Silver Iodide Complexes in DMSO and DMF Solutions

Ferenc Gaizer and Georg Johansson

KEMISK BIBLIOTEK
Den Kgl. Veterinær- og Landbohøjskole

Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Gaizer, F. and Johansson, G., 1988. Silver Iodide Complexes in DMSO and DMF Solutions. – Acta Chem. Scand., Ser. A 42: 259–268.

The structures of silver iodide complexes formed in DMSO and DMF solutions at different I:Ag ratios have been investigated by X-ray diffraction methods. With iodide in excess the scattering data are consistent with the formation of mononuclear, planar, triangular AgI_3^{2-} complexes. At low I:Ag ratios polynuclear complexes are formed in which the Ag atoms are joined by iodide bridges. Possible structures for these complexes consistent with the scattering data are discussed.

Silver iodide dissolves in DMSO (dimethyl sulfoxide) and DMF (*N,N*-dimethylformamide) in the presence of an excess of iodide. Solutions can be prepared in fairly high concentration, often more than 1 M. The first attempts to identify the complexes formed in DMSO solutions and to determine their stability constants were based on potentiometric measurements. Rumbaut and Peters[1] assumed the formation of the species $Ag_2I_3^-$, AgI_2^- and AgI_3^{2-}. Le Demezet *et al.*,[2] however, substantiated formation of the species $Ag_3I_4^-$ besides the mononuclear ones. On the basis of measurements carried out over a wide range of total silver ion concentration,[3] binuclear and trinuclear complexes were excluded and the formation of the species $Ag_6I_8^{2-}$ was suggested. Another series of potentiometric measurements,[4] in which iodide ions were titrated with silver ions, led to the conclusion that the complexes $Ag_6I_8^{2-}$, $Ag_5I_7^{2-}$, $Ag_4I_6^{2-}$, $Ag_2I_4^{2-}$, AgI_2^-, AgI_3^{2-} and, in small amounts, AgI were formed.

In the present paper the structures of the complexes in the solutions will be discussed on the basis of results from a series of X-ray scattering measurements on concentrated solutions with different I:Ag ratios.

Table 1. Compositions of solutions (mol l^{-1}), chosen stoichiometric unit of volume, V/Å^{-3}, and number of atoms in the stoichiometric unit.

	Solution							
	4:1	2.67:1	2:1	1.5:1	NaI	$AgNO_3$	2:1	1.5:1
Ag	0.50	0.750	1.000	1.000	–	3.000	1.000	1.000
I	2.00	2.006	2.039	1.500	0.70	–	2.017	1.505
Na	1.50	1.256	1.039	0.500	0.70	–	1.017	0.505
DMSO	13.00	12.98	12.88	13.18	13.66	12.79	–	–
DMF	–	–	–	–	–	–	12.01	12.20
V/Å^3	830.3	827.7	814.6	1106.8	790.2	844.0	823.3	1102.7
Ag	0.250	0.374	0.490	0.667	–	1.525	0.496	0.664
I	1	1	1	1	0.33	–	1	1
Na	0.75	0.63	0.51	0.33	0.33	–	0.50	0.33
DMSO	6.50	6.47	6.32	8.79	6.50	6.50	–	–
DMF	–	–	–	–	–	–	5.96	8.10

Experimental

The solutions were prepared from weighed amounts of sodium iodide and silver iodide of analytical grade, and DMSO and DMF of spectroscopic purity. The I:Ag ratio was varied between 4 and 1.5 for the DMSO, and between 2 and 1.5 for the DMF solutions. A nearly saturated solution of sodium iodide in DMSO without added silver, and a solution of $AgNO_3$ in DMSO without added iodide were prepared for use as reference solutions. The compositions are given in Table 1.

The X-ray scattering from the free surface of the solutions was measured with Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) using either a $\theta-\theta$ diffractometer equipped with a focusing single-crystal LiF monochromator described in previous papers,[5] or a Rigaku $\theta-\theta$ diffractometer using a graphite monochromator. Different slit widths were used to cover the complete θ range ($1° \leq \theta \leq 70°$; 2θ = the scattering angle). Measurements were taken at intervals in θ of 0.1° for $\theta \leq 20°$, and 0.25° for $\theta \geq 20°$.

