

Synthesis and crystal structure of an Ag(I) *p*-toluenesulphonate complex with 4-methylpyridine of composition [Ag(CH₃C₅H₄N)₂(CH₃C₆H₄SO₃)₂]

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The compound [Ag(4-*mepy*)₂(*pts*)] was prepared by direct reaction of silver(I) *p*-toluenesulphonate (Ag(*pts*)) and 4-methylpyridine (4-*mepy*), and was investigated by X-ray diffraction. The crystal structure is monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.4914(2)$, $b = 11.8786(3)$, $c = 17.0443(3)$ Å, $\beta = 90.221(2)$, $V = 1921.64(8)$ Å³. The structure contains distinct [{Ag(4-*mepy*)₂(*pts*)}]₂ units, which are interconnected via hydrogen bonds. The closest coordination environment of the metal atom is built up from two nitrogen atoms of pyridine rings and oxygen atoms of *p*-toluenesulphonate anions.

Silver(I) / Coordination compound / 4-Methylpyridine / *p*-Toluenesulphonate / Crystal structure

1. Introduction

Silver(I) compounds are useful reagents for catalytic systems in science and technology [1,2] and have been extensively investigated over recent years, due to their exclusive properties (optical, magnetic, etc. [3-5]). Sulfonates ($R-SO_3^-$) are widely used as weakly coordinated ligands in organometallic chemistry, and have typically been employed as counter anions to complicated coordination cations [6]. On the other hand, sulfonate surfactants are commonly used in daily life and can react with natural and synthetic silver compounds.

In order to study the coordination behavior of silver(I) *p*-toluenesulphonate towards 4-methylpyridine, we prepared [Ag(4-*mepy*)₂(*pts*)] (**I**) and determined its crystal structure.

2. Experimental section

2.1 Preparation of [Ag(4-*mepy*)₂(*pts*)] (**I**)

Colorless elongated prismatic crystals of the complex **I** were prepared by slow evaporation of a solution of silver(I) *p*-toluenesulphonate in 4-methylpyridine.

2.2 X-ray crystal structure determination

The crystallographic parameters and summaries of the data collection for **I** are presented in Table 1. Single

crystals of **I** were preliminarily studied by photographic methods and the diffraction data were collected on a KUMA-KM4/CCD diffractometer (graphite-monochromated Mo K_α radiation). The CrysAlisRED program was used for processing the data [7]. An absorption correction was applied by the analytical method [8]. The structure was solved by using SHELXL programs and refined by the least-squares method on F^2 by SHELXL with graphical user interfaces of OLEX² [9,10]. Full-matrix least-squares refinements based on F^2 were carried out for the positional and thermal parameters of all non-hydrogen atoms. The hydrogen atoms were revealed from difference Fourier syntheses and refined in the riding model along with the non-hydrogen atoms (fixed C–H distances and $U_{iso}(H)$ equal to $1.2U_{eq}(C)$). The structure was checked for additional symmetry using PLATON [11]. Atomic positional and displacement parameters for **I** are given in Table 2.

3. Results and discussion

The complex **I** crystallizes in the centrosymmetric space group $P2_1/n$, with one silver(I) atom in the asymmetric unit. The metal center coordinates two nitrogen atoms of two pyridine rings (Ag–N(11) 2.161(3) and Ag–N(21) 2.172(3) Å), so that the CH₃C₅H₄N rings are distorted from

Table 1 Crystallographic data and experimental details for **I**.

