

## A novel three-dimensional cadmium(II) coordination polymer incorporating 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene and thiocyanate

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In the title complex, poly[cadmium(II)- $\mu_2$ -1,4-bis(1,2,4-triazol-1-ylmethyl)benzene-di- $\mu_2$ -thiocyanato],  $[\text{Cd}(\text{NCS})_2(\text{C}_{12}\text{H}_{12}\text{N}_6)]_n$ , the  $\text{Cd}^{\text{II}}$  atom lies on an inversion centre in a distorted octahedral environment. Four N atoms from the thiocyanate and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) ligands occupy the equatorial positions, and two S atoms from symmetry-related thiocyanate ligands occupy the axial positions. The benzene ring of the bbtz ligand lies about an inversion centre. Single thiocyanate bridges link the  $\text{Cd}^{\text{II}}$  atoms into two-dimensional sheets containing novel 16-membered  $[\text{Cd}_4(\mu\text{-NCS-N:S})_4]$  rings. The bbtz ligands further link these two-dimensional sheets into an unprecedented covalent three-dimensional network for the cadmium–thiocyanate system.

### Comment

In the past decade, the design and synthesis of metal–organic frameworks based on the principles of crystal engineering

have made rapid progress. The interest in these compounds is due to their intriguing structural topologies and potential application as microporous, magnetic, non-linear and fluorescent materials (Kahn *et al.*, 2000; Yaghi *et al.*, 1998; Batten & Robson 1998; Moulton & Zaworotko, 2001). In the construction of one-, two- and three-dimensional frameworks, multi-dentate ligands are usually used to bridge metal centres to form polymeric structures. Cadmium thiocyanate adducts of organic ligands are an important class of compounds for the design and preparation of functional coordination frameworks (Zhang *et al.*, 1999). A number of cadmium(II) thiocyanate complex adducts of monodentate organic ligands, such as methyl-substituted pyridines (Taniguchi *et al.*, 1986, 1987), dibenzylamine (Taniguchi & Ouchi 1987), dimethyl sulfoxide (DMSO; Chenskaya *et al.*, 2000), 4-chloropyridine (Goher *et al.*, 2003), 1*H*-1,2,4-triazole (Haasnoot *et al.*, 1983) and imidazole (Chen *et al.*, 1999), have been reported. All of these adducts exhibit chain structures, where each pair of adjacent  $\text{Cd}^{\text{II}}$  atoms are bridged by two inversely related  $\mu\text{-SCN}^-$ - $\text{N:S}$  ligands and the remaining coordination sites are occupied by monodentate organic ligands. Few thiocyanate-bridged cadmium(II) complexes consist of a two-dimensional network (Mondal *et al.*, 2000; Yang *et al.*, 2001).

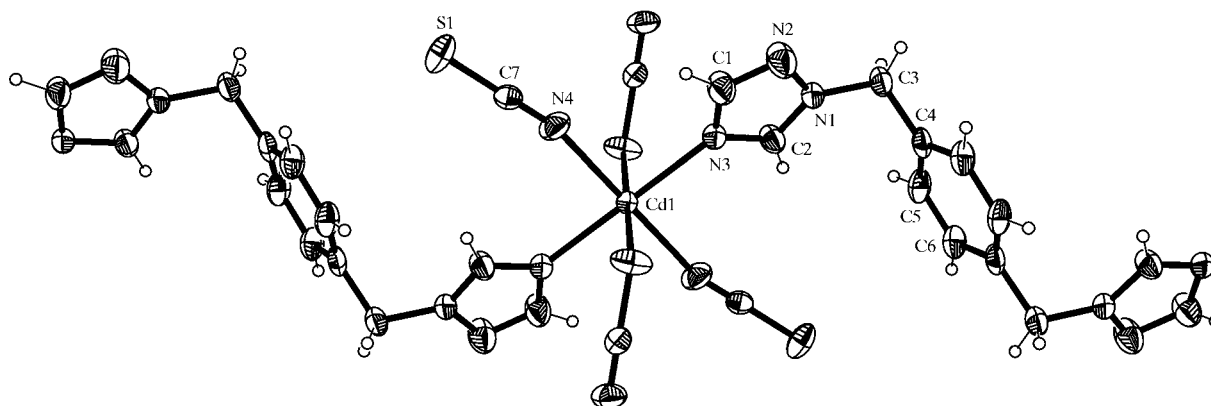
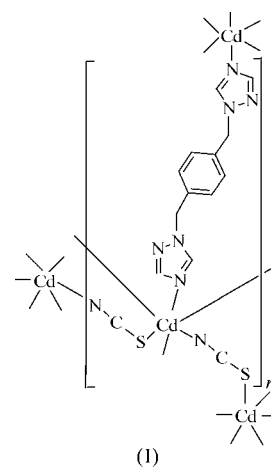