Treatment of data

The scattering data were processed with the KURVLR program[6] modified for use on a PC computer. Corrections were made for absorption, multiple scattering, polarization in the sample and in the monochromator, and for incoher-

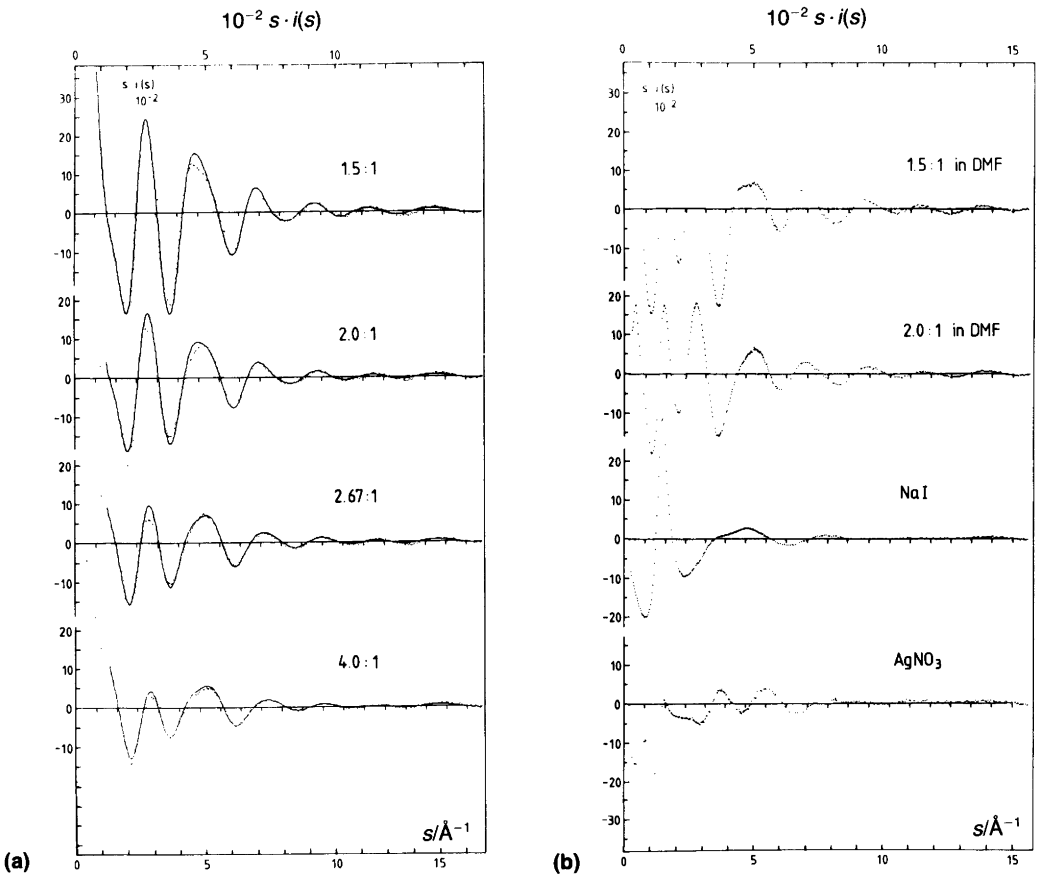

Fig. 1. Reduced intensity values, $s \cdot i(s)$. (a) Observed values for the DMSO solutions (dots) cmpared with theoretical values (solid lines) calculated for intramolecular interactions within DMSO, AgI_3^{2-} and $Ag_4I_5^-$ complexes using parameter values given in Table 2. (b) Observed values for the DMF solutions and for the reference solutions.

ent scattering. Normalization of the data to a chosen stoichiometric unit of volume was done with the use of the outermost part of the scattering curve. Corrections were made for low-frequency additions to the intensity curves which in the radial distribution functions lead to spurious peaks below 1.0 Å not attributable to interatomic distances.

Scattering factors, $f_i(s)$, for neutral atoms corrected for anomalous dispersion were used.[7] Values for incoherent scattering were corrected for the Breit-Dirac effect.

Reduced intensities, $i(s)$, were calculated from the observed intensities, $i(s)$, as:

$$i(s) = I(s) - \Sigma n_i[f_i^2(s) + \Delta f_i''^2].$$

Here $s = 4\pi\tau^{-1} \sin\theta$, f_i is the scattering factor for atom i corrected for the real part of the anomalous dispersion and $\Delta f_i''$ is the imaginary part of the anomalous dispersion.

Electronic radial distribution functions (RDF) were calculated as:

$$D(r) = 4\pi r^2 \varrho_0 + 2r\pi^{-1} \int_0^{Smax} si(s) \sin(rs)\, M(s)\, ds$$

where $\varrho_0 = (\Sigma n_i Z_i)^2/V$, where Z_i is the atomic number of atom i, V is the stoichiometric unit of volume, and the modification function $M(s) = f_o(0)^2 f_o(s)^{-2} \exp(-0.0075\, s^2)$.

Theoretical intensities for discrete interactions were calculated from:

$$i(s) = \Sigma\Sigma f_p f_q \sin(r_{pq}s)/(r_{pq}s) \exp(-{}^1/_2 l_{pq}{}^2 s^2)$$

where r_{pq} is the distance between the atoms p and q and l_{pq} is the root-mean-square variation in the distance. The corresponding peak shapes were calculated by a Fourier transformation in the same way as for the experimental intensities, using the same integration limits and the same modification function.

