

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF POLYMERIC SILVER(I) BUTYL XANTHATE

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Polymeric silver(I) butyl xanthate, $[\text{Ag}(\text{Bu-XA})]_n$, was synthesized and crystallographically characterized. The polymer shows chair conformation of eight-membered ring units and a novel mode of coordination, with a structural arrangement different from that in silver dialkyldithiocarbamate and dialkyldithiophosphates. The polymeric structure of the new complex is formed by corrugated planes.

Keywords: Silver(I) complexes; Butyl xanthate; Xanthates; Two-dimensional polymers; Crystal structure; X-Ray Diffraction.

Silver(I) compounds with dithio ligands, such as the dialkyldithiocarbamates (DTC)^{1,2} and dithiophosphates (DDP)³⁻⁵, are well known. Xanthate complexes of silver(I) have been much less extensively studied and only some spectroscopic results on $[\text{Ag}(\text{ROCS}_2)(\text{Ph}_3\text{P})_2]$ (R = Me, Et, Pr, iPr) have appeared⁶⁻⁸. In this paper we present the synthesis and crystal structure of the silver(I) complex with the butyl xanthate, $[\text{Ag}(\text{Bu-XA})]_n$, which is polymeric involving bridging to adjacent metal through sulfur. It appears to be the first structural report on a novel coordination mode.

EXPERIMENTAL

Instrumentation

The IR spectra (wavenumbers in cm^{-1}) were recorded with a Perkin-Elmer 17300 FTIR spectrometer. Carbon, nitrogen and hydrogen were determined by using a VARIO EL elemental analyzer. Silver was determined by using an American SP-I ICP analyzer.

Synthesis

Sodium butyl xanthate was synthesized by the reaction of butan-1-ol (10 ml), sodium hydroxide (0.40 g) and carbon disulfide (1.4 ml). Addition of a solution of AgNO_3 (0.85 g) gave a precipitate that was separated by filtration. The filtrate was allowed to slowly evaporate, which resulted in the formation of rhombic yellow-green flake crystals, suitable for the X-ray crystallographic study. IR spectrum (KBr pellet): 3447 bw, 2960 m, 1469 m, 1224 m, 1191 s, 1128 m, 1035 s, 1024 s, 940 m, 741 w, 656 w, 564 vw, 499 w. The bands in the $1200\text{--}1000\text{ cm}^{-1}$ region are due to the C–O stretching vibrations, and the bands in the $740\text{--}560\text{ cm}^{-1}$ region to C–S stretching vibrations⁹. For $\text{C}_5\text{H}_9\text{AgOS}_2\cdot\text{H}_2\text{O}$ (275.1) calculated: 21.83% C, 4.03% H, 39.21% Ag; found: 22.06% C, 3.98% H, 39.44% Ag.

X-Ray Crystallography

A yellow-green single crystal of $[\text{Ag}(\text{Bu-XA})]_n$ with the dimensions $0.38 \times 0.38 \times 0.37$ mm was mounted on a glass fiber. Data collection was performed on an CCD area detector with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.071073$ nm) at 296 K, using the $\omega/2\theta$ scan technique. The reflections were corrected for absorption by the Gaussian integration method, for Lorentz polarization and for secondary extinction effects. The structure was solved by the Patterson method and subsequent difference Fourier techniques and refined by the full-matrix least-squares method with anisotropic thermal factors for all non-hydrogen atoms; a number of the hydrogen atoms was placed in calculated position. All calculations were performed using the SHELXTL97 system¹⁰ of computer programs. Crystal data: $\text{C}_5\text{H}_9\text{AgOS}_2$ ($M_r = 257.11$), monoclinic system, space group $P2(1)/c$, $Z = 4$, $a = 1.55442(12)$ nm, $b = 0.62057(5)$ nm, $c = 0.84937(7)$ nm, $\beta = 96.358(1)^\circ$, $V = 0.81429(11)$ nm³, $D_c = 2.097$ g cm⁻³, $F(000) = 504$. The final values $R_1 = 0.0360$, $wR_2 = 0.0872$ were obtained. CCDC 170252 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The structure of $[\text{Ag}(\text{Bu-XA})]_n$ is a folded two-dimensional polymer with eight-membered ring units $\{\text{CS}_2\text{Ag}\}_2$ connected with sulfur bridging bonds (Figs 1, 2). Selected bond lengths and bond angles are given in Table I. The eight-membered ring is of chair conformation; the terminal butyl groups take *trans*-configuration. In the eight-membered ring, two butyl xanthate ligands bridge two silver atoms. Each of the silver atoms is trigonally coordinated to three sulfur atoms of three different xanthate ligands (Fig. 1). The three sulfur atoms and the silver atom are almost coplanar: the bond angles $\text{S}(1)\text{--Ag--S}(2)$, $\text{S}(1)\#1\text{--Ag--S}(2)$ and $\text{S}(1)\text{--Ag--S}(1)\#1$ are $133.30(4)$, $119.47(4)$ and $106.30(2)^\circ$, respectively. Xanthate ligands are always bidentate when forming chelates with divalent or trivalent metals¹¹. In $[\text{Ag}(\text{Bu-XA})]_n$, one sulfur atom [S(2)] of the ligand is monodentate and the

