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Poly[disilver(I)-μ_8-1,5-naphthalenedisulfonato]

Shan Gao,* Zhen-Zhong Lu, Li-Hua Huo, Zhi-Biao Zhu and Hui Zhao

School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China
Correspondence e-mail: shangao67@yahoo.com

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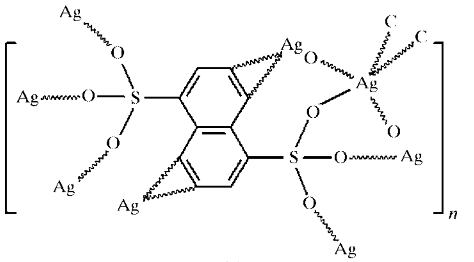
The title complex, poly[disilver(I)-μ_8-1,5-naphthalenedisulfonato-3,4-η:7,8-η:κ^6O:O':O'':O''':O'''':O'''''], $[Ag_2(C_{10}H_6O_6S_2)]_n$, exists as a three-dimensional framework of Ag^I atoms connected by η^{10},μ_8-1,5-naphthalenedisulfonate ligands through both Ag–sulfonate and Ag–η^2-arene interactions. Each Ag^I atom exhibits a distorted tetrahedral geometry defined by three O atoms of independent sulfonate groups and one C=C bond of the naphthalene group.

Comment

The study of the solid-state coordination and structural chemistry of organosulfonates has received growing attention over the past few years. Organosulfonate ions have proved able to generate not only highly robust and fascinating architectures but also 'softer' networks with sponge-like properties by connecting main group metals (Cai *et al.*, 2001) and some transition metal ions, such as barium(II) or silver(I), as reviewed by Côté & Shimizu (2003). Cai (2004, and references therein) recently reviewed the coordinating preferences of some aromatic mono- and disulfonates with main group metals and some transition metals, and also the structural and functional properties of cadmium sulfonates. Organodisulfonates exhibit a greater potential to form a higher-dimensional and more stable structure than do monosulfonates. However, there is little structural information about arenedisulfonate complexes involving the silver(I) ion, which often adopts distorted coordination geometries owing to the inherent lack of ligand field stabilization effects. Along with their soft Lewis acidic properties, Ag^+ ions may be a particularly good match for the flexible coordinative tendencies of sulfonate anions, leading to networks that may be readily capable of rearrangement.

We have obtained a novel complex, $[Ag_2(1,5\text{-nds}^{2-})]_n$ (1,5-nds is 1,5-naphthalenedisulfonic acid), (I), by the reaction of $AgNO_3$ with 1,5-naphthalenedisulfonic acid in ethanol. A search of the Cambridge Structural Database (Allen, 2002) reveals one other silver complex with the same ligand, namely $\{[Ag(1,5\text{-nds}^{2-})(MeCN)_2]\cdot H_3O^+\cdot 2H_2O\}_n$, in which the silver(I) ion adopts a tetrahedral geometry and the 1,5-nds^{2-} ligand displays a η^2,μ_2-coordination mode (each sulfonate group is monodentate), bridging the silver(I) ions to form a chain structure (Shimizu *et al.*, 1999).



(I)

In (I), however, the 1,5-nds^{2-} ligand adopts a η^{10},μ_8-coordination mode, leading to a three-dimensional framework through both Ag–sulfonate and Ag–η^2-arene interactions. To the best of our knowledge, (I) is the first metal complex involving the η^{10},μ_8-1,5-nds^{2-} ligand.

The local coordination around the Ag^I atom, together with the atom-numbering scheme of (I), is shown in Fig. 1. The asymmetric unit contains one Ag^I atom and one-half of a 1,5-naphthalenedisulfonate anion (1,5-nds^{2-}), the coordination being completed by inversion symmetry. The Ag^I atom is coordinated by three O atoms of independent sulfonate groups, with Ag—O bond lengths ranging from 2.377 (3) to 2.396 (3) Å [mean 2.385 (3) Å; Table 1]; these are shorter than the Ag—O bond lengths [2.380 (2)–2.439 (2) Å] in the one-dimensional silver complex with 1,5-nds^{2-} (see above), suggesting a stronger Ag—O$_{\text{sulfonate}}$ interaction. In addition, the Ag^I atom in (I) also interacts with a naphthalene group through a C=C π bond, with Ag—C distances of 2.478 (4) and 2.645 (4) Å, within the range reported for silver(I)–aromatic complexes (2.36–2.77 Å; Munakata *et al.*, 1997, 1998, 1999). The next closest contact between Ag^I and C atoms is 3.148 (3) Å. Therefore, the Ag^I atom exhibits a distorted tetrahedral geometry (regarding the C=C group as one donor). The silver(I) ion interacts with the shortest naphthalene C=C bond, as reported in related silver(I) complexes

