The Crystal Structure of Bis(tetrahydrothiophene)silver(I) Tetrafluoroborate

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The crystal structure of $[Ag(C_4H_8S)_2]BF_4$ has been determined from X-ray intensity data collected at 200 K with a four-circle diffractometer. The space group is $P2_12_12_1$ with $Z=4$; $a=7.497(2)$, $b=11.432(3)$ and $c=15.249(3)$ Å. The refinement converged to $R=0.031$. The coordination geometry around silver is close to trigonal planar, with Ag−S distances in the range 2.44−2.56 Å and S−Ag−S angles in the range 116−125°. Three-coordination is achieved through bridging by one of the two crystallographically independent sulphur atoms, and infinite chains $\cdots$S−Ag−S−Ag$\cdots$ are formed along a. These chains are van der Waals packed with the BF_4^- ions situated in voids in the vicinity of the Ag(I). The two closest distances, B$\cdots$Ag in adjacent chains, are 3.73 and 6.69 Å, respectively, indicating that the BF_4^- ions have little bridging effects between the chains.

From a comparison with other compounds, in which S is the only donor atom, it is concluded that Ag(I) is quite variable in its coordination geometry with S. The coordination geometries observed are bent, trigonal planar and tetrahedral for coordination numbers 2, 3 and 4, respectively.

This is the first paper in a series dealing with the coordination geometry in silver(I)−tetrahydrothiophene systems. The nature of the anion is systematically changed from one with very poor donor properties, e.g. BF_4^-, to those with good donor properties, e.g. I^-.

In such a series there is an increasing competition between the tetrahydrothiophene molecule (THT) and the anions for the coordination sites around Ag(I). The aim is to elucidate the correlation between the concepts hard−soft as derived from thermodynamic parameters of complex formation in solution[1,2] and the observed coordination geometries (coordination figures and bond distances). The crystal structure of $[Ag(THT)_2]BF_4$ is reported below.

EXPERIMENTAL

The title compound was prepared by dissolving Ag_2O in an aqueous solution of HBF_4. $Ag^+BF_4^-$ was then extracted into THT. After centrifugation the water phase was discarded, the THT-phase was diluted with CH_2Cl_2, dried over molecular sieves and filtered through a G4 glass filter. The methylene chloride was then evaporated under reduced pressure (20 mmHg) at room temperature. Finally, crystals of $[Ag(THT)_2]BF_4$ were obtained by evaporating the excess tetrahydrothiophene at a reduced pressure of 0.08 mmHg. Recrystallization from ethyl acetate gave single crystals. The silver content was determined by potentiometric titrations with a sodium chloride solution. Before a titration the tetrahydrothiophene was destroyed by heating the compound with concentrated HNO_3 and H_2O_2. The titration results were evaluated according to Gran,[3] giving 29.1±0.1 % Ag in close agreement with the theoretical value of 29.07 %.

The final intensity data set was collected at 200 K on a CAD 4 diffractometer equipped with a nitrogen gas blower device. A data set collected at room temperature gave very poor resolution of the C-atoms, which is most probably due to conformational reorientations of the ring, similar to that observed in 1-pyrrolidinyldithiocarbamate compounds.[4] Laue symmetry and systematic extinctions are consistent with the space group $P2_12_12_1$. Cell dimensions were obtained from

Table 1. Crystal data, collection and reduction of intensity data and least-squares refinement.

Crystal size/mm	$0.42 \times 0.42 \times 0.45$
a/Å	7.497(2)
b/Å	11.432(3)
c/Å	15.249(3)
V/Å^3	1307
D_m/g cm^{-3}	1.77
Z	4
$\bar{\lambda}$/Å	0.7093
μ/cm^{-1}	18.47
Range of transmission factor	0.522−0.606
θ interval/°	3.0−27.0
$\omega-2\theta$ scan width, $\Delta\omega$/°	$0.8+0.5 \tan \theta$
σ_c $(I)/I$ requested in a scan	0.030
Maximum recording time/s	120
Number of measured reflexions	3412
Number of reflexions with $I \geqslant 1.5\sigma_c(I)$, m	1368
Number of parameters refined, n	148
$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_p|$	0.0311
$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$	0.0309
$S = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{\frac{1}{2}}$	1.1