Derivation of the structures

Reduced intensities, $s \cdot i(s)$, for each solution, normalized to the stoichiometric unit of volume given in Table 1, are shown in Fig. 1. The corresponding RDF's for the DMSO solutions are given in Fig. 2.

The RDF's for the DMF solutions are compared in Fig. 3 with those for the DMSO solutions, after subtracting the intramolecular interactions of the solvent molecules. For the same I:Ag ratio the RDF's are very similar. The same complexes are thus formed in both solvents and

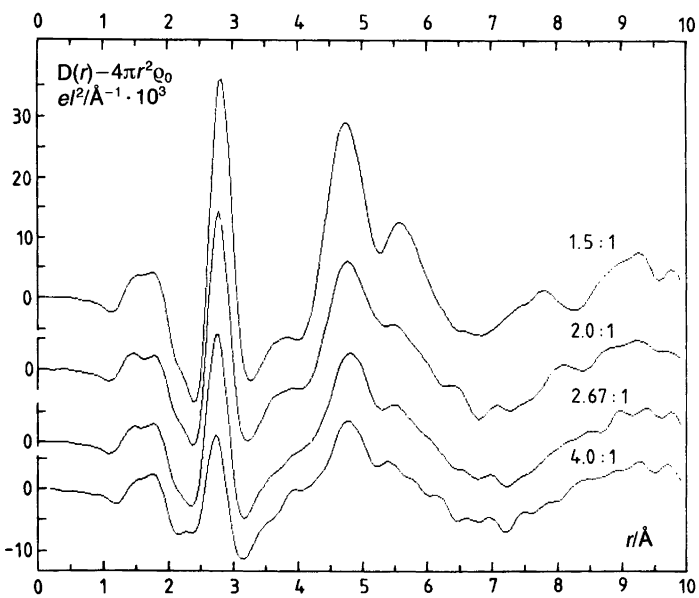

Fig. 2. Radial distribution functions, $D(r) - 4\pi r^2 \varrho_0$, for the silver iodide solutions in DMSO.

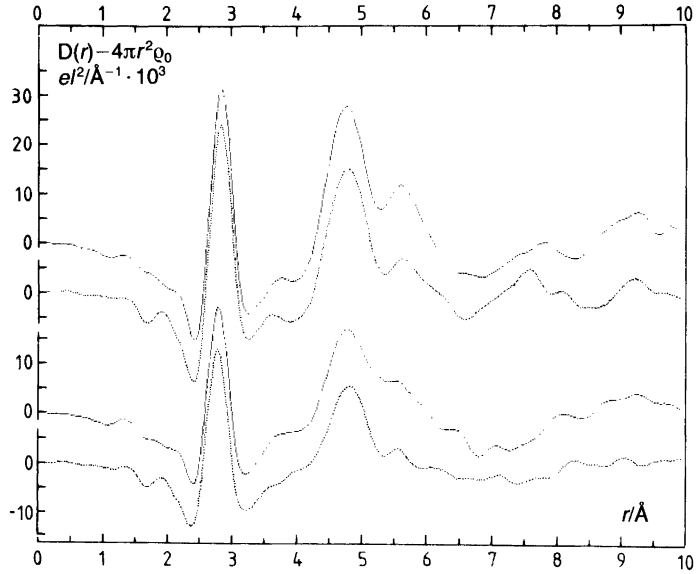

Fig. 3. Comparison between the $D(r)-4\pi r^2\varrho_0$ functions for the DMSO (solid lines) and the DMF (dotted lines) solutions after subtracting intramolecular interactions for the solvent molecules. The I:Ag ratios are 1.5:1 for the upper curves and 2:1 for the lower curves (see Table 1).

