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The Structure of Silver(I) Iodide and Bromide, and the Silver(I) Solvate in Tetrahydrothiophene Solution: an X-ray Scattering and Raman Spectroscopic Study

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Abstract

Structures of silver(I) iodide and bromide, and the solvated silver(I) ion are determined in tetrahydrothiophene solution with Large Angle X-ray Scattering (LAXS) technique. In a silver(I) perchlorate tetrahydrothiophene solution, silver(I) is solvated by four tetrahydrothiophene molecules in a regular tetrahedron. The main peak in the radial distribution function corresponds to four Ag–S distances at 2.526(7) Å. An S–S distance at 2.65(2) Å in the solvent bulk is also included in the main peak. This shows that an internal structure exists in the tetrahydrothiophene bulk. Silver(I) iodide and bromide are tetrameric complexes with a *stella quadrangula* configuration, in saturated solution. The distances in the $[AgI(SC_4H_8)]_4$ complex are Ag–I, 2.799(4); Ag–Ag, 3.072(6) and I–I, 4.638(19) Å and in the $[AgBr(SC_4H_8)]_4$ complex they are Ag–Br, 2.592(3); Ag–Ag, 2.866(5) and Br–Br, 4.25(4) Å. The Ag–I bond distance in the $[AgI(SC_4H_8)]_4$ complex is shorter in solution than in the solid solvate. This is because bulk tetrahydrothiophene is a markedly weaker donor than free tetrahydrothiophene due to the sulfur–sulfur interactions in the bulk, shown to be around 2.65 Å. Raman spectroscopic studies on silver(I) and copper(I) iodide and silver(I) chloride tetrahydrothiophene solutions show that the polymeric structures predominate in concentrated solution and that they disintegrate upon dilution.

Introduction

The formation of silver(I) and copper(I) halide and thiocyanate complexes has been studied in dilute tetrahydrothiophene, THT, solution. Two strongly entropy stabilized mononuclear complexes are formed in all these systems [1]. The neutral complexes are extraordinarily stable in a solvent with a low dielectric constant, $\epsilon \approx 8$ in THT, due to strong electrostatic forces between ions of different charge. The neutral complexes are fairly strongly solvated in THT [2]. Previous studies on strongly entropy stabilized complexes have shown that such complexes can undergo disproportionation or polymerization reactions when the concentration is increased, *i.e.* the number of solvent molecules per complex decreases [3, 4]. The stability of the neutral mononuclear silver(I) and copper(I) halide complexes in THT at different concentrations has been studied by means of Raman spectroscopic studies.

Silver(I) iodide solvated by tetrahydrothiophene is a tetramer in the solid state with the composition $[AgI(SC_4H_8)]_4$ [5]. Solvated copper(I) iodide is found to be a dimer, $[CuI(SC_4H_8)_2]_2$, in the solid state [6]. The structures of silver(I) iodide and bromide in concentrated tetrahydrothiophene solution are reported in this paper.

The structure of solid bis(tetrahydrothiophene)-silver(I) tetrafluoroborate has been reported to be a chain structure, with sulfur bridging two silver atoms [7]. Silver(I) is three-coordinated in a trigonal fashion in this structure. This chain structure is not expected to be found in solution. Silver(I) is four-coordinated in most solvate structures in both the solid state and in solution [4, 8–11]. The structure of the silver(I) tetrahydrothiophene solvate in solution is reported in this paper.

Experimental

Preparation of Solutions

The solutions were prepared by dissolving anhydrous silver(I) iodide, bromide and perchlorate to saturation in freshly purified tetrahydrothiophene [12]. The composition of the solutions studied by means of LAXS technique is given in Table I. Saturated solution of silver(I) iodide (1.77 M), silver(I) bromide (3.0 M), silver(I) chloride (0.56 M), and copper(I) iodide (1.20 M) were used as start solutions in the Raman spectroscopic studies. These solutions were then successively diluted for the Raman measurements.

