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

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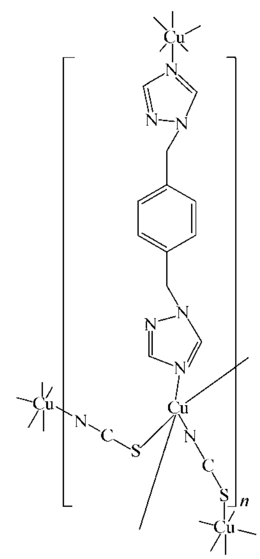
In the title complex, poly[copper(II)-di-μ_2-thiocyanato-μ_2-1,4-bis(1,2,4-triazol-1-ylmethyl)benzene], $[Cu(NCS)_2(C_{12}H_{12}N_6)]_n$, the Cu^{II} atom lies on an inversion centre in a tetragonally distorted octahedral environment. Four N atoms from thiocyanate and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) ligands fill the equatorial positions, and S atoms from symmetry-related thiocyanate ligands fill the axial positions. The benzene ring of the bbtz ligand lies about an inversion centre. Single thiocyanate bridges link the Cu^{II} atoms into two-dimensional sheets containing an unprecedented 16-membered $[Cu_4(\mu\text{-NCS-}N{:}S)_4]$ ring. The bbtz ligands further link the two-dimensional sheets into a three-dimensional network.

Comment

The design and construction of coordination polymers is of great interest because of their intriguing structural topologies and potential applications as functional materials (Yaghi *et al.*, 1998; Batten & Robson, 1998; Moulton & Zaworotko, 2001). The design of coordination polymers requires appropriate components, such as suitable bridging ligands, to link metal centres. The pseudohalide thiocyanate has been demonstrated to be an extremely versatile ligand, which can provide μ-NCS$^-$-*N*:*S*, μ-NCS$^-$-*N*:*N*, terminal N-bonded NCS$^-$ or terminal S-bonded NCS$^-$ modes (Zhang *et al.*, 1999). Many doubly thiocyanate-bridged copper(II) complexes have been characterized (Zhang *et al.*, 1999; Bie *et al.*, 2003). However, singly thiocyanate-bridged copper(II) compounds are relatively rare (Ribas *et al.*, 1995; Karan *et al.*, 2002).

The most widely used ligands for construction of coordination polymers are rigid rod-like N-atom donor organic ligands, and a variety of topological architectures have been synthesized (Fujita *et al.*, 1994; Li *et al.*, 2001). However, flexible ligands containing triazole or imidazole have not been well studied to date (Effendy *et al.*, 2004; Van Albada *et al.*, 2000; Shen *et al.*, 1999). In previous studies, we synthesized several coordination polymers with the flexible ligands 1,2-bis(1,2,4-triazol-1-yl)ethane (bte; Li *et al.*, 1999, 2003; Zhu *et al.*, 2004; Zhou *et al.*, 2004), 1,2-bis(imidazol-1-yl)ethane (bim; B.-L. Li *et al.*, 2004) and 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene (bbtz; Peng *et al.*, 2004; B.-Z. Li *et al.*, 2004). In the present paper, we report the preparation and crystal structure of a three-dimensional coordination polymer, $[Cu(NCS)_2(bbtz)]_n$, (I), which contains novel 16-membered $[Cu_4(\mu\text{-SCN-}N{:}S)_4]$ rings.



(I)

As shown in Fig. 1, the Cu^{II} atom lies on an inversion centre, in a tetragonally distorted octahedral environment, coordinated by four N atoms from symmetry-related thiocyanate and bis-monodentate bbtz ligands in the equatorial positions, and two S atoms from symmetry-related thiocyanate ligands in the axial positions. This coordination environment is similar to that in $[Cu(NCS)_2(4\text{-picoline})_2]_n$ [Cambridge Structural Database (CSD; Allen, 2002) refcode DUPFOJ10 (Koziskova *et al.*, 1990)], $[Cu(NCS)_2(imidazole)_2]_n$ (Bie *et al.*, 2003) and $[Cu(NCS)_2(4\text{-cyanopyridine})_2]_n$ (Li *et al.*, 2002). The Cu—N_{bbtz} bond lengths are 2.0074 (15) Å (Table 1), longer than the Cu—N_{NCS^-} bond lengths [1.9700 (15) Å] and similar to the Cu—N bond lengths in the three cited compounds. The NCS$^-$ ion acts as a bridging ligand in a μ-*N*:*S* mode in (I), as in the three cited compounds. In (I), however, single thiocyanate bridges link two Cu^{II} atoms, while double thiocyanate bridges connect two Cu^{II} atoms in the cited compounds. The Cu—S bond length in (I) is 2.9163 (6) Å, shorter than the sum of the van der Waals radii of the Cu and S atoms (3.4 Å) and similar to the values 2.968 (4)–3.258 (4) Å in $[Cu(NCS)_2(4\text{-picoline})_2]_n$, 3.14 (5) Å in $[Cu(NCS)_2(imidazole)_2]_n$, 2.950 (4) and 2.996 (4) Å in $[Cu(NCS)_2(4\text{-cyanopyridine})_2]_n$, and 3.021 (3) and 3.038 (3) Å in $[Cu(NCS)_2(2,2'\text{-bipyridine})]$ (CSD refcode FAZQOM; Ferlay *et al.*, 1999), in which the S atoms adopt the axial positions in a similarly distorted octahedron around the Cu^{II} atom. In Cu^{II} complexes, *N*-bonded thiocyanate groups mostly appear in equatorial positions, while the *S*-bonded