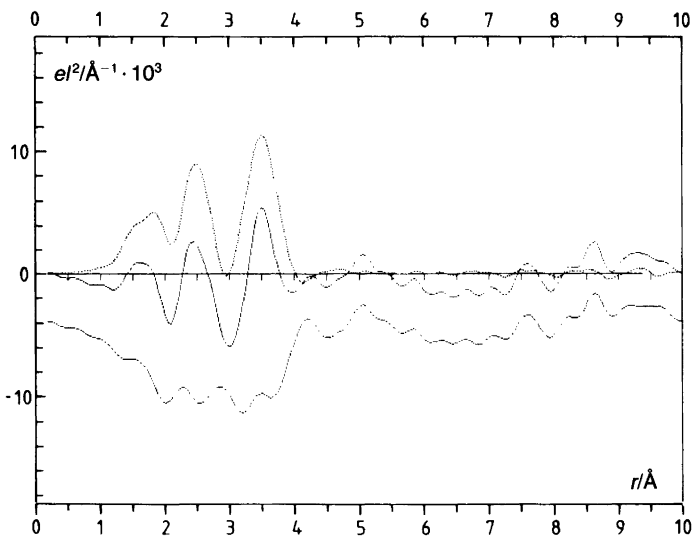

Fig. 4. The $D(r)-4\pi r^2\varrho_0$ functions for the $AgNO_3$ solution (solid line) compared with the sum of calculated peaks (dotted line) for intramolecular NO_3^- and DMSO interactions, and Ag−O and Ag−S interactions (Table 2). The lower curve gives the difference.

the solvent molecules have no decisive influence on the structures. For this reason the following discussion will be limited to the DMSO solutions.

For the silver nitrate solution the RDF (Fig. 4) shows two pronounced peaks, at 2.4 Å and 3.5 Å, in addition to those corresponding to distances within the DMSO molecule. The two peaks can be identified as corresponding to Ag−O and Ag−S distances within the solvated Ag^+ ion. They are compared in Fig. 4 with theoretical peaks, assuming the Ag^+ ion to be four-coordinated and using parameter values given in Table 2. Corresponding peaks cannot be distinguished in the RDF's for the silver iodide solutions.

For the sodium iodide solution the only pronounced peaks in the RDF result from intramolecular interactions within the DMSO molecules.

Table 2. Parameter values used for the calculation of intramolecular interactions. Distance = d(Å) and its corresponding rms value, l, are given. Distances which are not independent are given in parentheses. Estimated standard deviations in independently determined parameter values are also given in parentheses.

		d_{pq}	l_{pq}
DMSO	S–O	1.52(2)	0.045(5)
	S–C	1.84(2)	0.06(1)
	C–H	1.08	0.07
	C–O	2.65	0.08
	C–C	2.74	0.09
$Ag(DMSO)_4^+$	Ag–O	2.42(1)	0.17(3)
	Ag–S	3.49(1)	0.26(4)
AgI_3^{2-}	Ag–I	2.775(5)	0.14(2)
	I–I	4.806(10)	0.28(3)
$Ag_4I_4(I)_{\sim 1}$	Ag–I	2.86(1)	0.14(2)
	Ag–Ag	(2.94)	0.20
	I–I	4.74(2)	0.24(4)
	Ag–I	(4.70)	0.24
	Ag–(I)	(2.95)	0.17
	I–(I)	(4.67)	0.28
	Ag–(I)	5.61(5)	0.22(5)
	I–(I)	(7.65)	0.35

In Fig. 5, theoretical peaks, calculated with the parameter values for the DMSO molecule given in Table 2, are compared with the D(r) function. Subtraction of the theoretical peaks leaves only one remaining rather diffuse peak at about 2.3 Å, which can probably be related to Na–O interactions. Pure DMSO gives a very similar RDF but without the 2.3 Å peak.

For the analysis of the radial distribution functions for the silver iodide solutions the intramolecular DMSO interactions were eliminated with the use of the sodium iodide solution. By subtracting its RDF, normalized to contain the same number of DMSO molecules in the stoichiometric unit as that of the silver iodide solution, a difference curve was obtained without the DMSO interactions and with the intramolecular interactions of the silver iodide complexes appearing as sharp peaks on a slowly varying background curve (Fig. 6). The corresponding curves, obtained for the four different DMSO solutions, are shown in Fig. 7a. Each of them contains only two pronounced peaks, viz. one at about 2.8 Å, which is the expected Ag–I bonding distance, and the other at about 4.8 Å, the expected I–I contact distance. Since the curves are normalized to one I atom in the stoichiometric unit, the peak sizes will reflect the surroundings of an average I atom in the solution. Comparison with calculated peaks shows the number of Ag–I bonds in which

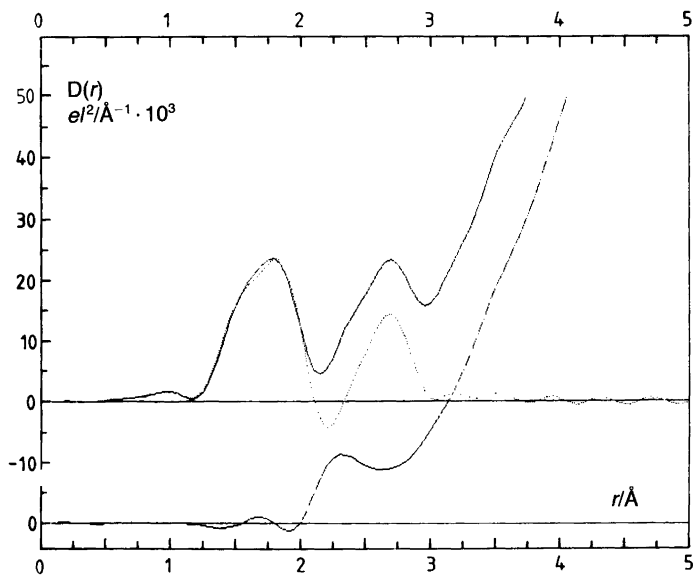

Fig. 5. The D(r) function for the sodium iodide solution in DMSO (upper full-drawn curve) compared with calculated peaks for intramolecular DMSO interactions (upper dotted curve). The difference is given by the lower curve.

