

The Coordination and Complex Formation of Silver(I) in Aqueous Perchlorate, Nitrate, and Iodide Solutions

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X-Ray scattering data, collected in a θ - θ diffractometer at 25 °C from 3 and 9 M aqueous solutions of silver perchlorate and silver nitrate, are shown to be consistent with a coordination number of four for the silver ion, with Ag-O bonding distances of about 2.4 Å. In the nitrate solutions the anions are coordinated to Ag⁺ as monodentate ligands. In the perchlorate solutions the perchlorate ion does not enter the first coordination sphere except when required for stoichiometric reasons. The concentrated solutions can dissolve silver iodide up to a concentration of about 1 M. The scattering data indicate that in these solutions "cationic complexes" Ag₄I³⁺ are formed having well-defined Ag-I distances of 2.79 Å, but no distinct Ag-Ag distances.

The hydration number of silver(I) in aqueous solution has been determined by several methods but the results are not consistent and seem to depend on the method employed.¹ In a recent X-ray diffraction study of concentrated (~3.5 M) aqueous silver perchlorate and nitrate solutions¹ the Ag-O(H₂O) distances were found to be 2.41-2.45 Å and a model of two water molecules coordinated to Ag⁺ was used to explain the experimental data. Later, electron spin echo modulation (ESEM) studies on glassy and polycrystalline ice matrices of Ag salts² showed the Ag⁺ ion to be surrounded by eight equivalent deuterons at 3.1 Å, corresponding to a tetrahedral coordination of water molecules around Ag⁺.

Very recently, an extended X-ray absorption fine structure (EXAFS) study has been performed on concentrated aqueous silver perchlorate and nitrate solutions,³ which indicated that three to four water molecules are bound to each Ag⁺ ion with Ag-O distances of 2.31-2.36 Å.

Raman and infrared spectra from aqueous AgNO₃ solutions with various solute concentrations have been interpreted in terms of an equilibrium between hydrated ions and ion pairs Ag⁺NO₃⁻.⁴ Diffusion data for concentrated AgNO₃ solutions also indicate a variable extent of ion-pairing in concentrated solutions.⁵ On the other hand, Raman spectral studies of concentrated aqueous AgClO₄ solutions have given no evidence for Ag⁺ClO₄⁻ pairing.⁶

In the previous X-ray diffraction study,¹ which was made on a 3.5 M AgNO₃ solution, no direct ion-pairing was assumed, and one aim of the present work has been to reexamine the coordination around Ag⁺ in aqueous AgNO₃ and AgClO₄ solutions with the use of X-ray diffraction techniques. The previous measurements have been extended to more concentrated solutions (~9 M), where the extent of ion pairing and the relative contributions to the scattering from interactions within the Ag⁺ coordination sphere should be more pronounced than in the more dilute solutions.

Leden and Parck⁷ studied the solubility of AgI in aqueous 4 M (Ag,Na)ClO₄ solutions. The pronounced increase in AgI solubility with increasing AgClO₄ concentration in the range 10⁻³–4 M was attributed to the formation of cationic complexes Ag_mI_n^{(m-n)+} with a maximum ionic charge of 3+. Self-diffusion studies⁸ indicated that no condensation into polynuclear (*i.e.* polyiodic) species occurs in solutions of similar composition, and the 3+ complex should thus be Ag₄I³⁺. Lieser⁹ determined the solubility of silver halide in aqueous AgNO₃ solutions of concentrations up to 2 M. The cationic complexes Ag₂I⁺ and Ag₃I²⁺ were assumed to account for the shape of the solubility curve for AgI. The nature of these proposed complexes is, however, rather unclear. Crystalline compounds Ag₃I(ClO₄)₂·2H₂O, Ag₂INO₃ and Ag₃I(NO₃)₂, which have been isolated from solutions of this kind, contain no discrete cationic complexes and their structures seem rather to be determined by anion packing geometries.^{10–12} A recent X-ray diffraction study¹³ of (K,Na)NO₃ based melts containing dissolved AgNO₃ and AgI at 280 °C revealed a preferential association with an average of four Ag⁺ to every I⁻ with well-defined Ag–I bond distances of 2.8 Å in agreement with previous interpretations of thermodynamic data in terms of Ag₄I³⁺ complexes.¹⁴ No Ag–Ag correlation in the coordination sphere of I⁻ could be observed, however. These remarkable structural features raise doubts about the applicability of classical coordination chemistry concepts to the proposed Ag₄I³⁺ complexes, and it is of interest to investigate if these features result from some fundamental properties of ionic liquids or are characteristic of Ag_nI⁽ⁿ⁻¹⁾⁺ species in gener-

al. Hence, another aim of this investigation has been to clarify the structures of the proposed cationic complexes in concentrated AgClO₄–AgI–H₂O and AgNO₃–AgI–H₂O solutions by comparing the X-ray scattering from such solutions with that from iodide-free solutions.