Figure 1

A view of the local coordination of the  $\text{Cd}^{\text{II}}$  atom in (I), with displacement ellipsoids drawn at the 50% probability level. Only the atoms of the asymmetric unit have been labelled.

2004), 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (Li *et al.*, 2005) and 1,2-bis(benzotriazol-1-yl)ethane (Zhou *et al.*, 2004). As a part of our work towards the rational design and preparation of functional coordination frameworks, we recently reported two novel thiocyanate cadmium complexes, namely  $[\text{Cd}(\text{NCS})_2(\text{bte})]_n$  [bte is 1,2-bis(1,2,4-triazol-1-yl)ethane; Li *et al.*, 2004] and  $[\text{Cd}_{1.5}(\text{NCS})_3(\text{bbta})_{1.5}]_n$  [bbta is 1,2-bis(benzotriazol-1-yl)ethane; Zhou *et al.*, 2004]. In the present paper, we report the preparation and crystal structure of the novel title three-dimensional coordination polymer,  $[\text{Cd}(\text{bbtz})(\text{NCS})_2]_n$ , (I), in which 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) ligands bridge a two-dimensional network containing 16-membered  $[\text{Cd}_4(\mu\text{-SCN-N:S})_4]$  rings.

As shown in Fig. 1, the  $\text{Cd}^{\text{II}}$  atom of (I) lies on an inversion centre, in a distorted octahedral environment, coordinated by four N atoms from two symmetry-related thiocyanate ligands and bis-monodentate bbtz ligands in the equatorial positions, and two S atoms from two symmetry-related thiocyanate ligands in the axial positions. This coordination environment is similar to that in the chain structures of the cadmium(II) thiocyanate complex adducts of monodentate organic ligands, such as  $[\text{Cd}(\text{NCS})_2(\text{L})_2]_n$  [ $L = 2\text{-}, 3\text{-}$  or  $4\text{-methylpyridine}$  (Taniguchi *et al.*, 1986, 1987), dibenzylamine (Taniguchi & Ouchi, 1987), 4-chloropyridine (Goher *et al.*, 2003), 1*H*-1,2,4-triazole (Haasnoot *et al.*, 1983) and imidazole (Chen *et al.*, 1999)], and that in the two-dimensional network cadmium thiocyanate complexes  $\{[\text{Cd}(\text{NCS})_2(\text{nicotinamide})_2] \cdot \text{H}_2\text{O}\}_n$  and  $[\text{Cd}(\text{NCS})_2(\text{isonicotinamide})_2]_n$  (Yang *et al.*, 2001). The  $\text{NCS}^-$  anion acts as a bridging ligand in the  $\mu\text{-N:S}$  mode in (I), with single thiocyanate bridges linking two  $\text{Cd}^{\text{II}}$  atoms to form the two-dimensional network. The  $\mu\text{-N:S}$  coordination mode for the  $\text{Cd}^{\text{II}}$  atom is one of the usual coordination fashions (Zhang *et al.*, 1999), since the  $\text{Cd}^{\text{II}}$  atom is in the centre of the hard–soft range in the acid–base concept.