Empirical formula	C ₁₉ H ₂₁ AgN ₂ O ₃ S
Formula weight	465.31
Temperature, K	150
Wavelength, Å	0.71073 (Mo K _α)
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Diffractometer	KM-4, CCD
Unit cell dimensions:	
<i>a</i> , Å	9.4914(2)
<i>b</i> , Å	11.8786(3)
<i>c</i> , Å	17.0443(3)
<i>α</i> , °	90
<i>β</i> , °	90.221(2)
<i>γ</i> , °	90
Volume, Å ³	1921.64(8)
<i>Z</i>	4
Calculated density, g·cm ⁻³	1.608
Absorption coefficient, mm ⁻¹	1.18
<i>F</i> (000)	944
Crystal size, mm	0.10 × 0.12 × 0.25
Color, shape	Colorless, prism
Theta range for data collection, °	2.9–36.5
Limiting indices	–12 ≤ <i>h</i> ≤ 15, –15 ≤ <i>k</i> ≤ 19, –25 ≤ <i>l</i> ≤ 28
Refinement method	Full-matrix least-squares on <i>F</i> ²
Measured reflections	13714
Independent reflections	4820
Observed reflections	3902
[<i>I</i> > 2σ(<i>I</i>)]	
Free parameters	238
Weighting scheme	[σ ² (<i>F</i> _o ²) + (0.061 <i>P</i>) ² + 0.293 <i>P</i>] ⁻¹
Goodness-of-fit on <i>F</i> ²	1.02
Final <i>R</i> indices	<i>R</i> = 0.045,
[<i>I</i> > 2σ(<i>I</i>)]	w <i>R</i> = 0.117
Residual electron density, e Å ⁻³	1.72 and -0.79

linear coordination geometry with N–Ag–N bond angles of 165.2(1)° (Table 3). The oxygen atom of the *p*-toluenesulphonate anion (Ag...O(31) 2.712(3) Å) completes the Ag(I) surrounding to T-shaped, while the second O atom of the same anion is situated at a slightly longer distance from the Ag atom (2.867(3) Å). Taking into account one more weaker Ag...O interaction (2.903(3) Å) of the metal with an O atom of a symmetrically related anion, two {Ag(4-*mepy*)₂(*pts*)} fragments are connected into a unique centrosymmetric [{Ag(4-*mepy*)₂(*pts*)}]₂ unit (Fig. 1). Thus, the Ag(I) atoms may be considered to be five-coordinated. Within the [{Ag(4-*mepy*)₂(*pts*)}]₂ dimer, a

metallophilic Ag...Ag interaction (Ag(1)...Ag(1)′ 3.065(5) Å [12]) is observed. The Ag...Ag distance is considerably shorter than the sum of the Van der Waals radii of silver (1.72 Å) [13,14], but is slightly longer than the Ag–Ag distances in metallic silver (2.866 Å) and the bonds found in silver(I) carboxylates [15].

Similar topological units have been described in the structure of silver(I) *p*-toluenesulphonate with 2-aminopyridine [Ag(2-*apy*)₂(*pts*)]₂ (II) [16]. The centrosymmetric dimeric unit in II consists of two silver coordination polyhedra, interconnected thanks to the bridging function of sulphonate oxygen atoms (Ag–O bond distances in the range 2.559–2.596(2) Å).

