

catena-Poly[[(nitrate- $\kappa^2 O, O'$)-silver(I)- μ -2,2'-[1,4-phenylene-bis(methylenethio)]bis(5-methyl-1,3,4-thiadiazole)- $\kappa^2 N^3:N^3'$]

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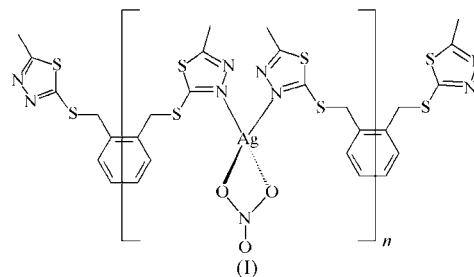
In the title complex, $[\text{Ag}(\text{NO}_3)(\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}_4)]_n$, the Ag^{I} atom lies on a twofold axis and shows a distorted tetrahedral coordination, comprised of two N-atom donors from two thiadiazole groups of separate ligands and two O-atom donors from one nitrate ligand. Each bis(thioether) ligand also lies on a twofold axis and bridges two adjacent Ag atoms to form an infinite chain along the c axis, with an $\text{Ag} \cdots \text{Ag}$ separation of 11.462 (4) Å. Adjacent one-dimensional chains are further linked into double-chain motifs through weak $\text{Ag} \cdots \text{S}$ and π - π stacking interactions.

Comment

The rational design of coordination architectures is one of the most exciting fields in current coordination and supramolecular chemistry (Braga *et al.*, 1998). Ligand design is an important aspect in adjusting the coordination framework, and the different numbers and relative orientations of coordination donors in the ligands may lead to the formation of unique frameworks with tailored properties and functions (Blake *et al.*, 1999; Sun *et al.*, 2001; Li *et al.*, 2003; Xie *et al.*, 2004). Di/triaryl and heteroaryl thioether ligands have shown interesting coordination ability with metal ions (Hong, Zhao *et al.*, 2000; Bu, Hou *et al.*, 2002; Bu, Chen *et al.*, 2002), and the range of heteroaryl groups studied has been enlarged in recent years from pyridine derivatives (Sharma *et al.*, 1999; Constable *et al.*, 2002; Xie & Bu, 2003; Bu *et al.*, 2003) to other heterocyclic thioether ligands (Yang *et al.*, 1997; Hong, Su *et al.*, 2000; Dong *et al.*, 2003; Fan *et al.*, 2003; Zou *et al.*, 2004). In previous work, we have synthesized a bis(thioether) ligand, PBT, which contains two 2-(5-methyl-1,3,4-thiadiazolyl)sulfanyl groups separated by an *o*-xylylene spacer (Zheng & Liu, 2003). In this paper, we report the crystal structure of the title compound, (I), which is a new Ag complex with this ligand.

In (I), atoms Ag1, N3 and O2 lie on a twofold axis (Fig. 1). The compound is a one-dimensional polymer and the geometry of the Ag^{I} cation is a distorted tetrahedron,

comprised of two N donors from two thiadiazole rings of separate PBT ligands and two O-atom donors from one nitrate, with $\text{Ag}-\text{N}$ and $\text{Ag}-\text{O}$ bond distances within the ranges expected for such coordination (Carlucci *et al.*, 1998; Engelhardt *et al.*, 1985; Gotsis & White, 1987).



As in uncoordinated PBT (Zheng & Liu, 2003), the two terminal 2-(5-methyl-1,3,4-thiadiazolyl)sulfanyl groups in (I) point in opposite directions from the benzene plane, in order to reduce the steric repulsion between them. The dihedral angle between the two thiadiazole planes is 50.5 (2)°, and that between the terminal group and the central benzene plane is 86.6 (3)°. Each PBT ligand bridges two adjacent Ag atoms through $\text{Ag}-\text{N}_{\text{thiadiazole}}$ coordination to form an infinite chain along the c axis, with an $\text{Ag} \cdots \text{Ag}$ separation of 11.462 (4) Å (e.g. Ag1A \cdots Ag1B in Fig. 2).

In the crystal packing of (I), adjacent one-dimensional chains are potentially linked into a double-chain motif (Fig. 2) through weak $\text{Ag} \cdots \text{S}$ interactions [3.54 (3) Å; Orpen *et al.*, 1989; Suenaga *et al.*, 1999; Zheng *et al.*, 2003] and π - π stacking interactions [the interplanar distance between parallel neighbouring thiadiazole rings from two chains is 3.33 (3) Å and the corresponding centroid-to-centroid distance is 3.72 (4) Å]. All Ag atoms are coplanar and all ligands contribute symmetrically to the plane of the Ag atoms. The two terminal thiadiazole groups of the PBT ligands lie above and below this plane.

