

catena-Poly[[silver(I)- μ_3 -2,2'- [*o*-phenylenebis(methylenethio)]- dianiline- κ^4 N:S,S':N'] nitrate chloroform solvate]

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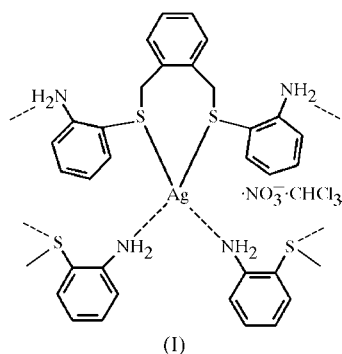
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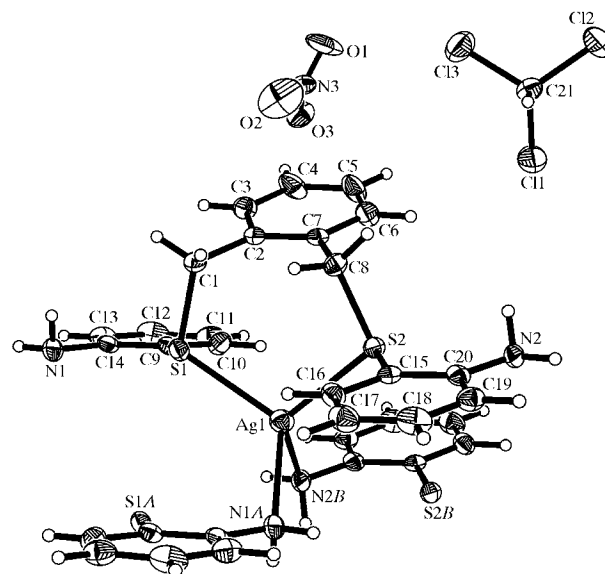
In the title complex, $[[\text{Ag}(\text{C}_{20}\text{H}_{20}\text{N}_2\text{S}_2)](\text{NO}_3)\cdot\text{CHCl}_3]_n$, the coordination about the Ag atom is a slightly distorted tetrahedron, involving the two S atoms of the ligand and two N-atom donors from two amine groups of two adjacent complexes related by centrosymmetry, so building up a chain running all along the crystal structure.

Comment

As a favourable and currently popular connecting node for the construction of coordination polymers, the Ag^{I} ion shows a good coordination tendency with S- or N-atom donors. The study of Ag complexes of nitrogen-containing heterocyclic thioether ligands has mainly focused on pyridine derivatives (Sharma *et al.*, 1999; Constable *et al.*, 2002; Xie *et al.*, 2004; Xie & Bu, 2003; Bu *et al.*, 2003), although examples with other heterocyclic thioether ligands have also been reported (Hong *et al.*, 2000; Zou *et al.*, 2004). Dithioethers, a type of ditopic ligand, can be used as bridging ligands in the construction of coordination polymers with soft metal ions, and a series of bis(phenylthio)alkane and bis(heteroarylthio)alkane flexible ligands and their Ag complexes have been prepared and characterized



(Li *et al.*, 2003; Bu, Hou *et al.*, 2002; Bu, Chen *et al.*, 2002). In this paper, we report the crystal structure of the title novel Ag

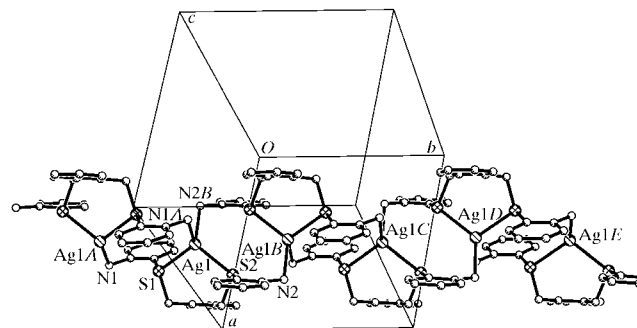

Figure 1

A view of the title complex, with 30% probability displacement ellipsoids. Atoms labelled with the suffixes A or B are at the symmetry positions $(1-x, 1-y, 2-z)$ and $(1-x, 2-y, 2-z)$, respectively.

complex, (I), with a relatively rigid bis(heteroarylthioether) ligand, [*o*-phenylenebis(methylenethio)]dianiline (L).

Complex (I) is a one-dimensional metallopolymer, and the geometry at the Ag^{I} ion can be best described as a slightly distorted tetrahedron comprising the two S-atom donors of the ligand and two N-atom donors from two amino groups of two adjacent complexes, with the NO_3^- counter-anion not taking part in coordination (Fig. 1). The Ag–N bond distances are 2.382 (5) and 2.428 (5) Å, and the Ag–S bond distances are 2.537 (2) and 2.546 (2) Å, which are in the ranges expected for such coordination (Carlucci *et al.*, 1998; Engelhardt *et al.*, 1985; Gotsis & White, 1987).