Table 2 Fractional atomic coordinates and (equivalent) isotropic displacement parameters (\AA^2) for **I**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}^a$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}^a$
Ag(1)	0.36695(3)	0.44124(2)	0.46597(2)	0.0259(1)	C(32)	0.1967(3)	0.7666(3)	0.6630(2)	0.0248(7)
S(31)	0.21223(8)	0.54270(6)	0.62589(5)	0.0216(2)	H(32)	0.2759	0.7522	0.6957	0.030
O(32)	0.3622(3)	0.5595(2)	0.6126(2)	0.0315(6)	C(13)	0.1108(3)	0.6786(3)	0.3299(2)	0.0271(7)
O(31)	0.1469(2)	0.4761(2)	0.5641(1)	0.0261(5)	H(13)	0.0137	0.6979	0.3307	0.033
O(33)	0.1812(3)	0.5015(2)	0.7039(1)	0.0388(6)	C(25)	0.3840(4)	0.1467(3)	0.6235(2)	0.0272(7)
N(21)	0.4214(3)	0.2839(2)	0.5235(2)	0.0234(6)	H(25)	0.3273	0.1205	0.6655	0.033
N(11)	0.2996(3)	0.5693(2)	0.3839(2)	0.0214(6)	C(34)	0.0244(4)	0.8970(3)	0.6109(2)	0.0279(7)
C(16)	0.3853(3)	0.6153(3)	0.3298(2)	0.0243(7)	C(12)	0.1636(4)	0.6021(3)	0.3835(2)	0.0267(7)
H(16)	0.4812	0.5924	0.3286	0.029	H(12)	0.1017	0.5713	0.4216	0.032
C(31)	0.1355(3)	0.6789(3)	0.6197(2)	0.0216(6)	C(33)	0.1413(3)	0.8744(3)	0.6580(2)	0.0279(7)
C(22)	0.5394(4)	0.2282(3)	0.5032(2)	0.0266(7)	H(33)	0.1837	0.9337	0.6872	0.033
H(22)	0.5944	0.2565	0.4612	0.032	C(24)	0.5066(4)	0.0884(3)	0.6034(2)	0.0293(7)
C(15)	0.3397(4)	0.6940(3)	0.2764(2)	0.0249(7)	C(17)	0.1474(5)	0.8092(3)	0.2141(2)	0.042(1)
H(15)	0.4046	0.7257	0.2403	0.030	H(17A)	0.2004	0.8798	0.2185	0.063
C(23)	0.5836(4)	0.1319(3)	0.5410(2)	0.0300(7)	H(17B)	0.0471	0.8241	0.2225	0.063
H(23)	0.6671	0.0949	0.5244	0.036	H(17C)	0.1608	0.7771	0.1617	0.063
C(14)	0.1994(4)	0.7276(3)	0.2747(2)	0.0253(7)	C(37)	-0.0365(5)	1.0144(3)	0.6082(2)	0.0410(9)
C(26)	0.3454(3)	0.2416(3)	0.5827(2)	0.0260(7)	H(37A)	-0.0920	1.0236	0.5600	0.062
H(26)	0.2609	0.2790	0.5972	0.031	H(37B)	0.0402	1.0696	0.6090	0.062
C(35)	-0.0353(4)	0.8091(3)	0.5692(2)	0.0280(7)	H(37C)	-0.0972	1.0261	0.6538	0.062
H(35)	-0.1158	0.8233	0.5375	0.034	C(27)	0.5537(4)	-0.0145(3)	0.6485(2)	0.0411(9)
C(36)	0.0194(3)	0.7002(3)	0.5725(2)	0.0231(6)	H(27A)	0.6240	-0.0557	0.6178	0.062
H(36)	-0.0226	0.6413	0.5428	0.028	H(27B)	0.4724	-0.0633	0.6582	0.062
					H(27C)	0.5953	0.0088	0.6986	0.062

^a For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j), \text{ for hydrogen atoms } U_{\text{iso}} \text{ was set equal to } 1.2U_{\text{eq}}(\text{C}).$$