X-ray Scattering Experiments

The X-ray scattering from a free surface of solution was measured in a large angle theta–theta

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TABLE I. Composition (mol dm^{-3}) and Linear Absorption Coefficient, μ(Mo Kα) (cm^{-1}) for the Investigated Solutions

	Ag	X	ClO$_4$	SC$_4$H$_8$	μ
AgI	1.771	1.771		10.62	16.9
AgBr	1.451	1.451		10.82	16.9
AgClO$_4$	0.766		0.766	10.92	6.2

diffractometer [13] of Seifert GDS type. The solutions were enclosed in a cylindrical thin-walled glass container, in order to avoid evaporation. The glass container was exactly half-filled. The absorption of the glass container and its angle dependence have been determined previously [14]. Mo Kα (λ = 0.7107 Å) radiation was used as X-ray source. The scattered intensities were measured at discrete points in the region $4° < \theta < 65°$, separated by 0.0335 in s, where $s = 4\pi \sin\theta\lambda^{-1}$, and the scattering angle is 2θ. An extrapolation of the intensity data at $\theta < 4$ was necessary due to the upward meniscus in the glass container. A statistical error of 0.35% was achieved by measuring 40000 counts twice at each sampling point. The fraction of incoherent scattering contributing to the intensity determinations has been estimated in the usual manner [15].

Treatment of Scattering Data

The same data reduction procedure and corrections as described elsewhere were applied [15]. The experimental intensities were normalized to a stoichiometric unit of volume containing one silver atom. The scattering factors, corrections for anomalous dispersion and values for incoherent scattering were the same as used before [15]. Correction for multiple scattering was made for silver(I) perchlorate. Spurious peaks below 1.5 Å in the experimental radial distribution function, which could not be related to interatomic distances within the tetrahydrothiophene molecule or the perchlorate ion, have been removed by a Fourier transformation procedure [13]. The reduced intensity functions, $i(s)$, multiplied by the scattering variable, s, are shown in Fig. 1. The corresponding experimental radial distribution functions, RDF, $D(r)$-$4\pi r^2\rho_0$, were obtained by Fourier transformation of the reduced intensity functions, Fig. 2.

All calculations were carried out by means of the computer programs KURVLR [16] and STEPLR [17].

Raman Measurements

Raman spectra were recorded using d.c. amplification from a D.I.L.O.R. RTI 30 triple monochromator with 4 cm^{-1} spectral bandwith. The light source was the 647.1 nm line of a Coherent Radiation Innova 90-5 Kr-ion laser.

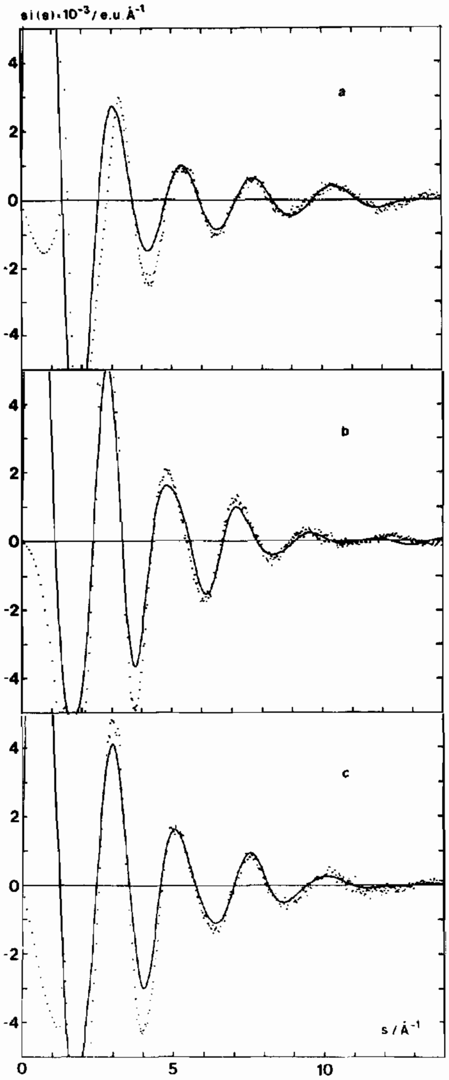

Fig. 1. Experimental (dots) and calculated (solid lines) values for the Ag(SC$_4$H$_8$)$_4^+$ (a), [AgI(SC$_4$H$_8$)]$_4$ (b) and [AgBr-(SC$_4$H$_8$)]$_4$ (c) complexes in tetrahydrothiophene. The parameters given in Table II were used for the theoretical curves.