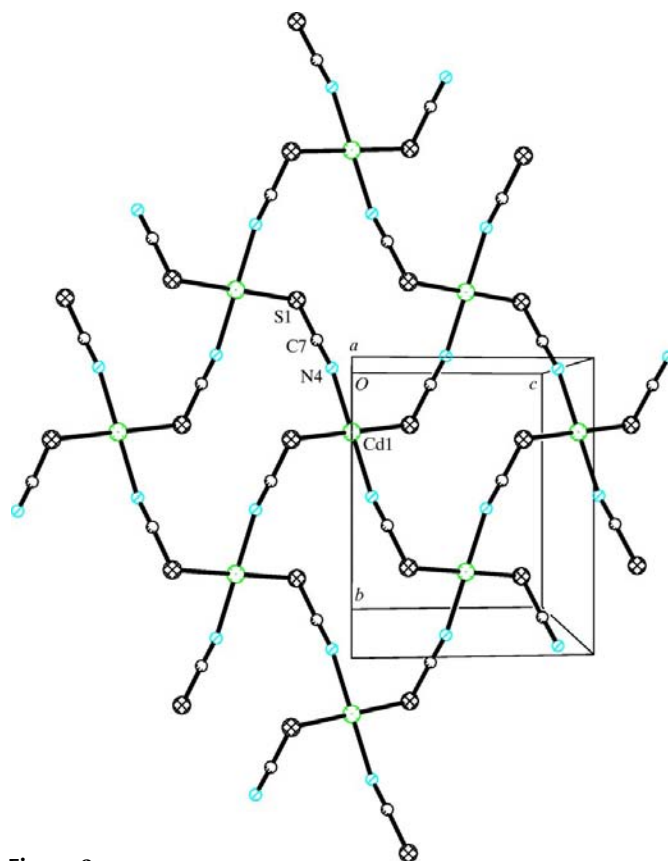
The  $\text{Cd}-\text{N}_{\text{bbtz}}$  bond lengths (Table 1) are similar to those in other cadmium(II) bbtz complexes (Li *et al.*, 2005), in  $[\text{Cd}(\text{NCS})_2(\text{bte})]_n$  (Li *et al.*, 2004) and in  $[\text{Cd}(\text{NCS})_2(\text{trz})_2]_n$  ( $\text{trz} = 1\text{H-}1,2,4\text{-triazole}$ ; Haasnoot *et al.*, 1983). The  $\text{Cd}-\text{N}_{\text{NCS}}$  bond lengths (Table 1) are also similar to those in double thiocyanate-bridged cadmium(II) complexes, such as  $[\text{Cd}(\text{NCS})_2(\text{L})_2]_n$  ( $L$  is a pyridine derivative, such as 2-, 3- or 4-methylpyridine and 4-chloropyridine; Taniguchi *et al.*, 1986, 1987; Goher *et al.*, 2003),  $[\text{Cd}(\text{NCS})_2(\text{dibenzylamine})_2]_n$  (Taniguchi & Ouchi, 1987),  $[\text{Cd}(\text{NCS})_2(\text{bte})]_n$  (Li *et al.*, 2004) and  $[\text{Cd}(\text{NCS})_2(\text{trz})_2]$  (Haasnoot *et al.*, 1983), in the triple thiocyanate-bridged cadmium(II) complex  $[\text{Cd}_{1.5}(\text{bbta})_{1.5}(\text{NCS})_3]_n$  (Zhou *et al.*, 2004), and in singly thiocyanate-bridged cadmium(II) complexes, such as  $[\text{Cd}(\text{NCS})_2(\text{dmen})]_n$  ( $\text{dmen} = N,N\text{-dimethylethylenediamine}$ ; Mondal *et al.*, 2000),  $\{[\text{Cd}(\text{NCS})_2(\text{nicotinamide})_2] \cdot \text{H}_2\text{O}\}_n$  and  $[\text{Cd}(\text{NCS})_2(\text{isonicotinamide})_2]_n$  (Yang *et al.*, 2001).

