

(μ -2,11-Dithia[3.3]paracyclophane- $\kappa^2S:S'$)bis[(6-carboxypyridine-2-carboxylato- κ^2N,O^6)silver(I)]: a mixed-ligand silver-based dinuclear compound

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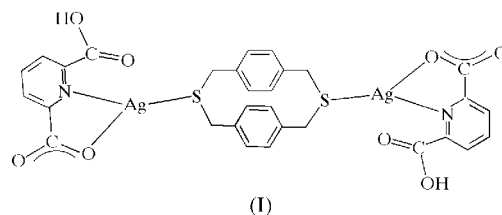
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In the title complex, $[\text{Ag}_2(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{C}_{16}\text{H}_{16}\text{S}_2)]$, each Ag^{I} atom is trigonally coordinated by one S atom of a 2,11-dithia[3.3]paracyclophane (dtpcp) ligand, and by one N and one O atom of a 6-carboxypyridine-2-carboxylate ligand. Dtpcp acts as a bidentate ligand, bridging two inversion-related Ag^{I} atoms to give a dinuclear silver(I) compound. The dinuclear moieties are interconnected *via* $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to form a two-dimensional zigzag sheet. Two such sheets are interwoven *via* π - π interactions between pyridine rings, affording an interwoven bilayer network.

Comment

The design of inorganic-organic hybrid frameworks, in particular the construction of polymeric silver(I) coordination networks, has become an increasingly active research area because of the potential applications of these polymers as functional materials with controllable properties and novel molecular structures (Khlobystov *et al.*, 2001; Hu *et al.*, 2003; Yaghi & Li, 1996; Zhao *et al.*, 2001). Recent developments in supramolecular chemistry have made it possible to select building blocks to assemble structures with specific networks. Many investigations in this field have focused on the construction of metal-organic complexes containing N- or S-atom donor ligands. Very recently, attention has been diverted to complexes based on mixed ligands. We chose here pyridine-2,6-dicarboxylic acid (H_2pdc), with an N-atom donor, and 2,11-dithia[3.3]paracyclophane (dtpcp), with an S-atom donor, as mixed ligands. Although metal complexes of H_2pdc have been studied extensively because of its ability to form stable chelates (Ducommun *et al.*, 1989; Sengupta *et al.*, 1983; Zhou & Kostic, 1988), structural characterizations of its silver(I) complexes are very rare (Wang *et al.*, 2004). On the

other hand, reports on polymeric silver(I) complexes of sulfur-bridged paracyclophane are also very sparse (Munakata *et al.*, 1996; Liu *et al.*, 2004a,b). We report here the crystal structure of the title compound, $[\text{Ag}_2(\text{dtpcp})(\text{Hpdc})_2]$, (I).



Compound (I) is a dinuclear complex having a center of symmetry and consisting of two Ag^{I} ions, one dtpcp molecule and two Hpdc^- anionic ligands (Fig. 1). One of the two carboxylic acid groups in the H_2pdc ligand is deprotonated, and the Hpdc^- anion is chelated to one Ag^{I} center through the pyridine N atom and an O atom of the deprotonated carboxyl group. Each Ag^{I} ion is three-coordinated in an approximately

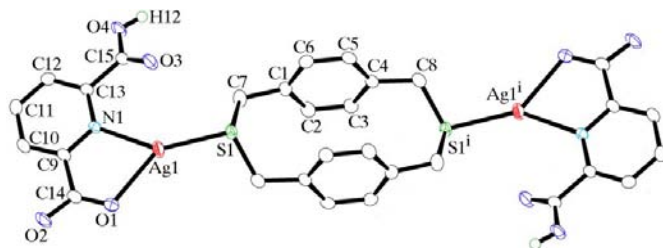


Figure 1
The structure and atom numbering of (I), showing displacement ellipsoids at the 50% probability level. H atoms, except those of the carboxylic acid groups, have been omitted for clarity. [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.]

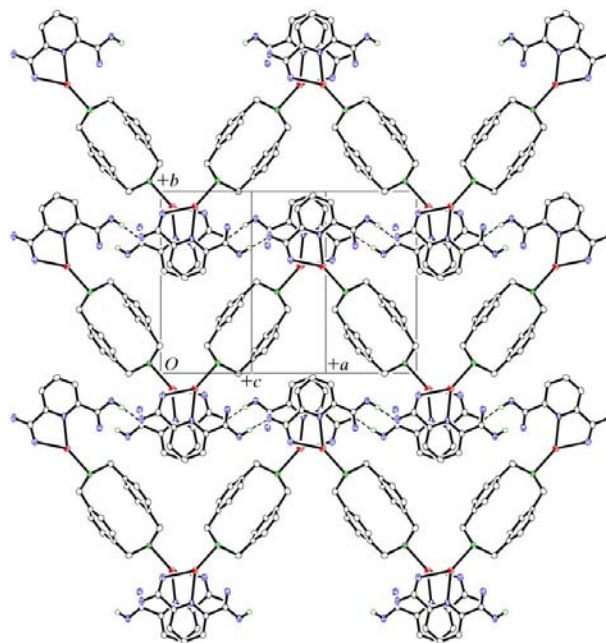


Figure 2
The interwoven bilayer network of (I). H atoms, except those of the carboxylic acid groups, have been omitted. Broken lines indicate $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