Results

X-ray Scattering Measurements

A peak at 2.5 Å corresponding to a Ag–S distance, and two shoulders at around 3.6 and 4.2 Å corresponding to Ag–C and S–S distances are found in the RDF for the silver(I) perchlorate solution. The distances and temperature factor coefficients of the Ag–S and Ag–C distances have been refined in the range $4.0 < s < 14.0$ Å^{-1}. The number of Ag–S and Ag–C distances has been set to 4.0 and 8.0 respectively, and they have not been refined. The parameters for the Ag(SC$_4$H$_8$)$_4^+$ solvate in tetrahydrothiophene solution are given in Table II.

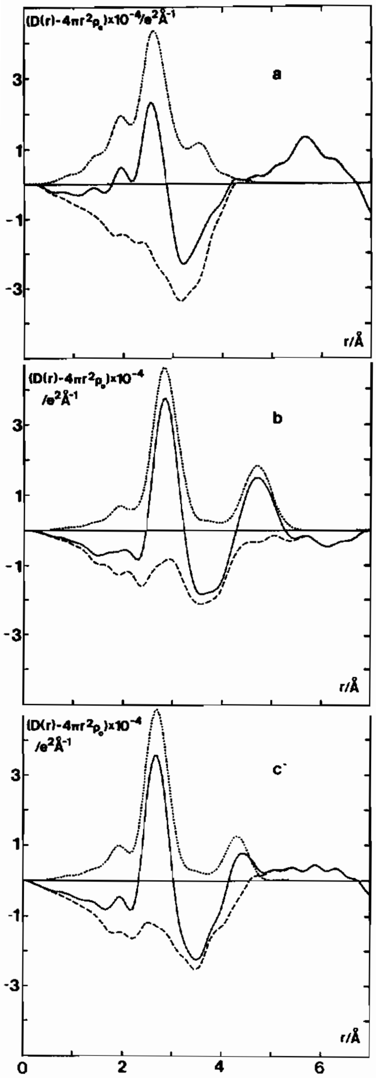

Fig. 2. $D(r)$-$4\pi r^2\rho_0$ functions and calculated peak shapes with parameters from Table II, for the $Ag(SC_4H_8)_4^+$ (a), $[AgI(SC_4H_8)]_4$ (b) and $[AgBr(SC_4H_8)]_4$ (c) complexes. Experimental curves (solid lines), model functions (dotted lines) and their differences (dashed lines) are given.

However, after the introduction of the $Ag(SC_4H_8)_4^+$ complex there remained a large peak in the difference between the experimental and calculated RDFs, and the fit between the experimental and calculated intensity functions was not satisfactory, Fig. 3. Previous thermodynamic studies have strongly indicated that tetrahydrothiophene has a pronounced bulk structure [18]. This bulk structure is most probably built up of sulfur–sulfur interactions between tetrahydrothiophene molecules. A sulfur–sulfur distance at 2.7 Å was introduced and the parameters were refined. The S–S distance was refined to 2.65(2) Å, b = 0.042(2) Å and n = 2.6(5). The RDF, with S–S interaction in the bulk included, is given in Fig. 2.

