem. Commun.* **9**, 844–847.
- Han, Z. B., Zhang, G. X., Zeng, M. H., Yuan, D. Q., Fang, Q. R., Li, J. R., Ribas, J. & Zhou, H. C. (2010). *Inorg. Chem.* **49**, 769–771.
- Ishikawa, N., Otsuka, S. & Kaizu, Y. (2005). *Angew. Chem. Int. Ed.* **44**, 731–733.
- Jones, L. F., Brechin, E. K., Collison, D., Harrison, A., Teat, S. J. & Wernsdorfer, W. (2002). *Chem. Commun.* pp. 2974–2975.
- Kaye, S. S., Dailly, A., Yaghi, O. M. & Long, J. R. (2007). *J. Am. Chem. Soc.* **129**, 14176–14177.
- Kaye, S. S. & Long, J. R. (2005). *J. Am. Chem. Soc.* **127**, 6506–6507.
- Lin, X., Jia, J. H., Zhao, X. B., Thomas Mark, K., Blake, A. J., Walker, G. S., Champness, N. R., Hubberstey, P. & Schörder, M. (2006). *Angew. Chem. Int. Ed.* **45**, 7358–7364.
- Lu, J., Zhao, K., Fang, Q. R., Xu, J. Q., Yu, J. H., Zhang, X., Bie, H. Y. & Wang, T. G. (2005). *Cryst. Growth Des.* **5**, 1097–1098.
- Lukin, O., Recker, J., Böhmer, A., Muer, W. M., Kubota, T., Okamoto, Y., Nieger, M., Fröhlich, R. & Vögtle, F. (2003). *Angew. Chem. Int. Ed.* **42**, 442–445.
- Ma, Y., Han, G. X. & Han, Z. B. (2008). *Russ. J. Coord. Chem.* **34**, 1–4.
- Ma, Y., Han, Z. B., He, Y. K. & Yang, L. G. (2007). *Chem. Commun.* pp. 4107–4109.
- Ma, S., Sun, D., Ambrogio, M., Fillinger, J. A., Parkin, S. & Zhou, H.-C. (2007). *J. Am. Chem. Soc.* **129**, 1858–1859.
- Min, K. S. & Suh, M. P. (2000). *J. Am. Chem. Soc.* **122**, 6834–6840.
- Ockwig, N. W., Friedrichs-Delgado, O., O’Keeffe, M. & Yaghi, O. M. (2005). *Acc. Chem. Res.* **38**, 176–182.
- Pan, L., Sander, M. B., Huang, X. Y., Milton Smith, J. L., Bittner, E., Bockrath, B. & Karl Johnson, J. (2004). *J. Am. Chem. Soc.* **126**, 1308–1309.
- Rao, C. N. R., Natarajan, S. & Vaidyanathan, R. (2004). *Angew. Chem. Int. Ed.* **34**, 1466–1496.
- Rosi, N. L., Eckert, J., Eddaoudi, M., Vodak, D. T., Kim, J., O’Keeffe, M. & Yaghi, O. M. (2003). *Science*, **300**, 1127–1129.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tabernor, J., Jones, L. F., Heath, S. L., Muryn, C., Aromí, G., Ribas, J., Brechin, E. K. & Collison, D. (2004). *Dalton Trans.* pp. 975–976.
- Tezuka, Y. & Oike, H. (2001). *J. Am. Chem. Soc.* **123**, 11570–11576.
- Wong-Foy, A. G., Matzger, A. J. & Yaghi, O. M. (2006). *J. Am. Chem. Soc.* **128**, 3494–3495.
- Yang, E. C., Zhao, H. K., Ding, B., Wang, X. G. & Zhao, X. J. (2007). *Cryst. Growth Des.* **7**, 2009–2015.
- Zhang, X. M., Hao, Z. M., Zhang, W. X. & Chen, X. M. (2007). *Angew. Chem. Int. Ed.* **46**, 3456–3459.