TABLE I
Selected bond lengths (in nm) and bond angles (in °)

Ag(1)–S(2)	0.24923(11)	S(1)–Ag(1)–S(1)#1	106.31(2)
Ag(1)–S(1)	0.25005(12)	S(2)–Ag(1)–Ag(1)#2	81.49(3)
Ag(1)–S(1)#1	0.25755(12)	S(1)–Ag(1)–Ag(1)#2	105.93(3)
Ag(1)–Ag(1)#1	0.31297(9)	S(1)#1–Ag(1)–Ag(1)#2	71.79(3)
S(1)–C(1)	0.1704(4)	C(1)–S(1)–Ag(1)	110.37(14)
S(1)–Ag(1)#3	0.2575(2)	C(1)–S(1)–Ag(1)#3	103.72(15)
S(2)–C(1)#4	0.1683(4)	Ag(1)–S(1)–Ag(1)#3	116.94(5)
O(1)–C(1)	0.1337(5)	C(1)#4–S(2)–Ag(1)	102.22(15)
O(1)–C(2)	0.1453(6)	C(1)–O(1)–C(2)	119.1(3)
C(1)–S(2)#5	0.1683(4)	O(1)–C(1)–S(2)#5	121.3(3)
C(2)–C(3)	0.1504(6)	O(1)–C(1)–S(1)	114.2(3)
C(3)–C(4)	0.1508(7)	S(2)#5–C(1)–S(1)	124.4(2)
C(4)–C(5)	0.1507(8)	O(1)–C(2)–C(3)	108.0(4)
		C(2)–C(3)–C(4)	111.4(4)
S(2)–Ag(1)–S(1)	133.30(4)	C(5)–C(4)–C(3)	113.5(5)
S(2)–Ag(1)–S(1)#1	119.47(4)		

Symmetry codes: #1: $-x + 1, y - 1/2, -z + 3/2$; #2: $-x + 1, -y - 1, -z + 1$; #3: $-x + 1, y + 1/2, -z + 3/2$; #4: $x, -y - 1/2, z - 1/2$; #5: $x, -y - 1/2, z + 1/2$.

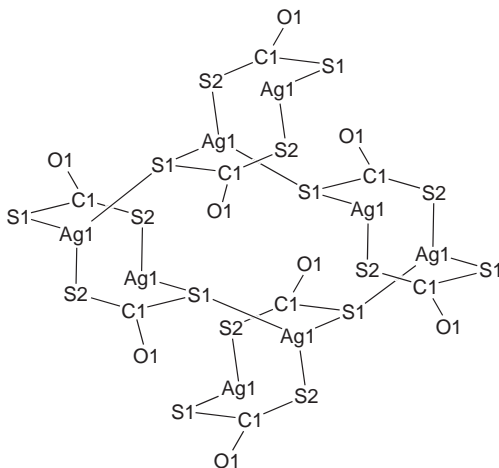


FIG. 1
The atom-numbering scheme for $[Ag(Bu-XA)]_n$. The butyl groups are omitted for clarity