TABLE II. Interatomic Distances, d (Å), Temperature Factor Coefficient for the Distances, b (Å^2), and Frequency of Distances Relative to One Silver(I) Atom, n, for the $AgClO_4$, AgBr and AgI Tetrahydrothiophene Solution. The Refined Parameters are those with e.s.d.s in Parentheses

Distance	d	b	n
$Ag(SC_4H_8)_4^+$			
Ag–S	2.526(7)	0.0070(8)	4.0
Ag–C	3.567(18)	0.009(2)	8.0
S–S	4.125	0.010	6.0
S–S (bulk)	2.65(2)	0.032	2.6(5)
$[AgI(SC_4H_8)]_4$			
Ag–I	2.824(4)	0.066(5)	3.0
Ag–S	2.65	0.012	1.0
Ag–Ag	3.070(11)	0.0075	1.5
I–S	4.62	0.015	3.0
I–I	4.71	0.093(23)	1.5
$[AgBr(SC_4H_8)]_4$			
Ag–Br	2.592(3)	0.0019(4)	3.0
Ag–S	2.65	0.012	1.0
Ag–Ag	2.866(5)	0.0047	1.5
Br–S	4.28	0.015	3.0
Br–Br	4.25(4)	0.015	1.5

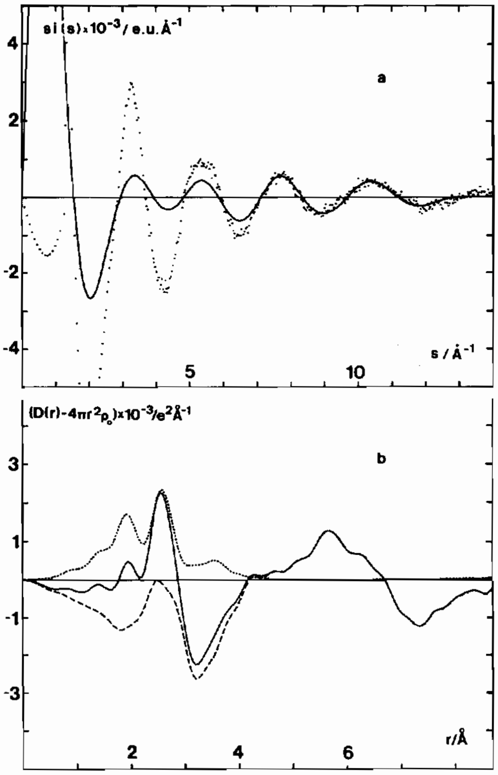

Fig. 3. (a) Experimental (dots) and calculated (solid line) values for the $Ag(SC_4H_8)_4^+$ complex without S–S bulk interactions in tetrahydrothiophene. (b) $D(r)$ $4\pi r^2\rho_0$ functions and calculated peak shapes for the $Ag(SC_4H_8)_4^+$ complex without S–S bulk interactions; the same marks as in Fig. 2 are used.

Two major peaks at 2.8 and 4.6 Å are found in the RDF of the silver(I) iodide solution. These peaks correspond to Ag–I, and I–I and I–S distances respectively. The area of the Ag–I peak corresponds to more than one Ag–I distance per silver, and the presence of I–I and I–S distances shows that silver(I) iodide has a polymeric structure in concentrated tetrahydrothiophene solution. The tetrameric $[AgI(SC_4H_8)]_4$ complex found in the solid state [5] was used as the model for the silver(I) iodide complex in concentrated tetrahydrothiophene solution. The distances and temperature factor coefficients of the Ag–I, Ag–Ag, I–I and I–S distances have been refined in the range $4.0 < s < 15.0$ Å^{-1} by a least-squares procedure. The number of the distances was kept fixed for all distances in the model. Fixed parameters were also introduced for the interatomic distances in tetrahydrothiophene, and intermolecular S–S distances in the tetrahydrothiophene bulk. The parameters for the $[AgI(SC_4H_8)]_4$ complex in tetrahydrothiophene solution are given in Table II.