Table 2. Positional and isotropic thermal parameters with estimated standard deviations.
$B_{eq} = \frac{4}{3} \Sigma\Sigma \beta_{ij} a_i \cdot a_j$

Atom	x	y	z	B_{eq}/Å^2
Ag	0.3948(1)	0.2709(1)	0.0821(1)	4.29(1)
S1	0.4883(4)	0.3311(2)	0.2289(1)	6.42(7)
C11	0.6375(11)	0.2223(11)	0.2742(5)	8.79(35)
C12	0.5278(20)	0.1577(10)	0.3413(7)	11.22(51)
C13	0.4041(20)	0.2351(12)	0.3750(6)	10.95(44)
C14	0.3167(14)	0.2960(13)	0.3053(5)	11.31(50)
S2	0.0897(2)	0.3363(1)	0.0259(1)	3.80(4)
C21	0.1083(14)	0.4918(6)	−0.0019(5)	5.65(23)
C22	−0.0004(13)	0.5566(8)	0.0656(7)	7.56(32)
C23	−0.0024(14)	0.4884(9)	0.1460(6)	6.95(30)
C24	−0.0437(10)	0.3626(8)	0.1221(5)	5.65(23)
B	0.0798(13)	0.0193(7)	0.0963(5)	4.62(22)
F1	−0.0643(9)	0.0763(6)	0.1347(4)	8.62(21)
F2	0.2361(7)	0.0602(5)	0.1333(3)	7.18(16)
F3	0.0771(9)	0.0465(4)	0.0080(3)	6.06(14)
F4	0.0654(9)	−0.0971(4)	0.1070(4)	8.56(19)

least-squares of 25 θ-values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$ (Table 1). The CAD 4 diffractometer in the bisecting mode, measuring $\omega_{\bar{h}\bar{k}\bar{l}}$ at negative θ angle, was used. During the data collection three standard reflections were measured at regular intervals. No systematic variation in their intensities were observed. Information concerning the collection and reduc-

tion of the data is given in Table 1. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarisation and absorption effects, the latter by numerical integration. The values of $\sigma_c(I)$ are based on counting statistics. Reflections with $I \leqslant 1.5\sigma_c(I)$ were considered insignificantly different from the background and excluded from all subsequent calculations. The structure was solved by vector
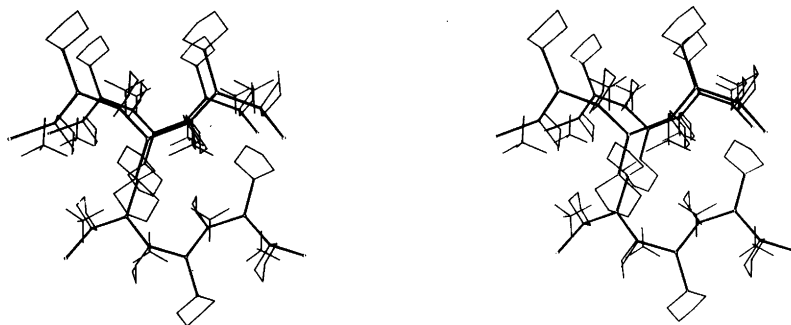
Fig. 1. Stereoscopic packing diagram of [Ag(C₄H₈S)₂]BF₄ viewed along *b*.

and difference Fourier methods. The atomic parameters for non-H atoms were refined using full-matrix least-squares. The atomic parameters of the H-atoms were calculated from the geometric criteria, C–H 0.9 Å and tetrahedral geometry around the C-atoms. These parameters were only included in the structure factor calculations.

The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with weights $w=[(\sigma_c^2/4|F_o|)^2+(0.007|F_o|)^2+0.5]^{-1}$. In the final refinement anisotropic temperature factors were applied to Ag, S, C, B and F. Scattering factors with corrections for anomalous dispersion, were taken from International Tables for X-Ray Crystallography.[5]

Details of the refinement are given in Table 1. The final positional and isotropic thermal parameters (anisotropic parameters have been recalculated to isotropic) are given in Table 2. Table 3 gives selected interatomic distances and angles. A list of structure factors and anisotropic thermal parameters may be obtained from the authors.