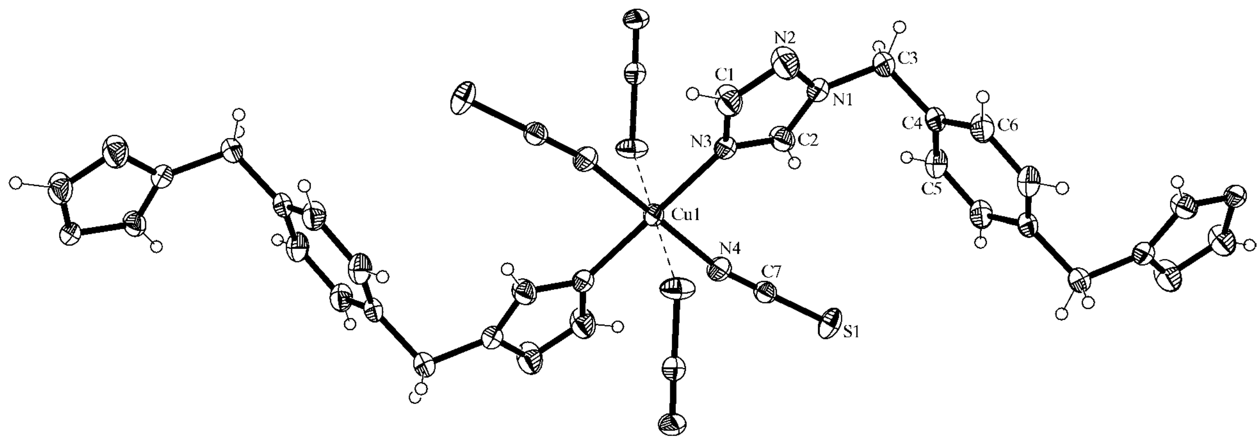


Figure 1
A view of the local coordination of the Cu^{II} atom in (I), with displacement ellipsoids drawn at the 50% probability level. Only the atoms of the asymmetric unit have been labelled.

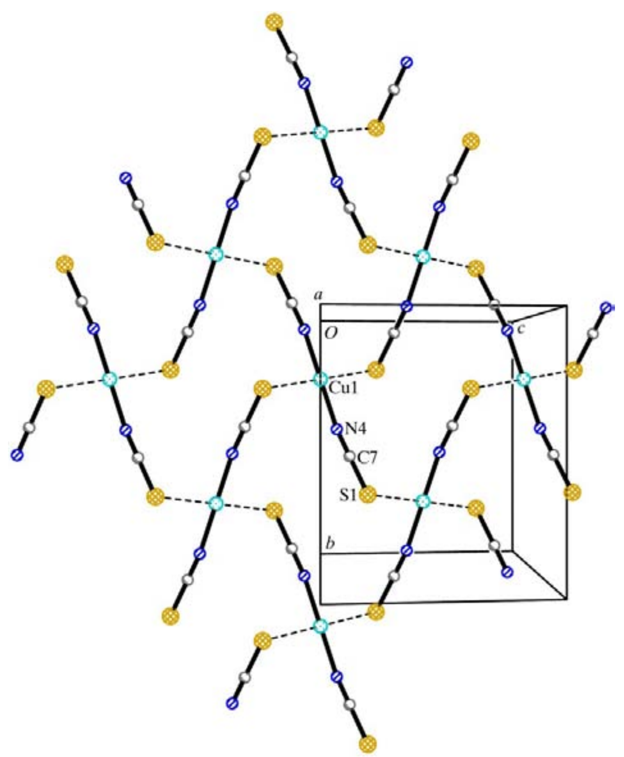


Figure 2
A perspective view of the two-dimensional sheet in (I) (see *Comment*). Only the Cu and thiocyanate atoms are shown for clarity.