trigonal configuration by one of the S atoms of the dtpcp ligand, and N and O atoms of the Hpdc⁻ anion (Table 1). The S1—C7···C8—S1ⁱ—C7ⁱ···C8ⁱ [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$] ring system exhibits a chair conformation, as observed in other dtpcp–silver(I) complexes (Liu *et al.*, 2004a,b). The dtpcp ligand acts as a μ_2 bridge linking two Ag atoms, with an Ag—S bond length of 2.4129 (6) Å, which is shorter than the range of 2.4787 (5)–2.5471 (6) Å observed in other dtpcp–silver(I) complexes (Liu *et al.*, 2004a,b). The Ag—N [2.287 (2) Å] and Ag—O bond lengths [2.353 (1) Å] in (I) are also shorter than those observed in another H₂pdc–silver(I) complex (Wang *et al.*, 2004). The shorter bond lengths around the Ag^I center may be attributable to the fact that the coordination number of the Ag atom in (I) is smaller than in other reported dtpcp- or H₂pdc–silver(I) complexes, in which the Ag^I ions are four-coordinate in a distorted tetrahedral configuration.

Each dinuclear silver(I) complex is interconnected with four adjacent ones through O4—H12···O2($x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$) hydrogen bonds (Table 2), propagating as a zigzag sheet. Two zigzag sheets are interwoven in an offset mode to give a bilayer network (Fig. 2). The chair conformation of the dtpcp ligand leads to a step-like arrangement of the two Ag(Hpdc) moieties (Fig. 1), allowing the formation of the bilayer structure. Within the bilayer, two pyridine rings from different sheets are partially overlapped, with an average interplanar distance of 3.30 Å, indicating strong π – π interactions between them. The bilayers are packed in an offset manner with respect to one another (Fig. 3). No short contacts were found between the bilayers.

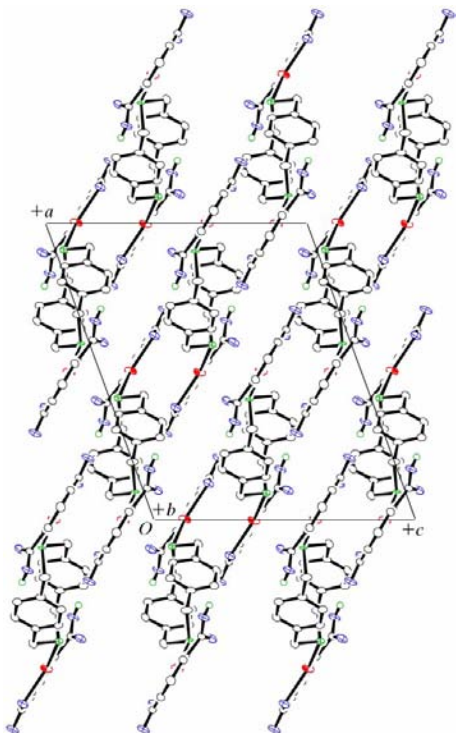


Figure 3

The crystal structure of (I), viewed along the *b* axis. H atoms, except those of the carboxylic acid groups, have been omitted.

Experimental

A mixed solution (4.5 ml) of mesitylene (3 ml) and dimethylformamide (1.5 ml), containing dtpcp (0.03 mmol, 8.2 mg) and H₂pdc (0.06 mmol, 10.0 mg), was introduced into a glass tube and layered with a methanol solution (4.5 ml) containing AgCF₃CO₂ (0.06 mmol, 13.2 mg). The glass tube was sealed under argon and left to stand at room temperature for 3 d, after which time colorless block-shaped crystals of (I) were isolated (yield 68%). Analysis calculated for C₃₀H₂₄Ag₂N₂O₈S₂: C 43.92, H 2.95, N 3.41%; found: C 43.66, H 2.91, N 3.38%.

Crystal data

[Ag₂(C₇H₄NO₄)₂(C₁₆H₁₆S₂)]
M_r = 820.38
 Monoclinic, *C*2/*c*
a = 17.025 (10) Å
b = 12.828 (7) Å
c = 14.096 (8) Å
 β = 110.075 (6)°
V = 2892 (3) Å³
Z = 4
D_x = 1.884 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 4714 reflections
 θ = 3.2–27.5°
 μ = 1.55 mm⁻¹
T = 150.2 K
 Block, colorless
 0.30 × 0.25 × 0.20 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
 ω scans
 Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.665, *T_{max}* = 0.733
 11 072 measured reflections
 3250 independent reflections

3038 reflections with *I* > 2σ(*I*)
R_{int} = 0.022
 θ_{\max} = 27.5°
h = -16 → 22
k = -16 → 16
l = -18 → 18

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.026
wR(*F*²) = 0.060
S = 1.09
 3038 reflections
 235 parameters
 Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 3.8032P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.002$
 $\Delta\rho_{\max} = 0.61 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|------------|-----------|-----------|
| Ag1—S1 | 2.4129 (6) | O2—C14 | 1.257 (2) |
| Ag1—O1 | 2.353 (1) | O3—C15 | 1.218 (3) |
| Ag1—N1 | 2.287 (2) | O4—C15 | 1.301 (2) |
| O1—C14 | 1.245 (3) | | |
| S1—Ag1—O1 | 142.50 (4) | O1—Ag1—N1 | 72.45 (5) |
| S1—Ag1—N1 | 144.31 (4) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O4—H12···O2 ⁱⁱ | 0.84 (3) | 1.66 (3) | 2.497 (2) | 180 (3) |

Symmetry code: (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.

All H atoms were found in difference Fourier maps and were subsequently included in the refinement with a fixed *U*_{iso}(H) value of 0.03 Å². The C—H bond lengths are in the range 0.89 (3)–1.00 (3) Å.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure

Corporation, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1220). Services for accessing these data are described at the back of the journal.

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