EXPERIMENTAL

All solutions were prepared by dissolving a weighed amount of AgClO₄, AgNO₃ or AgI (Merck, *pro analysi*) into a known volume of distilled water. The density of the solutions was measured by pycnometers. The compositions are given in Table 1.

MoK α radiation ($\lambda=0.7107$ Å) was used for the X-ray diffraction measurements. The scattered intensities were collected over the range $0.3 \leq s \leq 16.0$ Å⁻¹ ($s=4\pi \sin \theta/\lambda$). The measurements were repeated once to check the reproducibility of the data until total counts at each data point amounted to at least 100 000 counts. Details of the measurements and the diffractometer have previously been described.^{15,16} Samples A, B and D were measured in Göteborg and the others in Stockholm. Samples A, B and D were replaced several times during the measurements because of the reduction of Ag⁺ ions by the radiation.

Data treatment. Experimental intensities were corrected for background, absorption,¹⁷ double scattering,¹⁸ polarization and Compton scatterings,¹⁹ and were scaled to absolute units by comparison of the measured intensities with the total independent scattering in the high angle region ($s \geq 13.5$ Å⁻¹). The scattering factors for neutral atoms were taken from the International Tables for X-Ray Crystallography.²⁰ The values for incoherent scattering factors were taken from

Table 1. The composition of the sample solutions (mol dm⁻³). *V* is the stoichiometric volume (Å³) per silver atom, μ the linear absorption coefficient (cm⁻¹) and *d* the density (g cm⁻³).

Samples	Ag	I	Cl	N	O	H	<i>V</i>	<i>d</i>	μ
A. 3 M AgClO ₄	2.94		2.94		59.7	95.7	564	1.47	10.7
B. 9 M AgClO ₄	9.34		9.34		68.2	61.6	178	2.49	31.2
C. 9 M AgClO ₄ –1 M AgI	10.1	1.05	9.04		68.9	65.5	165	2.73	38.2
D. 3 M AgNO ₃	3.02			3.02	59.1	100	551	1.47	10.9
E. 9 M AgNO ₃	8.84			8.84	64.4	75.7	188	2.18	26.1
F. 11 M AgNO ₃ –1 M AgI	11.6	0.907		10.7	63.8	63.5	143	2.60	38.1

those given by Cromer and Mann²¹ for Ag and N, by Cromer²² for O, Cl and I, by Compton and Allison²³ for H. The incoherent scattering factors were corrected for the Breit-Dirac effect. Correction for anomalous dispersion was applied to all atoms, values of which were taken from the International Tables.²⁰

The electronic radial distribution functions, $D(r)$, were calculated by the conventional Fourier transform,

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_{\max}} s \cdot i(s) M(s) \sin(rs) ds \quad (1)$$

Here the modification function $M(s) = [f_{\text{Ag}}(0)^2 / f_{\text{Ag}}(s)^2] \exp(-0.003s^2)$, was used. Spurious ripples observed in a hard-core region of the $D(r)$ function were removed in the usual manner.¹⁹

Theoretical reduced intensities, $i(s)_{\text{calc}}$, for the models employed consist of two parts.

$$i(s)_{\text{calc}} = i(s)_1 + i(s)_2 \quad (2)$$

The first term, $i(s)_1$, includes contributions from short-range discrete structures given by the well-known Debye equation,

$$i(s)_1 = \sum n_j \sum \sum n_{pq} f_p f_q [\sin(sr_{pq}) / (sr_{pq})] \exp(-b_{pq}s^2) \quad (3)$$

with the distance, r_{pq} , the temperature coefficient, b_{pq} , related to the r.m.s. value $l_{pq} = (2 \cdot b_{pq})^{1/2}$ for the variation of the distance around an average, and the number of interactions, n_{pq} . n_j is the number of structural units "j" in the stoichiometric unit of volume, V . The second term, $i(s)_2$, includes intermolecular interactions approximated by an even electron distribution beyond a sphere of radius R_j surrounding the discrete structure.¹⁹

$$i(s)_2 =$$

$$\sum_j 4\pi V^{-1} [sR_j \cos(sR_j) - \sin(sR_j)] \cdot s^{-3} \cdot \exp(-B_j \cdot s^2) \cdot n_j \sum_p f_p (sr_p)^{-1} \sin(sr_p) \cdot \exp(-b_p \cdot s^2) \cdot \sum_i n_i f_i \quad (4)$$