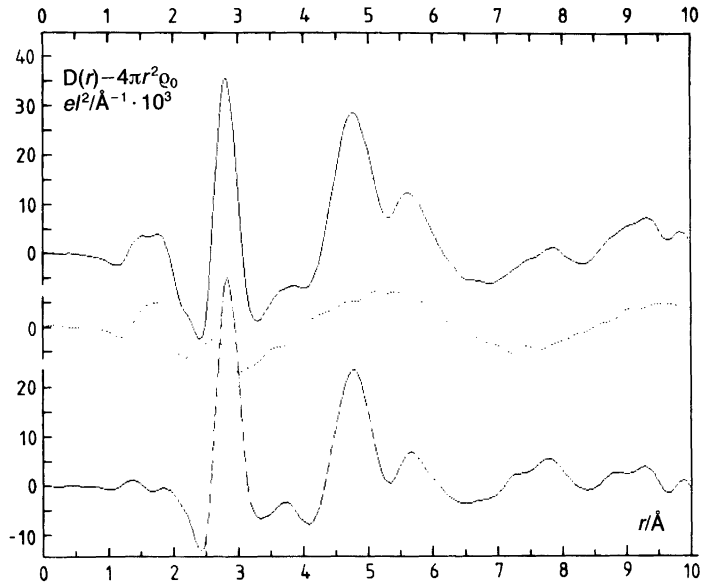

Fig. 6. The $D(r)-4\pi r^2 q_0$ functions for the 1.5:1 solution (upper solid line) and the NaI solution (dashed line), and the difference between them (lower curve).

the average I atom is involved to increase from 0.7 for the 4:1 solution to about 2 for the 1.5:1 solution. At least for the low I:Ag ratios, polynuclear complexes are thus formed with the Ag atoms joined by I bridges.

Fig. 7b gives the same difference curves normalized to one Ag atom in the stoichiometric unit. The four curves are now very similar, indicating that the intramolecular interactions in which an average Ag atom is involved do not change much when the I:Ag ratio changes. If only one polynuclear complex involving all Ag in the solution were present, the intramolecular peaks in the four curves in Fig. 7b should be identical. Although small, there are, however, significant changes in the peak shapes when the I:Ag ratio changes, which indicates that more than one complex must occur. An analysis of these changes in the 2.8 Å peak reveals two effects when the I:Ag ratio decreases: The distance is increased from 2.78 Å in the 4:1 solution to 2.86 Å in the 1.5:1 solution and a small additional interaction has appeared at about 3.0 Å. For the 4.8 Å interaction, the major change is a slight decrease in the distance from 4.80 Å to 4.74 Å without any marked change in the size of the peak. For the lowest ratio, 1.5:1, there are clear indications of the appearance of a peak at about 5.6 Å and, possibly, another one at about 7.6 Å.

In the 4:1 solution the number of Ag–I interactions per Ag atom is close to three, and the same value is found for the number of I–I interactions. The ratio between the I–I and the Ag–I distances is $4.80/2.78 = 1.73 \approx \sqrt{3}$. These observations are consistent with planar triangular coordination around Ag. In the 1.5:1 solution the distances have changed to 2.86 Å for Ag–I and 4.74 Å for I–I without any appreciable change in the number of Ag–I distances per Ag atom. The three-coordination is thus no longer planar triangular but pyramidal with the Ag atom about 0.8 Å above the center of the triangular base formed by the I atoms. This leads to the conclusion that the polynuclear complexes formed are built up from pyramidal AgI_3 units joined by common I atoms in such a way that no new distances besides those at 2.8 Å and 4.8 Å appear. This can be achieved if the I atoms in the polynuclear complexes have an approximately tetrahedral arrangement with the Ag atoms above the centers of the triangular faces of the tetrahedron, which points to a cubane-like structure as illustrated in Fig. 8.