In the RDF for the silver(I) bromide tetrahydrothiophene solution there is a major peak at 2.6 Å, corresponding to a Ag–Br distance, and a smaller peak at 4.3 Å, corresponding to Br–Br and Br–S distances. This shows that silver(I) bromide also has a polymeric structure in concentrated tetrahydrothiophene solution. The structure of tetrahydrothiophene solvated silver(I) bromide in the solid state has not been reported. Both tetrameric and dimeric models have been tested, since $[AgCl(SC_4H_8)_2]_2$ is a dimer and $[AgI(SC_4H_8)]_4$ is a tetramer in the solid state [5, 6]. This test clearly showed that the tetrameric complex $[AgBr(SC_4H_8)]_4$ gave the best fit. The distances and temperature factor coefficients of Ag–Br, Ag–Ag, Br–Br and Br–S distances have been refined in the range $4.0 < s < 15.0$ Å^{-1}. The same parameters as in the $[AgI(SC_4H_8)]_4$ complex were kept fixed, including the S–S distance in the tetrahydrothiophene bulk. The parameters for the $[AgBr(SC_4H_8)]_4$ complex in tetrahydrothiophene solution are given in Table II.

Raman Measurements

Raman spectra have been recorded for solutions of varying C_M, all with $C_L/C_M = 1$. The stretching modes ν_1(Ag–X) were found at 210, 145 and 118 cm^{-1} for X = Cl, Br and I respectively. The ν_1(Cu–I) mode was found at 130 cm^{-1}. In order to determine the stability of the complex present in concentrated solution, the ratio a/C_M is formed, where a is the integrated area of the ν_1(M–X) peak (in arbitrary units). Since a is proportional to C_M, this ratio will be constant as long as the complex distribution is the same as in the concentrated solution, studied by means of X-ray scattering. The a/C_M ratio decreases in the range 0.1 M $< C_M <$ 0.5 M indicating a drastic change in the complex distribution in this range, Fig. 4. It is not possible to obtain a complete Raman spectrum of AgBr in tetrahydrothiophene solution because of decomposition in the laser-beam.

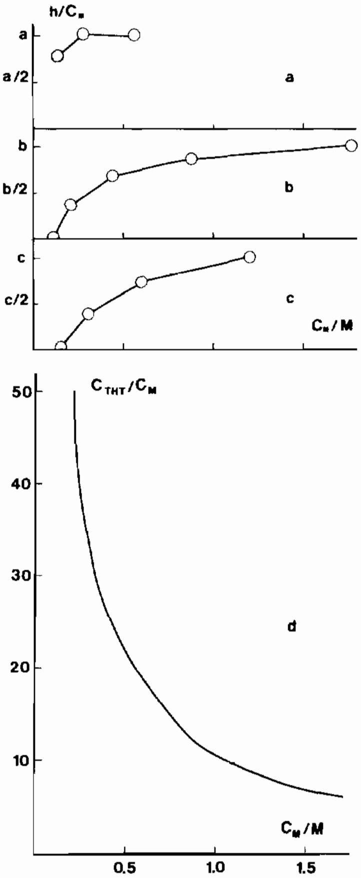

Fig. 4. (a)–(c) Ratios h/C_M between the peak areas of the ν_1(Ag–X) bonds of the polymeric AgCl (a), AgI (b) and CuI (c) complexes in solutions of $C_L/C_M = 1$, and the total metal concentration. The values of h/C_M are on an arbitrary scale. (d) The number of tetrahydrothiophene molecules per metal atoms is given as a function of C_M.

Discussion

The structure of the silver(I) tetrahydrothiophene solvate is a regular tetrahedron in solution, contrary to the trigonal coordination of the silver(I) tetrahydrothiophene solvate in the solid state. The Ag–S distance in the $Ag(SC_4H_8)_4^+$ complex, 2.526(7) Å, is slightly longer than the average Ag–S distance 2.506 Å in the solid $Ag(SC_4H_8)_2BF_4$. The maximum coordination number of a metal ion is, in most cases, found in the solvate structures in solution. In some cases the maximum coordination number is not obtained in solid solvates precipitated from saturated solutions, e.g. $Ag(SC_4H_8)_2BF_4$ [7] and $Au(CH_3CN)_2ClO_4$ [19].