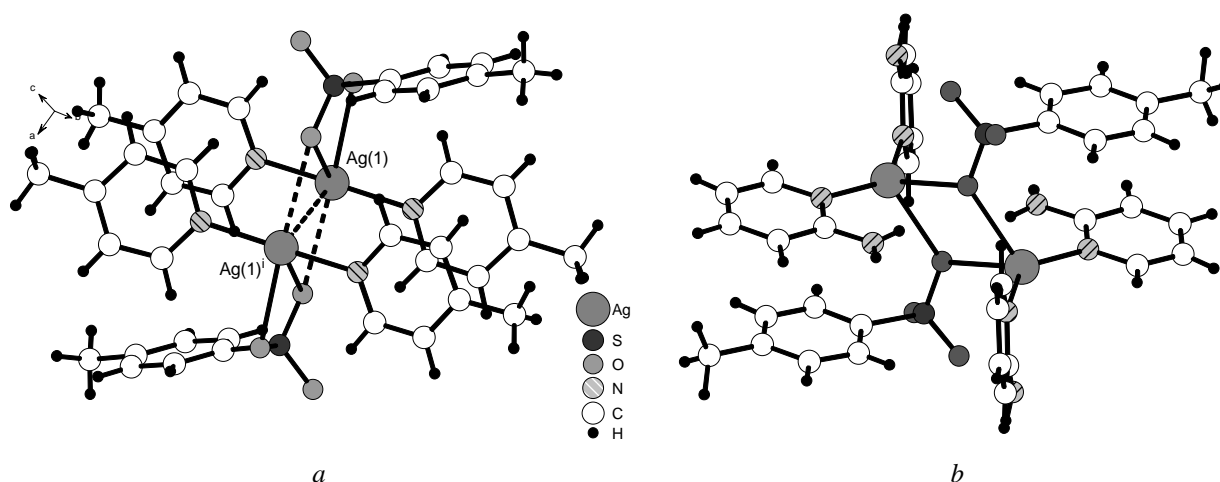


Fig. 1 Projection of dimeric topological units in the crystal structures of $[\text{Ag}(4\text{-mepy})_2(\text{pts})]$ (**I**) (a) and $[\text{Ag}(2\text{-apy})_2(\text{pts})]_2$ (**II**) (b). Symmetry codes: (i) $1-x, 1-y, 1-z$.

The narrower range of oxygen-metal distances in the structure of **II** confirms the linkage function of only one oxygen atom of the $-\text{SO}_3^-$ group. In contrast to **II**, in the complex **I** the *p*-toluenesulphonate anion plays a nearly bidentate bridging function (connects the Ag atoms by two oxygens) and has considerable influence on the location of the pyridine ring with respect to the central metal atom. Thus, the nearly linear *Pyr*-Ag-*Pyr* arrangement observed in **I** does not occur in **II**, where two coordinated pyridine rings are rotated with respect to one another by an angle of near 80° and the nitrogen atoms remain practically equidistant to the metal (Ag–N 2.203(3)–2.210(2) Å).

The structure of **I** is also stabilized by weak hydrogen bonds C–H...O [17] (H...O 2.39–2.56 Å, Table 4, Fig. 2). The most significant bonds connect the *p*-toluenesulphonate core of one organometallic dimer and oxygen atoms of the SO_3^- group of another building block. Weaker bonds link pyridine rings with $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ units in the same building block.

To analyze the interactions between the particles, the Hirshfeld surface was built for the $[\{\text{Ag}(4\text{-mepy})_2(\text{pts})\}]_2$ dimeric moiety in **I**, using CrystalExplorer software [18,19]. The most prominent interactions between O atoms and H atoms can be seen on the Hirshfeld surface plot as strong and medium red areas (Fig. 3). To show the intermolecular surface bond distances, fingerprint plots highlighting the regions for O...H, C...H, and H...H interactions, were produced. The contribution to the surface area by N...H contacts is 3.6%.

4. Supplementary material

CCDC number 1483368 contains supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on applications to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK Fax: int. code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Table 3 Selected bond lengths and angles in the structure of **I**.