groups are observed in the axial directions. The $Cu-N-C_{NCS}$ bond angle in (I) is 166.68 (16)°, in good agreement with the values in singly thiocyanate-bridged copper(II) complexes, *viz.* 163.6 (8) and 169.0 (7)° in [Cu(NCS)$_2$(2,2′-bipyridine)] (FAZQOM), 167.4 (14) and 169.1 (13)° in [Cu(NCS)$_2$(dach)]$_n$ (dach is 1,4-diazacycloheptane; Karan *et al.*, 2002), and 155.6 (5)° in [{Cu$_2$(tmen)$_2$NCS[μ-Cu(pba)]}(μ-SCN)]$_n$·3nH$_2$O {Cu(pba) is [1,3-propanediylbis(oxamato)]cuprate(II) and tmen is *N*,*N*,*N*′,*N*′-tetramethylenediamine; Ribas *et al.*, 1995}. The $Cu-S-C_{SCN}$ bond angle is 100.67 (6)°, comparable to the values of 97.9 (3), 90.3 (5) and 112.31 (7)° in the last three cited compounds. The thiocyanate ligand is normal.

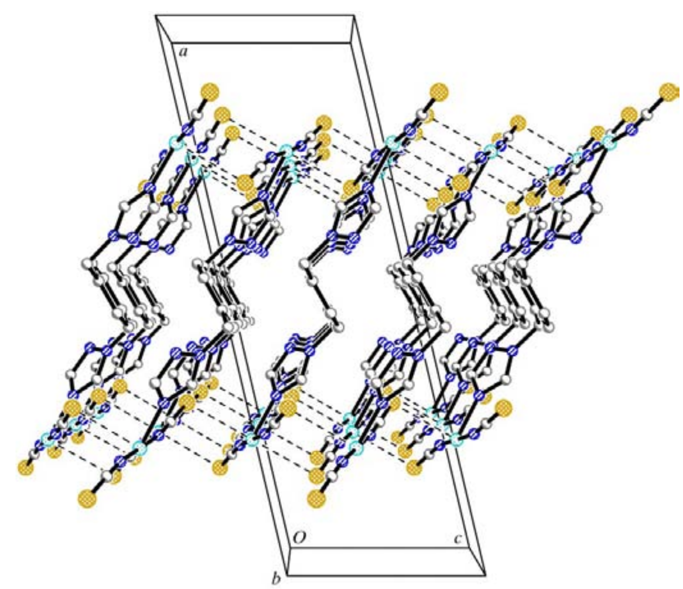


Figure 3
The three-dimensional network in (I) (see *Comment*). S, N and Cu atoms are fully hatched, partially hatched and not hatched, respectively. H atoms have been omitted for clarity.

Each NCS^- anion in (I) coordinates to two Cu^{II} atoms in a μ-NCS-*N*:*S* mode, and single thiocyanate bridges link the Cu^{II} centres into a two-dimensional sheet, resulting in an ‘hour-glass-shaped’ 16-membered [Cu$_4$(μ-NCS-*N*:*S*)$_4$] metallocycle (Fig. 2). To the best of our knowledge, such an arrangement of the metallocycle is unprecedented in copper–thiocyanate systems. Three similar structures with the [M_4(μ-NCS-*N*:*S*)$_4$] subunit have been reported for three transition metal complexes, *viz.* [Mn$_4$(μ-NCS-*N*:*S*)$_4$] in [Mn(NCS)$_2$(EtOH)$_2$] (McElearney *et al.*, 1979), and [Cd$_4$(μ-NCS-*N*:*S*)$_4$] in [Cd(NCS)$_2$(nicotinamide)$_2$]·H$_2$O and [Cd(NCS)$_2$(isonicotinamide)$_2$] (Yang *et al.*, 2001). The Cu···Cu separation through the NCS^- ligand is 6.0783 (6) Å in (I), compared with values ranging from 5.27 (2) Å in the singly thiocyanate-bridged copper(II) complex [Cu(NCS)$_2$(dach)]$_n$ to 6.113 Å in the doubly thiocyanate-bridged copper(II) complex [Cu(NCS)$_2$(2,2′-bipyridine)] (Diaz *et al.*, 1999).