The  $\text{Cd}-\text{S}_{\text{NCS}}$  bond lengths, and  $\text{Cd}-\text{N}-\text{C}_{\text{NCS}}$  and  $\text{Cd}-\text{S}-\text{C}_{\text{SCN}}$  bond angles (Table 1), are similar to those in the above-cited thiocyanate-bridged cadmium(II) complexes. As illustrated in Fig. 2, each  $\text{NCS}^-$  anion in (I) coordinates to two  $\text{Cd}^{\text{II}}$  atoms in a  $\mu\text{-N:S}$  mode and single thiocyanate bridges link the  $\text{Cd}^{\text{II}}$  centres into a two-dimensional sheet, resulting in

an hourglass-shaped 16-membered  $[\text{Cd}_4(\mu\text{-NCS-N:S})_4]$  metallacycle. Reports of such  $[\text{Cd}_4(\mu\text{-NCS-N:S})_4]$  metallacycle structures are rare. Two examples are  $[\text{Cd}(\text{NCS})_2(\text{nicotinamide})_2] \cdot \text{H}_2\text{O}$  and  $[\text{Cd}(\text{SCN})_2(\text{isonicotinamide})_2]$  (Yang *et al.*, 2001). The  $\text{Cd} \cdots \text{Cd}$  separation through the  $\text{NCS}^-$  ligand is 6.2266 (7) Å, which is similar to the values of 6.231 (1) and 6.310 (1) Å in the singly thiocyanate-bridged cadmium(II) complexes  $\{[\text{Cd}(\text{NCS})_2(\text{nicotinamide})_2] \cdot \text{H}_2\text{O}\}_n$  and  $[\text{Cd}(\text{NCS})_2(\text{isonicotinamide})_2]_n$  (Yang *et al.*, 2001).

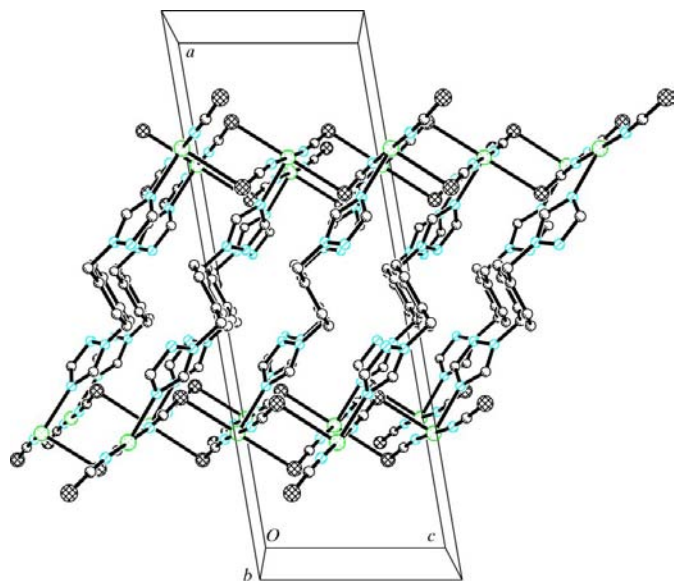
Because the methyl C atoms of the bbtz ligand can freely rotate to adjust to the coordination environment, bbtz can exhibit *trans-gauche* and *gauche-gauche* conformations. The bbtz ligands exhibit the *trans-gauche* conformation in (I), similar to the situation in the free bbtz molecule (Peng *et al.*, 2004), and in  $[\text{Cd}(\text{bbtz})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot 3\text{DMF}$  and  $[\text{Cd}(\text{bbtz})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{DMF}$  (DMF is dimethylformamide; Li *et al.*, 2005). However, the bbtz ligands show the *gauche-gauche* conformation in  $[\text{Cd}(\text{bbtz})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The bbtz ligands present both *trans-gauche* and *gauche-gauche* conformations in  $[\text{Cd}_3(\text{bbtz})_6(\text{H}_2\text{O})_6](\text{BF}_4) \cdot \text{H}_2\text{O}$  (Li *et al.*, 2005).