If the I–I and the Ag–I distances in an assumed cubane-like model (Fig. 8) are adjusted to the experimentally observed values of 4.74 Å and 2.86 Å, the resulting Ag–Ag distances within the complex will be 2.94 Å and the long Ag–I dis-

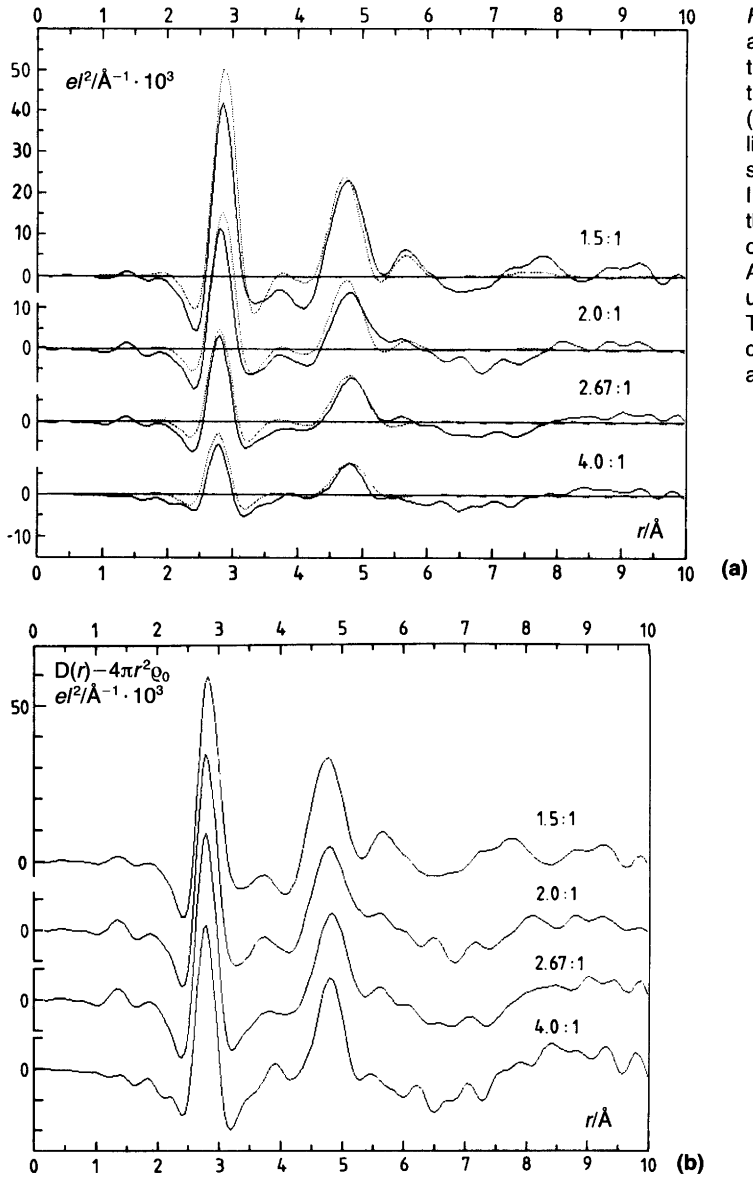

Fig. 7. Difference curves obtained after subtraction of the RDF for the sodium iodide solution from those for the DMSO solutions. (a) The difference curves (solid lines) normalized to a stoichiometric unit containing one I atom (Table 1). Dotted lines give the sum of theoretical peaks calculated for a combination of AgI_3^{2-} and $Ag_4I_5^-$ complexes using parameter values given in Table 2. (b) The same difference curves normalized to one Ag atom in the stoichiometric unit.

tances 4.70 Å. This is consistent with the experimental curves (Fig. 7), in which it can be seen that a lowering of the I:Ag ratio leads to an additional interaction at about 3.0 Å but does not result in any other marked changes. The appearance in the 1.5:1 solution of a peak at about 5.6 Å can then be explained if the fourth coordination site around the Ag atom in the model is partially occupied by I atoms. With a normal Ag–I bond length this would result in long Ag–I interactions at about 5.6 Å. It would also lead to long I–I interactions of a lower frequency at 7.6 Å (Fig. 7). An occupancy factor of about 0.25 would be consistent with the size of the 5.6 Å peak and would correspond to an approximate formula $Ag_4I_5^-$ for the complex.

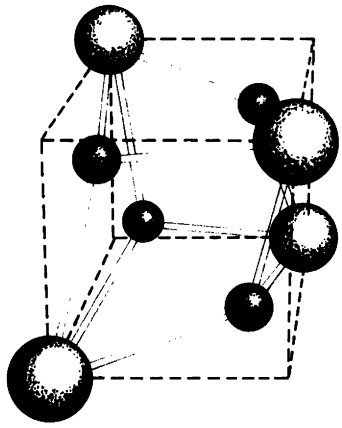

Fig. 8. A drawing of the idealized cubane structure for Ag_4I_4 showing the positions of the Ag atoms (small circles) and the I atoms (large circles).