Because the methyl C atoms of bbtz can rotate freely to adjust to the coordination environment, bbtz can exhibit *trans–gauche* and *gauche–gauche* conformations, similar to the ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix), as shown in the polyrotaxane $[Ag_2(bix)_3](NO_3)_2$ (Hoskins *et al.*, 1997*b*). The bbtz ligands exhibit the *trans–gauche* conformation in (I), similar to the situation in the free bbtz molecule (Peng *et al.*, 2004) and the bridging bbtz ligand in $[Co(N_3)_2(bbtz)_2]_n$, (II) (B.-Z. Li *et al.*, 2004). The three rings (two triazole rings and one benzene ring) of one bbtz ligand are not coplanar in (I), (II) or the free bbtz molecule. However, the dihedral angle between the two triazole planes is 0° by imposed crystallographic symmetry in (I) and in the free bbtz molecule, compared with 61.94 (19)° in (II). The dihedral angle between the benzene and triazole planes in (I) is 70.51 (7)°, similar to the value in the free bbtz molecule [77.81 (9)°] and those in (II) [67.26 (9) and 66.96 (7)°].

As illustrated in Fig. 3, each bbtz ligand in (I) coordinates to Cu^{II} atoms through its two triazole N atoms, thus acting as a bridging bidentate ligand to further link the $[Cu(\mu\text{-NCS-}N{:}S)_2]_n$ sheets into a three-dimensional network. A 34-membered ring is formed through four Cu atoms linked by two single μ-NCS-*N*:*S* bridges and two bbtz ligands. The Cu···Cu distance is 13.2178 (13) Å through the bridging bbtz ligand, similar to the corresponding metal–metal separations in (II) [14.4156 (18) Å] and the related bix complexes $[Zn(bix)_2(NO_3)_2]\cdot4.5H_2O$ [15.037 (2) Å; Hoskins *et al.*, 1997*a*], $[Ag_2(bix)_3(NO_3)_2]$ [14.626 (2) Å; Hoskins *et al.*, 1997*b*] and $[Mn(bix)_3(NO_2)_2]\cdot4H_2O$ (12.659 Å; Shen *et al.*, 1999). By way of comparison, two-dimensional sheets of $[Mn_4(\mu\text{-NCS-}N{:}S)_4]_n$ are separated by ethanol groups in $[Mn(NCS)_2(EtOH)_2]$ (McElearney *et al.*, 1979), and N—H···O amide hydrogen bonds between two-dimensional $[Cd_4(\mu\text{-NCS-}N{:}S)_4]_n$ sheets extend the two-dimensional networks to three-dimensional structures in $[Cd(NCS)_2(nicotinamide)_2]\cdot H_2O$ and $[Cd(NCS)_2(isonicotinamide)_2]$ (Yang *et al.*, 2001).

Experimental

A water–methanol solution (20 ml, 1:1 *v*/*v*) of 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 (20 ml, 1:1 *v*/*v*) of $CuSO_4\cdot5H_2O$ (0.150 g, 0.6 mmol) was added to the other leg of the tube. Well-shaped green crystals suitable for X-ray analysis were obtained after about two months. The product is stable in an ambient atmosphere and insoluble in most common inorganic and organic solvents. Analysis found: C 39.92, H 2.83, N 26.57%; calculated for $C_{14}H_{12}CuN_8S_2$: C 40.04, H 2.88, N 26.69%.

Crystal data

$[Cu(NCS)_2(C_{12}H_{12}N_6)]$	D_x = 1.705 Mg m^{-3}
M_r = 420.01	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3412 reflections
a = 23.005 (3) Å	θ = 3.4–27.5°
b = 9.2208 (12) Å	μ = 1.61 mm^{-1}
c = 7.9222 (11) Å	T = 193.2 K
β = 103.200 (3)°	Block, green
V = 1636.1 (4) Å^3	0.40 × 0.32 × 0.09 mm
Z = 4	

Data collection

Rigaku Mercury CCD diffractometer	1870 independent reflections
ω scans	1784 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (North *et al.*, 1968)	R_{int} = 0.023
	θ_{max} = 27.5°
T_{min} = 0.566, T_{max} = 0.869	h = −29 → 27
8843 measured reflections	k = −11 → 11
	l = −10 → 10