Bond	<i>d</i> , Å	Angle	ω , °	Bond	<i>d</i> , Å	Angle	ω , °
Ag(1)–Ag(1) ⁱ	3.107(1)	N(21)–Ag(1)–Ag(1) ⁱ	91.53(7)	C(31)–C(32)	1.402(4)	C(36)–C(31)–S(31)	121.7(2)
Ag(1)–N(21)	2.172(3)	N(11)–Ag(1)–Ag(1) ⁱ	99.40(7)	C(22)–C(23)	1.378(5)	C(32)–C(31)–S(31)	118.5(2)
Ag(1)–N(11)	2.161(3)	N(11)–Ag(1)–N(21)	165.2(1)	C(15)–C(14)	1.391(5)	C(15)–C(14)–C(17)	120.8(3)
Ag(1)–O(31)	2.712(2)	O(32)–S(31)–C(31)	105.4(1)	C(23)–C(24)	1.391(5)	C(13)–C(14)–C(15)	116.6(3)
Ag(1)–O(32)	2.867(3)	O(31)–S(31)–O(32)	112.1(2)	C(14)–C(13)	1.391(4)	C(13)–C(14)–C(17)	122.6(3)
Ag(1)–O(32) ⁱ	2.903(3)	O(31)–S(31)–C(31)	106.2(1)	C(14)–C(17)	1.499(5)	N21)–C(26)–C(25)	123.0(3)
S(31)–O(32)	1.456(3)	O(33)–S(31)–O(32)	113.1(2)	C(26)–C(25)	1.374(5)	C(34)–C(35)–C(36)	121.9(3)
S(31)–O(31)	1.455(2)	O(33)–S(31)–O(31)	113.2(2)	C(35)–C(36)	1.395(4)	C(31)–C(36)–C(35)	119.2(3)
S(31)–O(33)	1.449(2)	O(33)–S(31)–C(31)	106.1(2)	C(35)–C(34)	1.382(5)	C(33)–C(32)–C(31)	119.9(3)
S(31)–C(31)	1.777(3)	C(22)–N(21)–Ag(1)	120.2(2)	C(32)–C(33)	1.387(5)	C(12)–C(13)–C(14)	120.3(3)
N21)–C(22)	1.347(4)	C(26)–N(21)–Ag(1)	122.3(2)	C(13)–C(12)	1.382(5)	C(26)–C(25)–C(24)	120.2(3)
N21)–C(26)	1.341(4)	C(26)–N(21)–C(22)	117.3(3)	C(25)–C(24)	1.397(5)	C(35)–C(34)–C(33)	118.3(3)
N11)–C(16)	1.348(4)	C(16)–N(11)–Ag(1)	123.4(2)	C(34)–C(33)	1.394(5)	C(35)–C(34)–C(37)	121.7(3)
N11)–C(12)	1.348(4)	C(12)–N(11)–Ag(1)	119.2(2)	C(34)–C(37)	1.510(5)	C(33)–C(34)–C(37)	119.9(3)
C(16)–C(15)	1.374(5)	C(12)–N(11)–C(16)	117.4(3)	C(24)–C(27)	1.511(5)	N11)–C(12)–C(13)	122.6(3)
C(31)–C(36)	1.385(4)	N(11)–C(16)–C(15)	122.7(3)				

^a symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z+1$; (iii) $x-1, y, z$; (iv) $x-1, y, z-1$

Table 4 Geometry of selected H-contacts in the structure of **I**.

Contact D–H...A	Bond length, Å			Angle D–H...A, °	Atom coordinates of A
	D–H	H...A	D...A		
C(12)–H(12)...O(31) ⁱ	0.95	2.44	3.220(4)	139	$-x, -y+1, -z+1$
C(16)–H(16)...O(32) ⁱⁱ	0.95	2.54	3.317(4)	139	$-x+1, -y+1, -z+1$
C(22)–H(22)...O(32) ⁱⁱ	0.95	2.56	3.338(4)	140	$-x+1, -y+1, -z+1$
C(33)–H(33)...O(33) ⁱⁱⁱ	0.95	2.39	3.258(4)	152	$-x+1/2, y+1/2, -z+3/2$