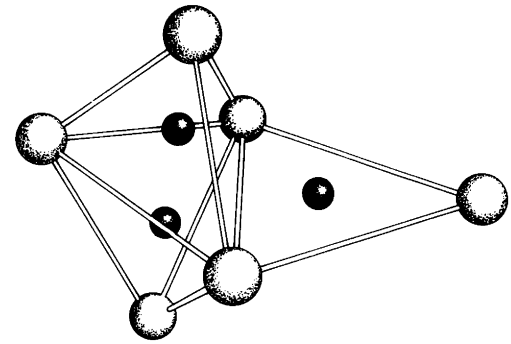

Fig. 10. The structure of the $Ag_3I_6^{3-}$ complex found in crystals of $NaAgI_2$–4DMSO. The structure is built up from two face-sharing AgI_4 tetrahedra and one edge-sharing AgI_3 triangle.

Cubane-like structures for polynuclear silver halide complexes have been found previously in crystals obtained from solutions of silver halides in various organic solvents. The structure of a tetrameric triphenylphosphine-silver iodide cluster has been described[8] in which the Ag and I atoms are arranged as shown in Fig. 8. Triphenylphosphine molecules are coordinated to the Ag atoms leading to distorted tetrahedral coordination. A chair-like arrangement, closely related to the cubane structure, has also been found. A similar cubane-like structure for a tetrameric tetrahydrothiophene-silver iodide cluster with distances closely similar to those found here has also been described.[9] One tetrahydrothiophene molecule is coordinated to each Ag, again leading to a distorted tetrahedral coordination.

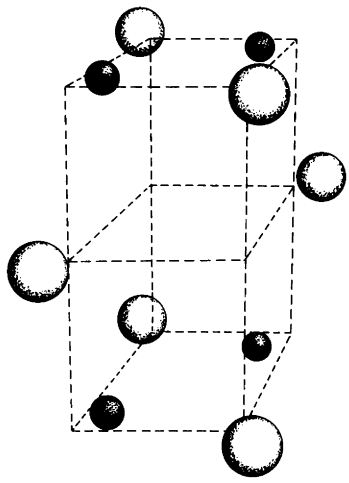

Fig. 9. A model for an $Ag_4I_6^{2-}$ complex based on the cubane structure and consistent with the scattering data for the 1.5:1 solution.

If we assume that AgI_3^{2-} and cubane-like $Ag_4I_5^-$ complexes are the only ones formed in the solutions investigated here, their concentrations in each solution can be estimated from the stoichiometry. Theoretical curves calculated with the use of the parameter values derived for the idealized models (Table 2) can then be compared with observed values. The results for the $s \cdot i(s)$ functions are shown in Fig. 1a and for the RDF's in Fig. 7a. The fairly good agreement between observed and calculated values over the whole range of concentrations supports the assumption of a cubane-like structure for the polynuclear complexes in the solutions. The actual complexes would probably be distorted and not have the high symmetry assumed for the idealized model, and an improved agreement could, presumably, be reached by adjustment of the parameters used. However, other similar complexes with the same basic structure can also be shown to be consistent with the data and cannot be excluded. For example, an $Ag_4I_6^{2-}$ complex with the structure shown in Fig. 9, consisting of two of the cubes in Fig. 8 with two of the Ag positions unoccupied, leads to equally good agreement between observed and calculated values for the 1.5:1 solution.[10]

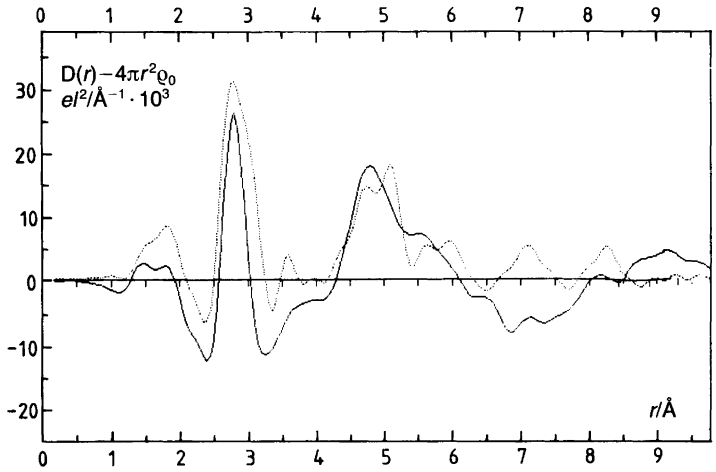

Fig. 11. A comparison between the sum of the peak shapes for the $Ag_3I_6^{3-}$ complex (dotted line), found in the crystal structure of $NaAgI_2 \cdot 4DMSO$, and for the $D(r)-4\pi r^2\varrho_0$ function for the 2:1 solution (solid line). For DMSO, the parameters given in Table 2 have been used.