Here the distance from the center of the structural unit "j" to the atom "p" of that unit is r_p with a corresponding temperature coefficient b_p , and n_i denotes the number of atoms "i" in V . An artificial temperature coefficient, B_j , was intro-

duced to account for the gradual emergence of the continuum. These calculations were carried out by the KURVLR program.¹⁹

For a direct analysis of the reduced intensities a least-squares method was applied, the function

$$U = \sum_{s_{\min}}^{s_{\max}} w(s) [i(s)_{\text{obs}} - i(s)_{\text{calc}}]^2 \quad (5)$$

being minimized by means of the NLPLSQ program.²⁴ A weighting function $w(s) = s^4$ was used. The s_{\min} and s_{\max} values are the lower and the upper limits of the s -range used in the refinement.

RESULTS AND DISCUSSION

Radial Distribution Functions (RDFs)

Fig. 1 (dots) shows experimental reduced intensities, $i(s)$, multiplied by s , for the solutions investigated. Figs. 2 and 3 (solid lines) give the corresponding radial distribution curves $D(r)$ and $D(r) - 4\pi r^2 \rho_0$. Each data set has been normalized to a stoichiometric unit of volume containing one Ag atom (Table 1).

Silver perchlorate solutions. In the distribution curves of 3 M and 9 M silver perchlorate solutions (A and B in Figs. 2 and 3), the expected Cl-O peak in the perchlorate group appears at about 1.45 Å. A second peak around 2.4 Å in both curves can be attributed to Ag-O interactions within the hydrated Ag⁺ ions and, in part, to O-O interactions within the tetrahedral perchlorate groups ($1.45 \text{ Å} \times (8/3)^{1/2} = 2.37 \text{ Å}$). In the 3 M solution the 2.9 Å peak is typical for aqueous solutions,²⁵ and can be attributed to first neighbour H₂O-H₂O interactions in the bulk water structure and to O-H₂O interactions between the oxoanions and surrounding water molecules.^{26,27} For the 9 M solution, the 2.9 Å peak is less pronounced, as expected. Several long-range interactions can contribute to the broad peak at 3.5-4.8 Å for the 3 M solution. For the 9 M solution the corresponding peak appears to be slightly enhanced at about 3.6 Å, which probably results from the formation of ion pairs, Ag⁺ClO₄⁻. This will be discussed in more detail later.

Silver nitrate solutions. The radial distribution curves for 3 and 9 M aqueous silver nitrate solutions (D and E) are shown in Figs. 2 and 3. A