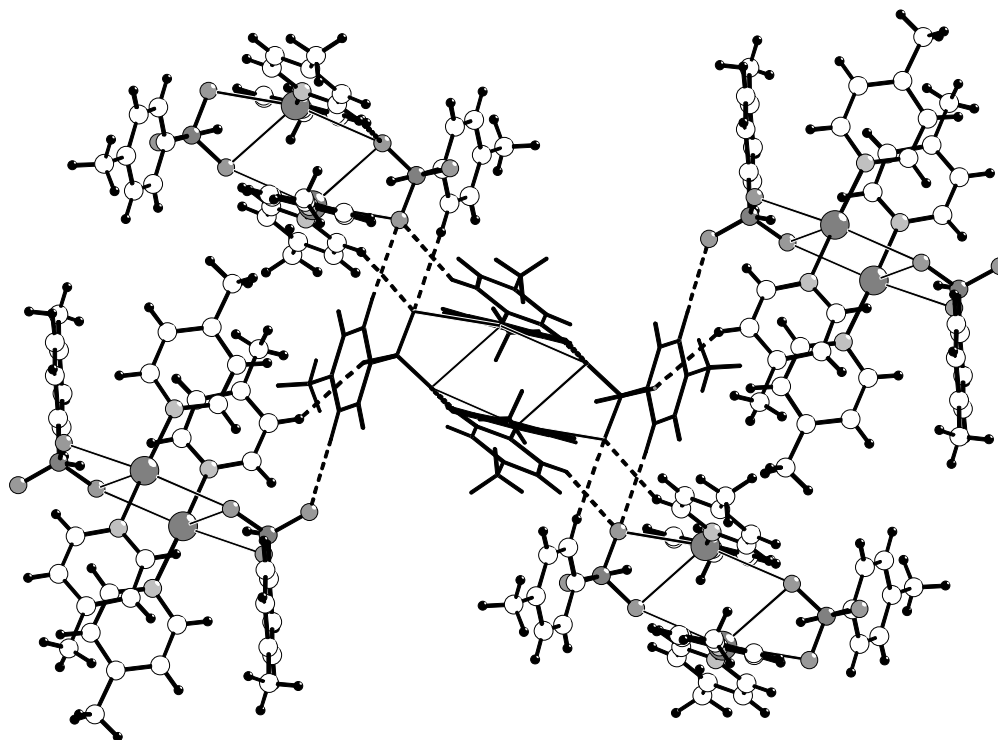


Fig. 2 Network of hydrogen bonds in the crystal structure of $[\text{Ag}(4\text{-mepy})_2(\text{pts})]$ (**I**).

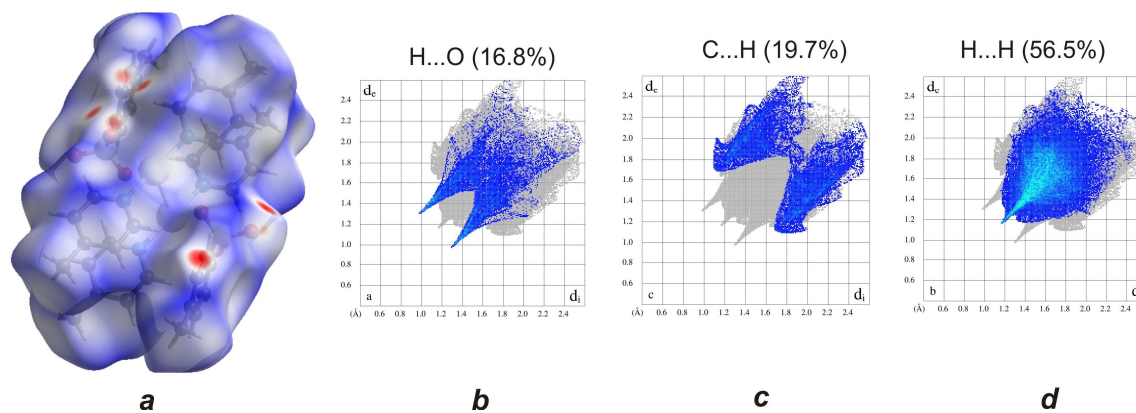


Fig. 3 Hirshfeld surface analysis of a $[\{\text{Ag}(4\text{-mepy})_2(\text{pts})\}]_2$ dimeric moiety in **I**. (a) Hirshfeld surface mapped with d_{norm} , which highlights both the donor and acceptor abilities. (b) Fingerprint plot for the $[\{\text{Ag}(4\text{-mepy})_2(\text{pts})\}]_2$ dimer resolved into O...H. (c) Fingerprint plot for the $[\{\text{Ag}(4\text{-mepy})_2(\text{pts})\}]_2$ dimer resolved into C...H contacts. (d) Fingerprint plot for the $[\{\text{Ag}(4\text{-mepy})_2(\text{pts})\}]_2$ dimer resolved into H...H contacts. The full fingerprint appears in gray beneath each decomposed plot.

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