In order to obtain a better basis for the formulation of possible structural models attempts were made to obtain crystals from the investigated solutions which might contain discrete polynuclear complexes. From DMSO solutions with an I:Ag ratio of about 2.7, crystals with the composition $NaAgI_2 \cdot 4DMSO$ could be prepared which, according to a crystal structure determination,[11] contain discrete complexes, $Ag_3I_6^{3-}$, built up as shown in Fig. 10. Two face-sharing AgI_4 tetrahedra are joined by a common edge to a planar AgI_3 triangle. For the three-coordinated Ag, the Ag−I distances are 2.80, 2.76 and 2.67 Å with an average value of 2.74 Å, which is close to the value 2.78 Å found here for AgI_3^{2-} in solution. For the tetrahedrally coordinated Ag atoms, the Ag−I distances range from 2.66 to 3.08 Å, with an average of 2.93 Å. The Ag−Ag distances between the two tetrahedrally coordinated Ag atoms are 2.96 Å, and the distances between any of these and the three-coordinated Ag atoms are 3.49 Å. Using the parameter values from the crystal structure determination the sum of the peak shapes for this $Ag_3I_6^{3-}$ complex was calculated, and it is compared in Fig. 11 with the RDF for the 2:1 solution. The shapes of the 2.8 and 4.8 Å peaks indicate a larger spread of Ag−I and I−I distances in the theoretical model than is observed for the solution. The many long distances within the $Ag_3I_6^{3-}$ complex seem to be indicated in the RDF for the solution but are much less pronounced, although this is a difference which to some extent can be adjusted by an increase in the assumed rms variations of the distances in the model. The comparison indicates that the $Ag_3I_6^{3-}$ complex may be present to some extent in the solution but cannot be a dominant complex.

The results demonstrate the difficulties in arriving at a unique interpretation of the scattering data. They result from the likely occurrence of more than one type of polynuclear complex in the solutions and from the contribution of several types of distances to the same peaks in the RDF's. The short Ag−Ag distances cannot be resolved from the Ag−I bonding distances, and long Ag−I distances within the complexes fall in the same region as the I−I contact distances. Because of the large number of parameters involved and the limited information contained in the one-dimensional solution diffraction curves, further refinement does not seem meaningful and would probably lead to overinterpretation of the data.

Conclusions

In the absence of iodide, the Ag^+ ion in DMSO solution is coordinated to four DMSO molecules by Ag−O bonds. On addition of an excess of iodide, planar trigonal AgI_3^{2-} complexes are formed, apparently without any coordinated solvent molecules. At lower I:Ag ratios polynuclear complexes form with the Ag^+ ions joined by I^- bridges and with short Ag−Ag distances of about 3.0 Å. According to the scattering data, the same

types of complexes occur in both DMSO and DMF solutions and are thus not dependent on the solvent molecules.

The Ag atoms have trigonal pyramidal or tetrahedral coordination in the polynuclear complexes, and the scattering data are consistent with cubane-like structures for the complexes. It seems likely, however, that more than one type of polynuclear complex is present in the solutions and the scattering data do not lead to a unique interpretation of the structures.

Acknowledgements. This work has been financially supported by the Swedish Natural Science Research Council. A grant from *Knut och Alice Wallenbergs Stiftelse,* which made it possible to purchase the Rigaku Theta–Theta diffractometer, is gratefully acknowledged. We thank Mr. Ernst Hansen and Mrs. Irena Desselberger for skilful technical assistance.

References

1. Rumbaut, N. A. and Peeters, H. L. *Bull. Soc. Chim. Belg. 76* (1967) 33.
2. Le Demezet, M., Madec, C. and L'Her, M. *Bull. Soc. Chim. Fr.* (1970) 365.
3. Gaizer, F. *Magy. Kem. Foly. 78* (1972) 54.
4. Gaizer, F. *Polyhedron 4* (1985) 1913.
5. Johansson, G. *Acta Chem. Scand. 25* (1971) 2787; *Ibid. 20* (1966) 553.
6. Johansson, G. and Sandström, M. *Chem. Scr. 4* (1973) 195.
7. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1968, Vol. 3; *Ibid.* 1974, Vol. 4.
8. Teo, B.-K. and Calabrese, J. C. *J. Am. Chem. Soc. 97* (1975) 1256.
9. Norén, B. and Oskarsson, Å. *Acta Chem. Scand., Ser. A 39* (1985) 701.
10. Gaizer, F. and Johansson, G. *Magy. Kem. Foly. 92* (1986) 193.
11. Johansson, G. *To be published.*

Received September 11, 1987.