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 1.4357P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.030	
$wR(F^2)$ = 0.079	
S = 1.07	$(\Delta/\sigma)_{max}$ < 0.001
1870 reflections	$\Delta\rho_{max}$ = 0.39 e Å^{-3}
116 parameters	$\Delta\rho_{min}$ = −0.38 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N4	1.9700 (15)	N1—C3	1.476 (2)
Cu1—N3	2.0074 (15)	N2—C1	1.316 (3)
Cu1—S1^{i}	2.9163 (6)	N3—C2	1.326 (2)
S1—C7	1.6317 (18)	N4—C7	1.156 (2)
N1—N2	1.360 (2)		
N4—Cu1—N3	89.79 (6)	C7—N4—Cu1	166.68 (16)
N4—Cu1—S1^{i}	87.99 (5)	N4—C7—S1	178.95 (18)
N3—Cu1—S1^{i}	89.37 (4)		

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

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 $U_{iso}(H) = 1.2U_{eq}(C)$. Two reflections ($\overline{6}02$ and $\overline{4}02$) were excluded by the image processing software.

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: GA1092). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
Bie, H. Y., Yu, J. H., Xu, J. Q., Lu, J., Li, Y., Cui, X. B., Zhang, X., Sun, Y. H. & Pan, L. Y. (2003). *J. Mol. Struct.* **660**, 107–112.
Bruker (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Diaz, C., Ribas, J., Sanz, N., Solans, X. & Font-Bardia, M. (1999). *Inorg. Chim. Acta*, **286**, 169–174.
Effendy, Marchetti, F., Pettinari, C., Pettinari, R., Ricciutelli, M., Skelton, B. R. & White, A. H. (2004). *Inorg. Chem.* **43**, 2157–2165.
Ferlay, S., Francese, G., Schmalle, H. W. & Decurtins, S. (1999). *Inorg. Chim. Acta*, **286**, 108–113.

Fujita, M., Kwon, Y. J., Washizu, S. & Ogura, K. (1994). *J. Am. Chem. Soc.* **116**, 1151–1152.
Hoskins, B. F., Robson, R. & Slizys, D. (1997*a*). *Angew. Chem. Int. Ed. Engl.* **36**, 2336–2338.
Hoskins, B. F., Robson, R. & Slizys, D. (1997*b*). *J. Am. Chem. Soc.* **119**, 2952–2953.
Karan, N. M., Mitra, S., Matsushita, T., Gramlich, V. & Rosair, G. (2002). *Inorg. Chim. Acta*, **332**, 87–91.
Koziskova, Z., Kozisek, J. & Kabesova, M. (1990). *Polyhedron*, **9**, 1029–1034.
Li, B., Zhou, J., Duan, C., Liu, Y., Wei, X. & Xu, Z. (1999). *Acta Cryst.* C**55**, 165–167.
Li, B.-L., Li, B.-Z., Zhu, X., Zhu, L.-M. & Zhang, Y. (2003). *Acta Cryst.* C**59**, m350–m351.
Li, B. L., Yin, G., Cao, H. Q., Liu, Y. J. & Xu, Z. (2001). *Inorg. Chem. Commun.* **4**, 451–453.
Li, B.-L., Zhu, X., Zhou, J.-H. & Zhang, Y. (2004). *Acta Cryst.* C**60**, m373–m374.
Li, B.-Z., Peng, Y.-F., Zhang, Y.-P., Li, B.-L. & Zhang, Y. (2004). *Acta Cryst.* C**60**, m560–m562.
Li, X. Y., Wang, P., Wang, Z. M., Yan, C. H., Zhang, L. D. & Guo, H. Y. (2002). *Chin. J. Chem.* **20**, 142–146.
McElearney, J. N., Balagot, L. L., Muir, J. A. & Spence, R. D. (1979). *Phys. Rev. B: Condens. Matter*, **19**, 306–317.
Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Peng, Y. F., Li, B. Z., Zhou, J. H., Li, B. L. & Zhang, Y. (2004). *Chin. J. Struct. Chem.* **23**, 985–988.
Ribas, J., Diaz, C., Solans, X. & Font-Bardia, M. (1995). *Inorg. Chim. Acta*, **231**, 229–232.
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.
Shen, H. Y., Liao, D. Z., Jiang, Z. H., Yan, S. P., Wang, G. L., Yao, X. K. & Wang, H. G. (1999). *Acta Chem. Scand.* **53**, 387–390.
Van Albada, G. A., Guijt, R. C., Haasnoot, J. G., Lutz, M., Spek, A. L. & Reedijk, J. (2000). *Eur. J. Inorg. Chem.* pp. 121–126.
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.
Zhu, X., Li, B.-Z., Zhou, J.-H., Li, B.-L. & Zhang, Y. (2004). *Acta Cryst.* C**60**, m191–m193.