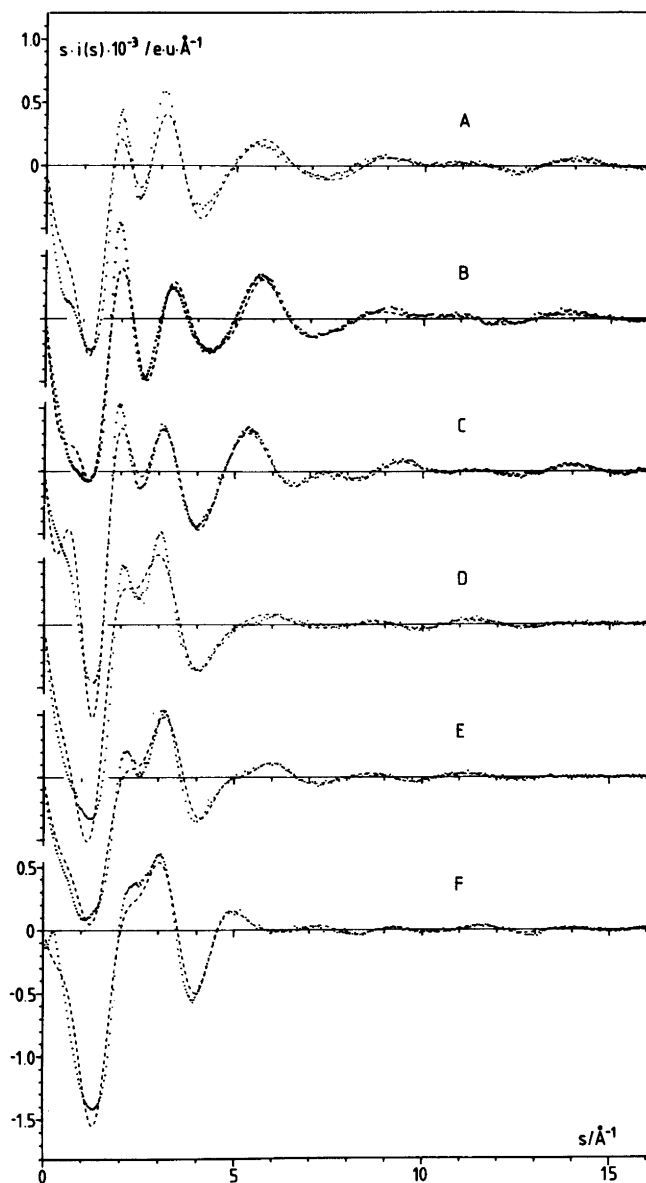


Fig. 1. Observed (dots) and calculated (dashed lines) $s \cdot i(s)$ values for the solutions investigated. Parameters given in Table 3 were used for the theoretical curves. All values are normalized to a stoichiometric unit of volume containing one Ag atom (Table 1).

small peak at $\sim 1.2 \text{ \AA}$, can be assigned to the N–O bonds of the nitrate group. The second peak, at 2.4 \AA , corresponds to Ag–O bonds within hydrated Ag^+ ions and, in part, to O–O interactions within the NO_3^- group ($1.2 \text{ \AA} \times 3^2 = 2.1 \text{ \AA}$). The 2.9 \AA peak is due to $\text{H}_2\text{O} - \text{H}_2\text{O}$

interactions in the water structure and to interactions between oxygen atoms in the nitrate group and surrounding water molecules, but also, as will be discussed later, to Ag–N and Ag–O interactions within Ag^+NO_3^- ion pairs. The broad peaks at $3.75 - 4.5 \text{ \AA}$ observed for the perchlorate

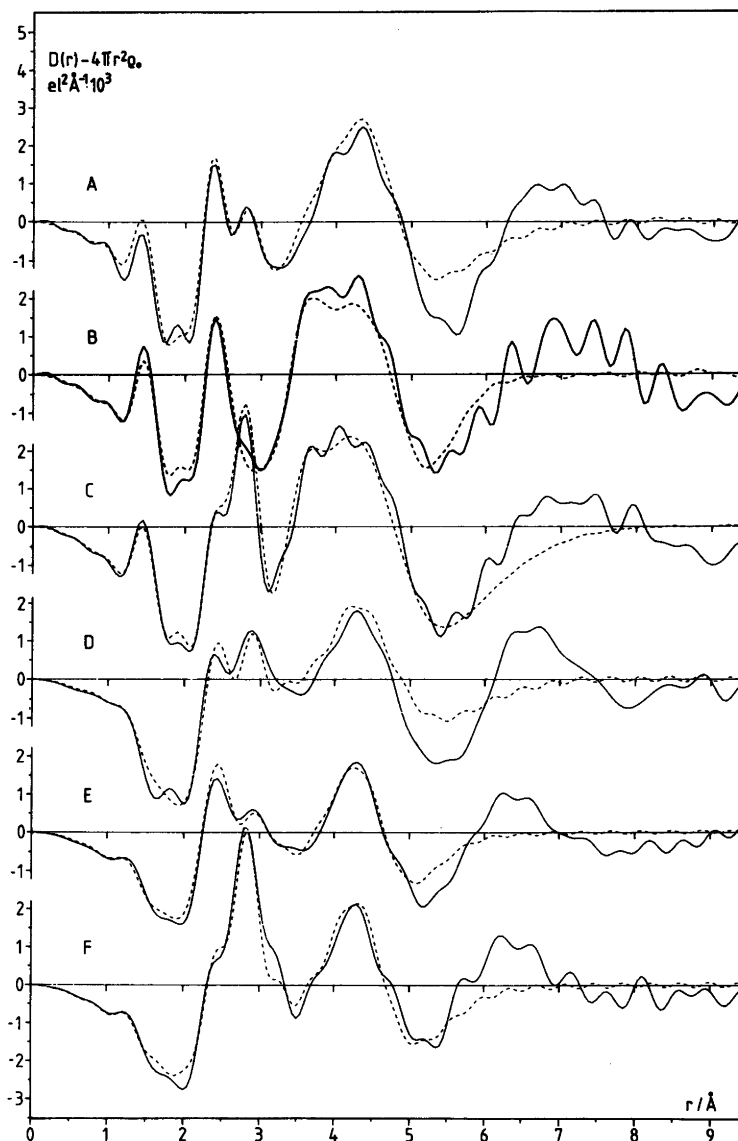


Fig. 2. $D(r) - 4\pi r^2 \rho_0$ functions. Experimental curves (solid lines) are compared with theoretical curves (dashed lines) obtained with the parameters given in Table 3. Normalization according to Table 1.

solutions appear also for the nitrate solutions, but, for the 9 M solution, they are less pronounced.