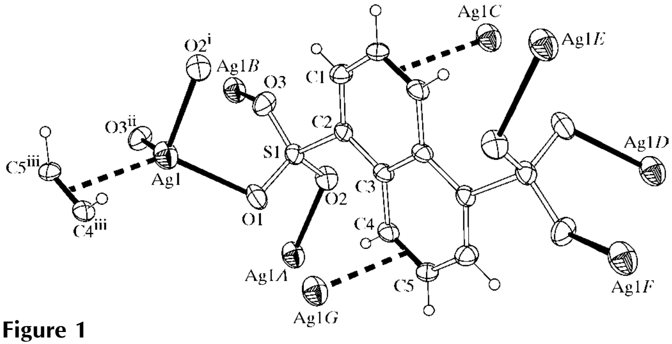


Figure 1
The local coordination around the sulfonate ligand (center) and the Ag^I atom (left) in (I). Ag···C=C interactions are denoted by dashed lines and displacement ellipsoids are shown at the 30% probability level. The atom-numbering scheme of the asymmetric unit is shown, together with the symmetry-equivalent atoms [symmetry codes: (*A*) $x+1$, y, z; (*B*) $1-x$, $-y$, $1-z$; (*C*) x, y, $z-1$; (*D*) $1-x$, $1-y$, $-z$; (*E*) $-x$, $1-y$, $-z$; (*F*) x, $y+1$, $z-1$; (*G*) $1-x$, $1-y$, $1-z$].

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(Munakata *et al.*, 1997, 1998, 1999; Iuliucci *et al.*, 1996; Ciolowski *et al.*, 1996; Pietsch & Rappé, 1996; Hoffmann *et al.*, 1993; Lewandos *et al.*, 1982). However, the naphthalene ring system has a standard pattern of bond lengths, whereby the shortest are always those labelled in the current structure as C1=C2 and C4=C5 (Allen *et al.*, 1997). Thus, coordination by the silver ion does not seem to have changed this pattern significantly. The silver ion may coordinate preferentially to this bond because it is shorter and more electron rich.

The dihedral angle between the plane of the naphthalene ring system and the plane defined by the three O atoms of the SO_3^- group is 83.6 (3)°. As shown in Fig. 2, the six O atoms of two SO_3^- groups are coordinated to the Ag^I ions, and the two SO_3^- groups function as a μ_6-bridge and construct a layer structure parallel to (011), with alternating organic–inorganic components. The inorganic portion consists of eight-membered rings [represented as (Ag—O—S—O)$_2$], which exhibit 'chair-like' profiles. The eight-membered rings propagate parallel to the *a* axis by sharing one edge (Ag—O—S) with neighboring rings, forming Ag1···Ag1*A*, Ag1···Ag1*B*, Ag1*A*···Ag1*B* and Ag1*B*···Ag1*F* distances of 5.208 (3), 4.507 (3), 4.406 (3) and 13.310 (3) Å, respectively [symmetry codes: (*A*) $x + 1, y, z$; (*B*) $1 - x, -y, 1 - z$; (*F*) $x, y + 1, z - 1$]. The naphthalene ring moiety of the 1,5-nds^{2-} group shows a η^4,μ_2-coordination mode, bridging two Ag^I ions, with an Ag1*C*···Ag1*D* separation of 6.883 (3) Å [symmetry codes: (*C*) $x, y, z - 1$; (*D*) $1 - x, 1 - y, -z$], and forming a three-dimensional network. The dihedral angle between the plane of the naphthalene ring system and the Ag1/C4/C5 plane is 77.3 (3)°. In consequence, 1,5-nds^{2-} ions act as η^{10},μ_8-bridges and link the silver ions into a three-dimensional framework through both Ag–sulfonate and Ag–arene interactions (Fig. 3).

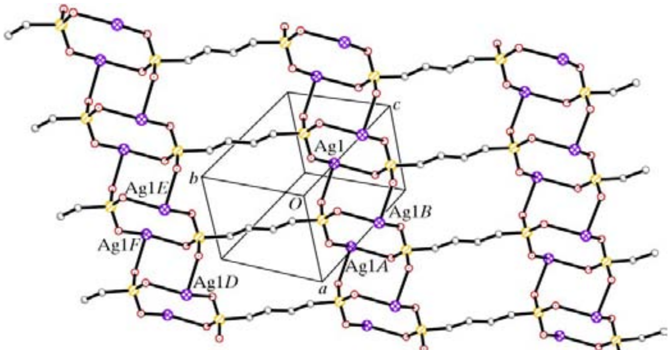

Figure 2
A perspective view of the organic–inorganic layer of (I). The C—Ag interactions and the H atoms have been omitted, and the naphthalene ring systems are represented by the central four C atoms only. (The symmetry codes are as in Fig. 1.)