In contrast with other Ag^{I} complexes with bis(thiadiazolylthioether) ligands (Zheng *et al.*, 2003), only one N atom of the thiadiazole ring coordinates to the Ag atom in (I). The reason may be that, in PBT, two thiadiazole rings are bridged by a relatively rigid *o*-xylylene spacer and stretched towards the same side of the benzene ring (*cis* conformation), and this therefore makes the methyl group on the thiadiazole stretch

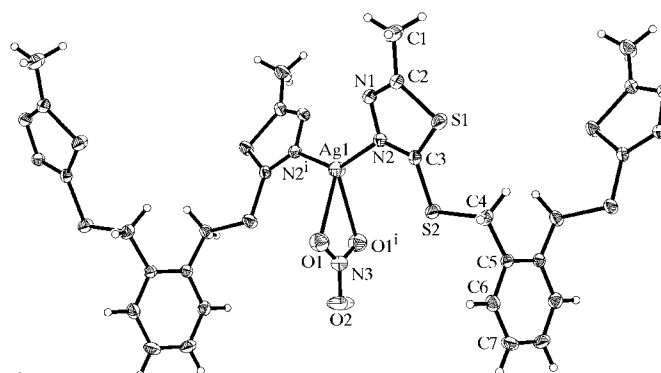


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. [Symmetry code: (i) $x, y, z - 1$.]

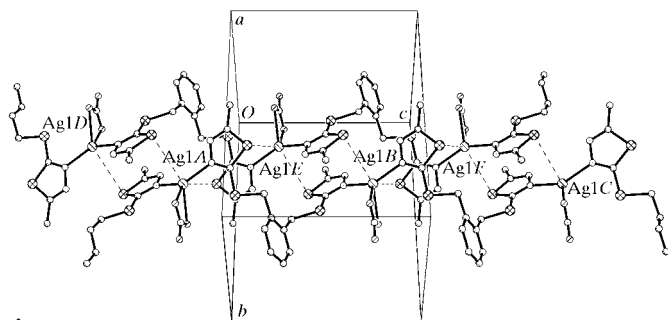


Figure 2

A view of the double-chain motif linked through Ag...S weak interactions in (I), with all H atoms omitted for clarity. Atoms labelled with the suffixes A, B, C, D, E or F are at the symmetry positions $(-x, y, \frac{3}{2} - z)$, $(-x, y, \frac{1}{2} - z)$, $(-x, y, \frac{7}{2} - z)$, $(x, -y, z - \frac{1}{2})$, $(x, -y, \frac{1}{2} + z)$ and $(x, -y, \frac{3}{2} + z)$, respectively.

outside. The bulkiness of the methyl group probably hinders the coordination of the neighbouring N atom.

Experimental

The ligand PBT was prepared in our previous work (Zheng & Liu, 2003) by the reaction of 5-methyl-2-mercapto-1,3,4-thiadiazole and bis(dibromomethyl)benzene. A solution of AgNO₃ (90 mg, 0.5 mmol) in methanol (10 ml) was carefully layered on a solution of PBT (183 mg, 0.5 mmol) in chloroform (10 ml), and the mixture was kept in the dark. Colourless crystals of (I) suitable for X-ray analysis were obtained after about two weeks (yield 55%). Elemental analysis calculated: C 31.32, H 2.61, N 13.05%; found: C 31.17, H 2.68, N 12.83%. IR (KBr pellet, ν , cm⁻¹): 2946 (m), 2868 (w), 1730 (w), 1631 (m), 1497 (m), 1468 (s), 1436 (vs), 1408 (vs), 1376 (vs), 1286 (vs), 1250 (vs), 1190 (s), 1158 (m), 1111 (vs), 1052 (s), 1030 (s), 982 (m), 817 (m), 786 (s), 713 (s), 611 (s).

Crystal data

[Ag(NO₃)(C₁₄H₁₄N₄S₄)]
 M_r = 536.41
 Monoclinic, C2/c
 a = 10.670 (5) Å
 b = 15.720 (7) Å
 c = 11.462 (5) Å
 β = 90.627 (7)°
 V = 1922.4 (15) Å³
 Z = 4
 D_x = 1.853 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 538 reflections
 θ = 2.7–24.9°
 μ = 1.51 mm⁻¹
 T = 293 (2) K
 Block, colourless
 0.25 × 0.15 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996; Blessing, 1995)
 T_{min} = 0.704, T_{max} = 0.889
 3722 measured reflections
 1710 independent reflections
 1389 reflections with I > 2σ(I)
 R_{int} = 0.022
 θ_{max} = 25.0°
 h = -12 → 12
 k = -18 → 10
 l = -12 → 13

Refinement

Refinement on F²
 R[F² > 2σ(F²)] = 0.025
 wR(F²) = 0.054
 S = 1.02
 1710 reflections
 124 parameters
 H-atom parameters constrained
 w = 1/[σ²(F_o²) + (0.025P)²]
 where P = (F_o² + 2F_c²)/3
 (Δ/σ)_{max} = 0.002
 Δρ_{max} = 0.37 e Å⁻³
 Δρ_{min} = -0.41 e Å⁻³

H atoms were placed geometrically and refined using a riding model, with C–H distances in the range 0.93–0.97 Å and with U_{iso}(H) = 1.2U_{eq}(C).