Solutions with dissolved silver iodide. The radial distribution curves for the two solutions AgNO₃-AgI and AgClO₄-AgI (C and F) are shown in Figs. 2 and 3. The RDF's are very similar to those of the 9 M AgClO₄ and the 9 M

AgNO₃ solutions, except for a distinct peak at 2.8 Å. This distance is close to the sum of the covalent radii of Ag and I, which is 2.85 Å,²⁸ and also to Ag-I distances found in several AgI containing crystals.¹⁰ Hence, the 2.8 Å peak is taken as evidence of the existence of well-defined Ag-I bonds in the AgClO₄-AgI and the AgNO₃-AgI solutions.

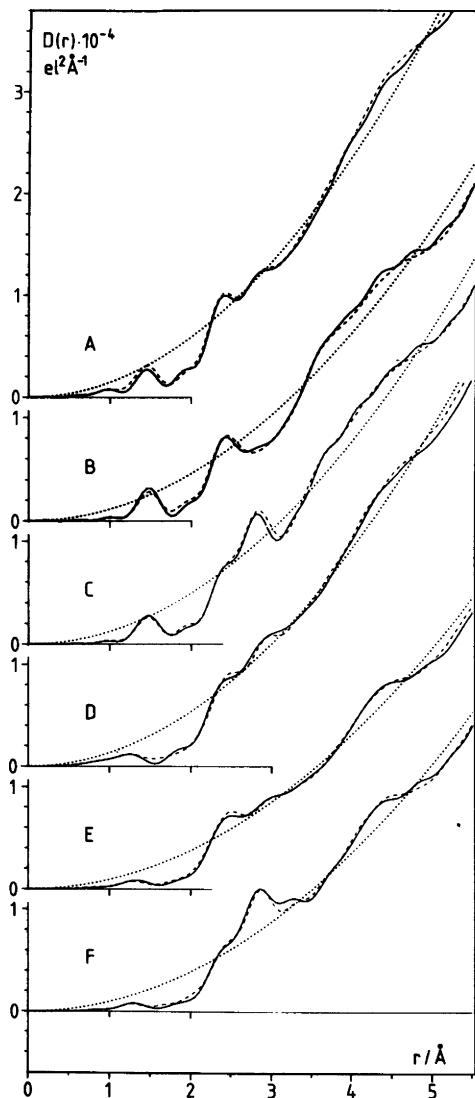


Fig. 3. $D(r)$ functions. Experimental curves (solid lines), theoretical curves (dashed lines) obtained with parameters given in Table 3, and $4\pi r^2 \rho_0$ functions (dotted lines) are given. Normalization as in Table 1.

Ag–O Coordination

The peak due to the Ag–O bonds within the hydrated Ag^+ ions occurs at around 2.40 Å irrespective of the anions and of the concentration of Ag^+ (Figs. 2 and 3). The value of 2.40 Å is in good agreement with values obtained from

the previous X-ray diffraction,¹ EXAFS³ and ESEM² studies.

The crystal structures of many oxygen-coordinated Ag compounds have been determined although no structure has been found to contain hydrated Ag^+ ions. Ag–O distances and coordination geometries found are summarized in Table 2. Two-fold oxygen coordination leads to a linear structure with the Ag–O distances falling within the range 2.04–2.20 Å. When four or more oxygen atoms are bonded to Ag^+ , the Ag^+ ions tend to have regular or distorted tetrahedral, octahedral, or antiprism geometries. For each coordination number the Ag–O bond lengths fall within a limited range with average values of 2.13, 2.40, 2.48 and 2.50 Å for two-, four-, five- and six-fold coordination, respectively (Table 2). Thus the value of 2.40 Å found for the Ag–O distances in the aqueous solutions indicates a fourfold rather than a twofold coordination. In the solid state, the geometry of Ag^+ ions coordinated by four or more oxygen atoms is irregular and depends on counter ions in the compounds. In aqueous solutions an irregular geometry would seem less likely though it might occur instantaneously. A distorted octahedral model for an AgO_6 moiety has been proposed for molten Ag_2SO_4 .⁴⁶ Our preliminary analysis of the peak for the 9 M AgClO_4 solution showed, however, that the octahedral model was not applicable and the EXAFS study has supported this conclusion.³ The solution scattering measurements thus seem to be most consistent with a fourfold coordination around Ag^+ .