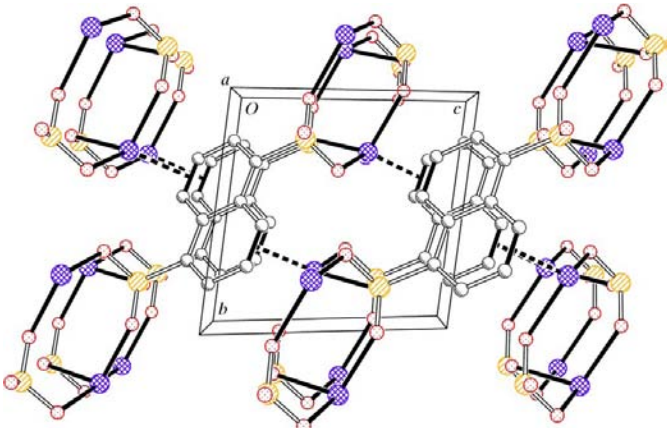

Figure 3
The packing of (I), showing the three-dimensional framework; H atoms have been omitted.

Experimental

The title complex, (I), was synthesized by the addition of $AgNO_3$ (2 mmol) to an ethanol solution of 1,5-naphthalenedisulfonic acid (6 mmol). The mixed solution was protected from light and allowed to evaporate slowly at room temperature; colorless prismatic crystals of (I) were isolated after about six days. Analysis calculated for $C_{10}H_6Ag_2O_6S_2$: C 23.93, H 1.02%; found: C 23.79, H 10.6%.

Crystal data

$[Ag_2(C_{10}H_6O_6S_2)]$
$M_r = 502.01$
Triclinic, $P\overline{1}$
$a = 5.2082$ (10) Å
$b = 7.3705$ (15) Å
$c = 7.8068$ (16) Å
$\alpha = 96.35$ (3)°
$\beta = 106.91$ (3)°
$\gamma = 92.79$ (3)°
$V = 283.93$ (11) Å^3
$Z = 1$
$D_x = 2.936$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 2193 reflections
$\theta = 3.7$–27.4°
$\mu = 3.84$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.37 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.329$, $T_{max} = 0.501$
2425 measured reflections
1264 independent reflections
1243 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.092$
$S = 1.05$
1264 reflections
92 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.7228P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.69$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.032 (4)

Table 1
Selected geometric parameters (Å, °).

Ag1—O1	2.377 (3)	C3—C3^{iv}	1.432 (7)
Ag1—O2^{i}	2.382 (3)	C3—C4	1.438 (5)
Ag1—O3^{ii}	2.396 (3)	C4—C5	1.368 (6)
Ag1—C4^{iii}	2.478 (4)	C5—C1^{iv}	1.415 (5)
Ag1—C5^{iii}	2.645 (4)	S1—O3	1.456 (3)
C1—C2	1.367 (5)	S1—O2	1.459 (3)
C1—C5^{iv}	1.415 (5)	S1—O1	1.467 (3)
C2—C3	1.427 (5)		
O1—Ag1—O2^{i}	99.85 (10)	O3^{ii}—Ag1—C5^{iii}	86.91 (12)
O1—Ag1—O3^{ii}	94.92 (11)	C4^{iii}—Ag1—C5^{iii}	30.75 (13)
O1—Ag1—C4^{iii}	123.14 (12)	O3—S1—O2	113.08 (19)
O1—Ag1—C5^{iii}	147.95 (11)	O3—S1—O1	112.68 (19)
O2^{i}—Ag1—C5^{iii}	108.49 (11)	O2—S1—O1	111.78 (18)
O2^{i}—Ag1—C4^{iii}	112.45 (11)	S1—O1—Ag1	111.48 (18)
O2^{i}—Ag1—O3^{ii}	114.39 (11)	S1—O2—Ag1^{v}	119.46 (17)
O3^{ii}—Ag1—C4^{iii}	110.94 (12)	S1—O3—Ag1^{ii}	123.88 (17)

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, 1 - y, -z$; (v) $1 + x, y, z$.

H atoms were placed in calculated positions [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C)] and refined using the riding-model approximation. Any influence of the Ag atom on the H-atom geometry at the coordinated double bond was neglected.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1673). Services for accessing these data are described at the back of the journal.

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