The three rings (two triazole rings and one benzene ring) of one bbtz ligand are not coplanar, either in (I) or in the free bbtz molecule (Peng *et al.*, 2004). However, the dihedral angle between the two triazole planes is  $0^\circ$  by imposed crystallographic symmetry [both in (I) and in the free bbtz molecule],



**Figure 2**

A perspective view of the two-dimensional sheet in (I) (see *Comment*). Only the Cu and thiocyanate atoms are shown for clarity.



**Figure 3**  
The three-dimensional network in (I).

with the dihedral angles between the benzene and triazole planes [70.48 (10)°] being similar to those in the free bbtz molecule [77.81 (9)°].

As illustrated in Fig. 3, each bbtz ligand in (I) coordinates to two Cd<sup>II</sup> atoms through its two triazole N atoms, thus acting as a bridging bidentate ligand, further linking the [Cd( $\mu$ -NCS-*N*:*S*)<sub>2</sub>]<sub>n</sub> sheets into a novel covalent three-dimensional network. To the best of our knowledge, construction of such a covalent three-dimensional network by bridging ligands and the [Cd( $\mu$ -NCS-*N*:*S*)<sub>2</sub>]<sub>n</sub> two-dimensional network are unprecedented in cadmium–thiocyanate systems. A 34-membered ring is formed through four Cd<sup>II</sup> atoms linked by two single  $\mu$ -*N*:*S* bridges and two bbtz ligands. The Cd $\cdots$ Cd distance is 13.5938 (15) Å through the bridging bbtz ligand, similar to the corresponding range of 11.568 (1)–14.845 Å in the bbtz cadmium(II) complexes reported previously (Li *et al.*, 2005). By way of comparison, N–H $\cdots$ O amide hydrogen bonds between two-dimensional [Cd<sub>4</sub>( $\mu$ -NCS-*N*:*S*)<sub>4</sub>]<sub>n</sub> sheets extend the two-dimensional networks into three-dimensional structures in [Cd(NCS)<sub>2</sub>(nicotinamide)<sub>2</sub>] $\cdot$ H<sub>2</sub>O and [Cd(NCS)<sub>2</sub>(isonicotinamide)<sub>2</sub>] (Yang *et al.*, 2001). The bidentate bte ligands link the [Cd( $\mu$ -NCS-*N*:*S*)<sub>2</sub>]<sub>n</sub> chains into a two-dimensional rhombic network in [Cd(NCS)<sub>2</sub>(bte)]<sub>n</sub> (Li *et al.*, 2004).

## Experimental

A water–methanol solution (1:1 *v/v*, 20 ml) of 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) (0.120 g, 0.50 mmol) and KNCS (0.194 g, 2.0 mmol) was added to one leg of a H-shaped tube and a water–methanol solution (1:1 *v/v*, 20 ml) of Cd(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.185 g, 0.6 mmol) was added to the other leg of the tube. Well shaped yellow crystals of (I) suitable for X-ray analysis were obtained after about one month. The product is stable in an ambient atmosphere and is insoluble in most common inorganic and organic solvents. Analysis found: C 35.76, H 2.53, N 23.78%; calculated for C<sub>14</sub>H<sub>12</sub>CdN<sub>8</sub>S<sub>2</sub>: C 35.87, H 2.58, N 23.91%.

## Crystal data

[Cd(NCS)<sub>2</sub>(C<sub>12</sub>H<sub>12</sub>N<sub>6</sub>)]  
*M<sub>r</sub>* = 468.87  
 Monoclinic, *C*2/*c*  
*a* = 22.749 (4) Å  
*b* = 9.5867 (15) Å  
*c* = 7.9484 (14) Å  
 $\beta$  = 99.787 (5)°  
*V* = 1708.2 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.823 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 3252 reflections  
 $\theta$  = 3.4–25.4°  
 $\mu$  = 1.54 mm<sup>-1</sup>  
*T* = 193 (2) K  
 Block, yellow  
 0.35 × 0.16 × 0.10 mm

## Data collection

Rigaku Mercury CCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.723, *T<sub>max</sub>* = 0.861  
 8122 measured reflections  
 1553 independent reflections