The coordination of the two S-atom donors of the ligand to the Ag atom forms a seven-membered chelate ring ($\text{Ag1/S1/C1/C2/C7/C8/S2}$), with an S··S distance of 4.088 (2) Å. Atoms C1, S1, Ag1, S2 and C8 are almost coplanar. The two


Figure 2

A view of the chain of (I), with all H atoms omitted. Atoms labelled with the suffixes A, B, C, D and E are at the symmetry positions $(1-x, 1-y, 2-z)$, $(1-x, 2-y, 2-z)$, $(x, 1+y, z)$, $(1-x, 3-y, 2-z)$ and $(x, 2+y, z)$, respectively.

terminal aniline groups of the ligand are oriented in opposite directions relative to the chelate plane and are almost perpendicular to this plane, with dihedral angles of 82.3 (3) and 83.6 (4)°. The planes of these two groups are almost parallel to each other, with a dihedral angle of 14.5 (2)°, and the angles between them and the central *o*-phenylene linker are 23.1 (3) and 9.4 (2)°.

The coordination of the Ag atom to donors from three different ligands results in the assembly of an intriguing extended polymeric structure, which consists of a complex system of interconnected rings, as shown in Fig. 2. In addition, a ten-membered centrosymmetric dinuclear ring is formed by two Ag atoms linked by two N—C—S bridges, with an Ag...Ag interatomic distance of 4.945 (4) Å.

Experimental

The *o*-phenylene ligand, *L*, was prepared according to a literature method (McAuliffe *et al.*, 1978; Pal *et al.*, 1994), by the reaction of *o*-aminobenzenethiol and 1,2-dibromomethylbenzene (yield 58%; m.p. 371–373 K). Spectroscopic analysis, ¹H NMR (CDCl₃, δ): 3.98 (SCH₂–, 4H, s), 4.13 (NH₂–, 4H, s), 6.62–6.72 (C–C₆H₄–C, 4H, m), 6.99–7.19 (N–C₆H₄–S, 8H, m). For the preparation of (I), a solution of AgNO₃ (90 mg, 0.5 mmol) in methanol (10 ml) was carefully layered on a solution of *L* (140 mg, 0.5 mmol) in chloroform (10 ml), and the mixture was kept in darkness. Colourless single crystals of (I) suitable for X-ray analysis were obtained after about two weeks in 48% yield. Analysis calculated for (I): C 39.27, H 3.27, N 6.54%; found: C 38.95, H 3.32, N 6.33%. Spectroscopic analysis, IR (KBr pellet, ν, cm^{–1}): 3447 (*w*), 3373 (*m*), 3270 (*m*), 3157 (*w*), 3064 (*w*), 2976 (*w*), 1606 (*s*), 1570 (*m*), 1479 (*vs*), 1447 (*s*), 1385 (*vs*), 1355 (*vs*), 1315 (*s*), 1233 (*s*), 1161 (*m*), 1044 (*m*), 1002 (*m*), 913 (*m*), 815 (*m*), 745 (*vs*), 692 (*m*).

Crystal data

[Ag(C ₂₀ H ₂₀ N ₂ S ₂)](NO ₃)·CHCl ₃	<i>Z</i> = 2
<i>M_r</i> = 641.75	<i>D_x</i> = 1.761 Mg m ^{–3}
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 9.441 (6) Å	Cell parameters from 865 reflections
<i>b</i> = 9.805 (6) Å	<i>θ</i> = 2.3–24.6°
<i>c</i> = 13.936 (9) Å	<i>μ</i> = 1.37 mm ^{–1}
<i>α</i> = 102.385 (11)°	<i>T</i> = 293 (2) K
<i>β</i> = 98.580 (12)°	Block, colourless
<i>γ</i> = 101.351 (11)°	0.30 × 0.25 × 0.20 mm
<i>V</i> = 1210.4 (13) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	4269 independent reflections
<i>φ</i> and <i>ω</i> scans	2561 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: empirical via multi-scan [SADABS (Sheldrick, 1996; Blessing, 1995)]	<i>R</i> _{int} = 0.033
<i>T</i> _{min} = 0.685, <i>T</i> _{max} = 0.772	<i>θ</i> _{max} = 25.0°
5074 measured reflections	<i>h</i> = –7 → 11
	<i>k</i> = –11 → 11
	<i>l</i> = –16 → 14

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.053	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0802 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.152	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 0.96	(Δ/ <i>σ</i>) _{max} = 0.001
4269 reflections	Δ <i>ρ</i> _{max} = 1.20 e Å ^{–3}
298 parameters	Δ <i>ρ</i> _{min} = –0.65 e Å ^{–3}

H atoms were placed in geometric positions and refined using a riding model, with N—H distances of 0.90 Å and C—H distances in the range 0.93–0.98 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,N).

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); 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: NA1660). Services for accessing these data are described at the back of the journal.

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