A previous thermodynamic study has strongly indicated that tetrahydrothiophene and other sulfides have a pronounced bulk structure [18]. The $Ag(SC_4H_8)_4^+$ complex cannot alone give a satisfactory fit to the experimental intensity function and RDF, Fig. 3. The S–S distance in the tetrahydrothiophene bulk is about 2.65 Å, and the number of distances is about two per tetrahydrothiophene molecule. This confirms that tetrahydrothiophene has a bulk structure built up of sulfur–sulfur interactions. These interactions are weaker than the hydrogen bonds in aqueous solution [18].

The Raman spectroscopic measurements have clearly shown that the neutral silver(I) halide and copper(I) iodide complexes polymerize when the concentration of the solute increases and the number of solvent molecules per metal ion decreases, Fig. 4. The mononuclear neutral silver(I) and copper(I) halide complexes are strongly entropy stabilized, and it is therefore not surprising that such complexes will undergo some kind of reaction when the concentration is increased. A more enthalpy stabilized complex is then formed. This pattern has previously been found in the HgX^+, X = Cl, Br, I, SCN, complexes in DMSO [20], the $HgSC_4H_9^+$ complex in pyridine [21], and in the AgI_2^- complex in acetonitrile [4]. The complexes formed in concentrated solution have more bonds between the metal ion and the ligand than in the complex stable in dilute solution.

The structure of the neutral tetrameric silver(I) iodide complex in tetrahydrothiophene solution is similar to that reported in the solid state. Tetrahydrothiophene is a weaker donor in bulk than free, due to the intermolecular interactions in the bulk. The entity is thus weaker solvated in THT solution than in the solid state. This means that the Ag–I bond distances become shorter and the Ag–S bond distances longer in THT solution than in the solid. This is indeed also found, see Table III. Shorter bonds in solution, than in the solid state, are also found for $HgBr_2(SC_4H_8)_2$ [22]. The average Hg–Br bond distance 2.55 Å in the solid state is slightly shorter in solution, 2.53 Å.

It has not been possible to determine the structure of the tetrahydrothiophene solvated silver(I) bromide in the solid state due to formation of plastic crystals with the composition, $AgBr(SC_4H_8)$. In THT solution, a tetrameric silver(I) bromide complex is formed with, most probably, a *stella quadrangula* configuration similar to the silver(I) iodide complex. The Ag–Br bond lengths are short, compared to silver(I) tetrahedrally coordinated by four bromide ions. In $[Ni(en)_2][AgBr_2]_2$, the silver(I) is coordinated by bromide ions in a distorted tetrahedron [23]. The Ag–Br distance varies between 2.69 and 2.74 Å, with 2.72 as an average value. Comparisons between $[AgBr(SC_4H_8)]_4$ in solution and in the solid state are not possible, but similar silver(I) bromide structures with other ligands have earlier been found in the solid state. The $[AgBr(Ph_3P)]_4$ [24] and $[AgBr(Et_3P)]_4$ [25] complexes have a cubane configuration in the solid state. The Ag–Br bonds vary between 2.68 and 2.96 Å in $[AgBr(Ph_3P)]_4$ and between 2.42 and 2.90 Å in $[AgBr(Et_3P)]_4$.

TABLE III. Interatomic Distances (Å) of Silver(I) Salts in Tetrahydrothiophene Solution and in some Corresponding Solid Solvates

	Ag–X	Ag–Ag	Ag–L	X–X
$Ag(SC_4H_8)_4^+$ (THT)			2.53	
$Ag(SC_4H_8)_2BF_4$ (s)[a]			2.51	
$[AgBr(SC_4H_8)]_4$ (THT)	2.59	2.87	2.65	4.25
$[AgBr(PPh_3)]_4$ (s)[b]	2.80	3.82	2.42	4.28
$[AgBr(PEt_3)]_4$ (s)[c]	2.74	3.48	2.40	4.20
$[AgI(SC_4H_8)]_4$ (THT)	2.80	3.07	2.65	4.71
$[AgI(SC_4H_8)]_4$ (s)[d]	2.90	3.11	2.55	4.74

[a]Ref. 7. [b]Ref. 24. [c]Ref. 25. [d]Ref. 5.

Acknowledgements

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