1457 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.023  
 $\theta_{\max}$  = 25.4°  
*h* = −26 → 27  
*k* = −11 → 11  
*l* = −9 → 9

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.023  
*wR*(*F*<sup>2</sup>) = 0.056  
*S* = 1.04  
 1553 reflections  
 116 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 1.9445P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Cd1–N3	2.3047 (19)	N1–C3	1.476 (3)
Cd1–N4	2.308 (2)	N2–C1	1.318 (4)
Cd1–S1 <sup>i</sup>	2.7394 (7)	N3–C2	1.320 (3)
S1–C7	1.646 (3)	N3–C1	1.330 (3)
N1–C2	1.320 (3)	N4–C7	1.149 (3)
N1–N2	1.353 (3)		
N3–Cd1–N4	90.53 (8)	C7–S1–Cd1 <sup>ii</sup>	100.06 (8)
N3–Cd1–S1 <sup>i</sup>	90.00 (5)	C7–N4–Cd1	165.8 (2)
N4–Cd1–S1 <sup>i</sup>	92.57 (6)	N4–C7–S1	177.8 (2)

Symmetry codes: (i) *x*, −*y*, *z* +  $\frac{1}{2}$ ; (ii) −*x* +  $\frac{3}{2}$ , *y* −  $\frac{1}{2}$ , −*z* −  $\frac{1}{2}$ .

H atoms were placed in idealized positions and refined as riding, with C–H distances of 0.95 (triazole and benzene) and 0.99 Å (methane), and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TY1011). Services for accessing these data are described at the back of the journal.

## References

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.

- Bruker (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, H.-J., Yang, G. & Chen, X.-M. (1999). *Acta Cryst.* **C55**, 2012–2014.
- Chenskaya, A., Virovets, A. V., Gromilov, S. A., Podberezhskaya, N. V. & Cherkasova, T. G. (2000). *Inorg. Chem. Commun.* **3**, 482–485.
- Goher, M. A. S., Mautner, F. A., abu-Youssef, M. A. M., Hafez, A. K., Badr, A. M.-A. & Gspan, C. (2003). *Polyhedron*, **22**, 3137–3143.
- Haasnoot, J. G., de Keyzer, G. C. M. & Verschoor, G. C. (1983). *Acta Cryst.* **C39**, 1207–1209.
- Kahn, O. (2000). *Acc. Chem. Res.* **33**, 647–657.
- Li, B. L., Peng, Y. F., Li, B. Z. & Zhang, Y. (2005). *Chem. Commun.* pp. 2333–2335.
- Li, B. L., Zhu, X., Zhou, J. H., Peng, Y. F. & Zhang, Y. (2004). *Polyhedron*, **23**, 3133–3141.
- Mondal, N., Saha, M. K., Mitra, S. & Gramlich, V. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3218–3221.
- Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Peng, Y. F., Li, B. Z., Zhou, J. H., Li, B. L. & Zhang, Y. (2004). *Chin. J. Struct. Chem.* **23**, 985–988.
- Rigaku (2000). *CrystalClear*. Version 1.3. Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Taniguchi, M. & Ouchi, A. (1987). *Bull. Chem. Soc. Jpn.*, **60**, 1192–1194.
- Taniguchi, M., Shimoi, M. & Ouchi, A. (1986). *Bull. Chem. Soc. Jpn.*, **59**, 2299–2302.
- Taniguchi, M., Sugita, Y. & Ouchi, A. (1987). *Bull. Chem. Soc. Jpn.*, **60**, 1321–1326.
- Yaghi, O. M., Li, H., Davis, C., Richardson, D. & Groy, T. L. (1998). *Acc. Chem. Res.* **31**, 474–484.
- Yang, G., Zhu, H. G., Liang, B. H. & Chen, X. M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 580–585.
- Zhang, H., Wang, X. M., Zhang, K. C. & Teo, B. K. (1999). *Coord. Chem. Rev.* **183**, 157–195.
- Zhou, J. H., Zhu, X., Zhang, Y. N., Zhang, Y. & Li, B. L. (2004). *Inorg. Chem. Commun.* **7**, 949–952.