DESCRIPTION OF THE CRYSTAL STRUCTURE

There are two crystallographically different ligands in the structure. The S-atom of ligand 1 is bound only to one Ag(I) while the S-atom of ligand 2 is bridging two Ag(I) in such a way as to form infinite chains ⋯S–Ag–S–Ag⋯ along *a*. (Fig. 1). These chains are van der Waals packed with the BF₄⁻ ions in voids in the vicinity of Ag(I). The BF₄⁻ ion is not situated symmetrically between two chains but much closer to one of them. The smallest distances, B to Ag in adjacent chains are 3.73 and 6.69 Å, respectively. The bridging effect of the anion between the metal-ligand chains should thus be small.

The true symmetry of the AgS₃-core is C_1 but it may be described as having the pseudosymmetry D_{3h} (Fig. 2). The three Ag–S distances are 2.445(2), 2.519(2) and 2.555(2) Å, the shortest being associated with the unbridged S-atom. A similar short Ag–S bond, 2.457 Å, with an unbridged S-atom is observed in the polymer ⋯(F₅C₆)₂Au(μ-AgTHT)₂Au(C₆F₅)₂⋯.[6] The S–Ag–S angles are in the range 116–125° and Ag is situated only 0.06 Å from the plane defined by the S-atoms. If the two F atoms closest to Ag (2.80 and 2.85 Å) are taken into consideration the coordination polyhedron may be described as a distorted trigonal bipyramide. However, the
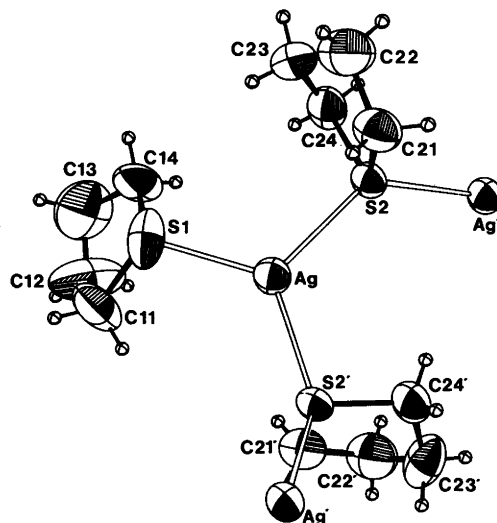

Fig. 2. The coordination around Ag viewed perpendicular to the LS-plane through Ag, S1, S2 and S2′.

Table 3. Selected bond distances (Å) and angles (°).
(′) $\frac{1}{2}+x, \frac{1}{2}-y, -z$ (″) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$

a. The coordination polyhedron

Ag−S1	2.445(2)	S1−Ag−S2	118.78(7)
Ag−S2	2.555(2)	S1−Ag−S2′	124.69(8)
Ag−S2′	2.519(2)	S2−Ag−S2′	116.26(3)

b. The THT molecules

S1−C11	1.810(11)	S1−C11−C12	105.0(7)
C11−C12	1.507(15)	C11−C12−C13	107.8(10)
C12−C13	1.380(19)	C12−C13−C14	110.1(9)
C13−C14	1.429(16)	C13−C14−S1	105.4(8)
C14−S1	1.781(10)	C14−S1−C11	92.4(5)
S2−C21	1.832(7)	S2−C21−C22	106.1(6)
C21−C22	1.507(14)	C21−C22−C23	108.5(8)
C22−C23	1.454(14)	C22−C23−C24	108.0(8)
C23−C24	1.516(14)	C23−C24−S2	103.9(6)
C24−S2	1.802(8)	C24−S2−C21	94.0(4)

c. The BF_4^- ion

B−F1	1.391(11)	F1−B−F2	109.1(6)
B−F2	1.382(11)	F1−B−F3	107.0(7)
B−F3	1.383(9)	F1−B−F4	110.5(7)
B−F4	1.344(9)	F2−B−F3	109.5(7)
		F2−B−F4	110.8(7)

d. Bond angles around the S atoms

Ag−S1−C11	109.5(3)	Ag−S2−Ag″	126.59(7)
Ag−S1−C14	109.2(3)	Ag−S2−C21	107.1(3)
C11−S1−C14	92.4(5)	Ag−S2−C24	105.8(3)
		Ag″−S2−C21	111.4(3)
		Ag″−S2−C24	106.9(3)
		C21−S2−C24	94.0(4)

Ag···F interactions must be considered very weak and will not be taken into account in the discussion of the coordination geometry of Ag.