other [S(1)] is bidentate. The Ag(1)–S(1) bond length, 0.25005(12) nm, is a little longer than Ag(1)–S(2), 0.24923(11) nm, due to bridging position of S(1). The sulfur atom [S(1)] is coordinated to another silver atom [Ag#] of the adjacent eight-membered ring. The Ag–S distances are in good agreement with those found in [AgS₂P(OC₃H₇)₂]₆, 0.2485(2)–0.2572(2) nm, and in [Ag[S₂C(OC₂H₅)₂]₆, 0.2471(3)–0.2554(3) nm. The C(1)–S(2) bond length, 0.1683(4) nm, is shorter than C(1)–S(1), 0.1704(4) nm. This shows that the singly bound sulfur atom has a dual, coordinating and bridging, role. The O(1)–C(1) bond length, 0.1337(5) nm, is shorter than O(1)–C(2), 0.1453(6) nm, which indicates a considerable double-bond character. A similar situation applies for [Ni(Et-XA)₂]⁹, although they are not isomorphous. We conclude that butyl xanthate adopts in [Ag(Bu-XA)]_n a novel coordination mode (Chart 1).

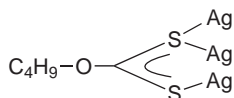


CHART 1

The Ag(1)–Ag(1)#2 distances, 0.31297 nm are longer than in silver metal, 0.2886 nm¹², and shorter than the van der Waals diameter of silver, 0.340 nm¹³. Hence, there is no metal–metal bond in the polymer. The adja-

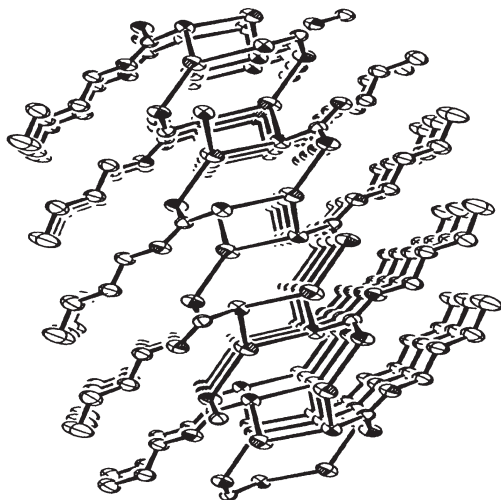


FIG. 2

A part of one of the extended polymer sheets present in the crystals of [Ag(Bu-XA)]_n

cent polymeric sheets are parallel, giving a layered arrangement (Fig. 3). The outer surfaces of each sheet are dominated by hydrophobic butyl groups and, thus, there are no intersheet interactions other than normal van der Waals forces. This absence of strong intermolecular interaction clearly contributes to the low melting point of the solid. Owing to its polymeric nature, $[\text{Ag}(\text{Bu-XA})]_n$ is not readily soluble in organic solvents.

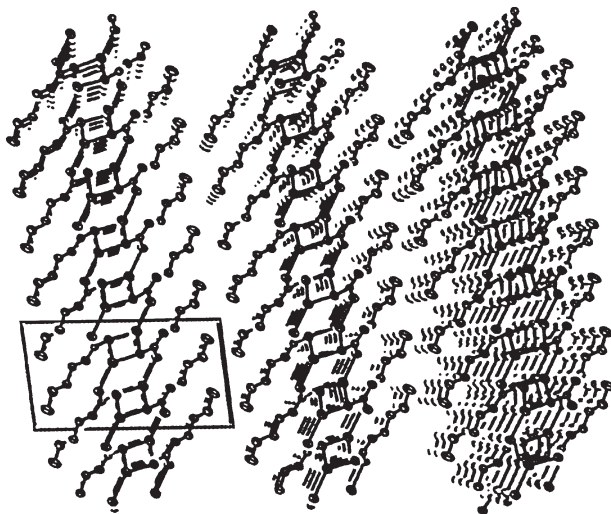


FIG. 3
View of the polymeric structure of $[\text{Ag}(\text{Bu-XA})]_n$

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