Table 1

Selected geometric parameters (Å, °).

Ag1–N2	2.200 (2)	Ag1–O1	2.506 (2)
N2 ⁱ –Ag1–N2	141.29 (11)	N2–Ag1–O1 ⁱ	114.85 (7)
N2–Ag1–O1	100.30 (7)	O1–Ag1–O1 ⁱ	50.71 (10)

Symmetry code: (i) -x, y, 3/2 - z.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1194). Services for accessing these data are described at the back of the journal.

References

Blake, A. J., Champness, N. R., Hubberstey, P., Li, W. S., Withersby, M. A. & Schröder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Braga, D., Grepioni, F. & Desiraju, G. R. (1998). *Chem. Rev.* pp. 1375–1405.
 Bruker (1998). SMART, SAINT and SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bu, X. H., Chen, W., Hou, W. F., Du, M., Zhang, R. H. & Brisse, F. (2002). *Inorg. Chem.* **41**, 3477–3482.
 Bu, X. H., Hou, W. F., Du, M., Chen, W. & Zhang, R. H. (2002). *Cryst. Growth Des.* **2**, 303–307.
 Bu, X. H., Xie, Y. B., Li, J. R. & Zhang, R. H. (2003). *Inorg. Chem.* **42**, 7422–7430.
 Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi, A. (1998). *Inorg. Chem.* **37**, 5941–5943.
 Constable, E. C., Housecroft, C. E., Kariuki, B. M., Kelly, N. & Smith, C. B. (2002). *Inorg. Chem. Commun.* **5**, 199–202.
 Dong, Y. B., Ma, J. P. & Huang, R. Q. (2003). *Inorg. Chem.* **42**, 294–300.
 Engelhardt, L. M., Pakawatchai, C., White, A. H. & Healy, P. C. (1985). *J. Chem. Soc. Dalton Trans.* pp. 117–123.
 Fan, J., Sun, W. Y., Okamura, T., Tang, W. X. & Ueyama, N. (2003). *Inorg. Chem.* **42**, 3168–3175.
 Gotsis, S. & White, A. H. (1987). *Aust. J. Chem.* **40**, 1603–1608.
 Hong, M. C., Su, W. P., Cao, R., Fujita, M. & Lu, J. X. (2000). *Chem. Eur. J.* **6**, 427–431.
 Hong, M. C., Zhao, Y. J., Su, W. P., Cao, R., Fujita, M., Zhou, Z. Y. & Chan, A. S. C. (2000). *J. Am. Chem. Soc.* **122**, 4819–4820.
 Li, J. R., Zhang, R. H. & Bu, X. H. (2003). *Cryst. Growth Des.* **3**, 829–835.
 Orpen, G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.
 Sharma, C. V. K., Broker, G. A., Huddleston, J. G., Baldwin, J. W., Metzger, R. M. & Rogers, R. D. (1999). *J. Am. Chem. Soc.* **121**, 1137–1144.
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Suenaga, Y., Kuroda-Sowa, T., Maekawa, M. & Munakata, M. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2737–2741.
 Sun, W. Y., Fan, J., Okamura, T., Xie, J., Yu, K. B. & Ueyama, N. (2001). *Chem. Eur. J.* **7**, 2557–2562.
 Xie, Y. B. & Bu, X. H. (2003). *J. Cluster Sci.* **14**, 471–482.
 Xie, Y. B., Zhang, C., Li, J. R. & Bu, X. H. (2004). *Dalton Trans.* pp. 562–569.
 Yang, C., Chen, X. M., Lu, X. Q., Zhou, Q. H. & Yang, Y. S. (1997). *J. Chem. Soc. Chem. Commun.* pp. 2041–2042.
 Zheng, Y., Du, M., Li, J. R., Zhang, R. H. & Bu, X. H. (2003). *Dalton Trans.* pp. 1509–1514.
 Zheng, Y. & Liu, H.-B. (2003). *Acta Cryst.* **E59**, o34–o35.
 Zou, R. Q., Li, J. R., Xie, Y. B., Zhang, R. H. & Bu, X. H. (2004). *Cryst. Growth Des.* **4**, 79–84.