With the exception of two very short C−C distances, C_{12}−C_{13} and C_{13}−C_{14}, bond distances and angles in the two THT-ligands are not significantly different (Table 3) and they agree well with those observed in other compounds.[7] The very short C−C distances observed are most probably an artifact caused by thermal motion.[4] Bond distances and angles within the BF_4^- ion are of the expected magnitudes.[8]

DISCUSSION

In a qualitative valence-bond description bond angles are highly dependent on hybridization of the atom under consideration. In the present case

the bond angles around Ag are close to 120° and the bonding to Ag may in such a model be described as three σ-bonds donated into sp^2 orbitals of the metal ion.

The bonding situation for the S-atoms in the two THT-ligands is different, S1 is bonded to three atoms while S2 is bonded to four. The bond angles around S1 are in the range 92−109° (Table 3). The S1 atom may thus be regarded as sp^3-hybridized with three electron pairs participating in σ-bonds and one essentially nonbonding. For S2 all four electron pairs participate in σ-bonds. The fairly large Ag−S2−Ag angle, 126.6° (Table 3), may be a consequence of the very small angle C21−S2−C24, 94.0°. Thus there is no indication of π-bonding in the studied compound.

The coordination situation in the present compound may be compared with the coordination to

Table 4. Comparison of intervals of observed Ag–S distances and S–Ag–S angles in compounds where S is the only donor atom.

Compound	$d(Ag–S)/Å$	$S–Ag–S/°$	Config.	Ref.
[Ag{SC(NH$_2$)$_2$}$_2$SCN]	2.462(2)–2.608(2)	115.6(1)–122.1(1)	trig.	9
[Ag{SC(NH$_2$)$_2$}$_3$]ClO$_4$	2.524(2)–2.684(2)	100.5(1)–115.9(1)	tetr.	11
[Ag$_8${S$_2$C=C(CN)$_2$}$_6$]$^{4-}$	2.462(4)–2.517(4)	115.5(1)–123.1(1)	trig.	13
[Ag{HO$_2$C(CH$_2$)$_3$S(CH$_2$)$_2$S(CH$_2$)$_3$CO$_2$H}$_2$]	2.55(2)–2.60(2)	86(1)–126(1)	tetr.	14
[Ag{SCNH(CH$_2$)$_2$NH}$_2$SCN]	2.478(2)–2.618(2)	118.6(2)–120.7(2)	trig.	10
[Ag(C$_4$H$_8$S)$_2$]BF$_4$	2.445(2)–2.555(2)	116.3(1)–124.7(1)	trig.	This study
NH$_4$[Ag(SCN)$_2$]	2.47(2)–2.74(3)	97–134	tetr.	12
[Ag$_{10}$(SiS$_4$)(Si$_2$S$_7$)]	2.411(8)–2.392(8)	153.4	bent. c.n.2	15

Ag(I) of the ligands thiourea, $SC(NH_2)_2$ and 2-thioimidazolidine, $SCNH(CH_2)_2NH$. With SCN⁻ these ligands form trigonal planar complexes with Ag(I), one of the coordinating sites being occupied by S from SCN⁻.[9,10] The S atoms in $SC(NH_2)_2$ and $SCNH(CH_2)_2NH$ may be regarded as sp²hybridized, with lone pairs suitable for σ-bonds to Ag(I). Both molecules also have extensive π-electron systems capable of participating in π-bonding with Ag(I). That π-bonding actually is of some significance in these compounds is supported by the observed angles between the least-square planes through the sulfur, carbon and nitrogen atoms of the thiourea parts of the ligands and the plane formed by the sulfur and silver atoms in the coordination polyhedra, which are less than 14° in both compounds. It may thus be concluded that three-coordination around Ag(I) with S-atoms occurs both with ligands forming and not forming π-bonds with Ag(I).

In Table 4 the coordination characteristics for some compounds in which Ag(I) is exclusively coordinating S are given. It is interesting to note that in the presence of the non-coordinating anion ClO_4^-, Ag(I) and $SC(NH_2)_2$ form a dimeric unit $[Ag_2\{SC(NH_2)_2\}_6]^{2+}$ in which Ag(I) is tetrahedrally coordinated by four S-atoms.[11] From this Table it may be concluded that Ag(I) is quite variable in its coordination geometry, varying between bent (c.n. 2), trigonal planar (c.n. 3) and tetrahedral (c.n. 4).

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