A further more quantitative analysis can be done in several ways, for example, by a direct analysis of the $s\cdot i(s)$ curves, resolving them into discrete frequencies by means of a least-squares procedure or by fitting calculated peaks for assumed intramolecular interactions to resolved peaks in the experimental $D(r)$ functions.¹⁹ The many different types of interactions, that have to be taken into account – the hydration of Ag^+ and its complex formation with the anions, the structure and hydration of the anions, remaining water structure etc. – require the introduction of a large number of parameters, which will not all be independent in a least-squares refinement procedure using the $s\cdot i(s)$ curves. Moreover, the Ag–O interactions cannot be expected to be solely dominant in the high-angle parts of the curves. Although such least-squares refinements

Table 2. Ag–O bond lengths (Å) and configurations in some O-coordinated Ag compounds.

Compounds	Ag–O distances	Mean values	Refs.
2-fold O-coordination – Linear			
NaAg ₃ O ₂	2.12(×2) 2.10(×2)	2.12 2.10	29
AgCrO ₂	2.04(×2)	2.04	30
LiAg ₃ O ₂	2.17(×2) 2.15(×2)	2.17 2.15	31
Ag ₈ W ₄ O ₁₆	Ag(6) 2.20(×2)	2.20	32
4-fold O-coordination – Distorted tetrahedral			
Ag ₃ P ₃ O ₉ ·H ₂ O	Ag(3) 2.452, 2.455, 2.465, 2.468	2.460	33
Ag ₈ W ₄ O ₁₆	Ag(4) 2.32(×2), 2.28(×2) Ag(5) 2.27(×2), 2.31(×2)	2.30 2.29	32
AgClO ₄	2.504(×4)	2.504	34
Ag ₂ CO ₃	2.254, 2.329, 2.479, 2.697	2.440	35
Ag ₃ PO ₄	2.345(×2), 2.403(×2)	2.374	36
4-fold O-coordination – Square planar			
AgCo ₃ H ₂ (AsO ₄) ₃	2.478(×2), 2.400(×2)	2.439	37
AgZn ₃ H ₂ (AsO ₄) ₃	2.474(×2), 2.397(×2)	2.436	37
5-fold O-coordination			
Ag ₃ P ₃ O ₉ ·H ₂ O	Ag(1) 2.333, 2.389, 2.408, 2.536, 2.645 Ag(2) 2.343, 2.387, 2.411, 2.535, 2.636	2.462 2.462	33
Te(OH) ₆ ·2Ag ₂ HPO ₄	Ag(1) 2.552, 2.434, 2.538, 2.507, 2.419 Ag(2) 2.427, 2.360, 2.478, 2.500, 2.701	2.490 2.493	38
Ag ₂ W ₂ O ₇	Ag(1) 2.31, 2.35, 2.37, 2.50, 2.86 Ag(2) 2.21, 2.23, 2.37, 2.75, 2.93	2.47 2.50	39
AgCoPO ₄	Ag(1) 2.314, 2.327, 2.582, 2.633, 2.678	2.507	40
6-fold O-coordination – Distorted octahedral			
Ag ₂ SO ₄	2.433(×2), 2.686(×2), 2.408(×2)	2.509	41
Ag ₂ Cr ₂ O ₇	Ag(1) 2.472, 2.415, 2.392, 2.456, 2.419, 2.595 Ag(2) 2.374, 2.393, 2.676, 2.535, 2.511, 2.499	2.458 2.498	42
Ag ₂ Mo ₂ O ₇	Ag(1) 2.28, 2.38, 2.46, 2.53, 2.62, 2.67 Ag(2) 2.32, 2.32, 2.43, 2.45, 2.76, 2.76	2.49 2.51	39
Ag ₃ P ₃ O ₉ ·H ₂ O	Ag(3) 2.26(×2), 2.68(×2), 2.75(×2)	2.56	33
7 or more-fold O-coordination – Anti-prism			
Ag ₈ W ₄ O ₁₆	Ag(1) 2.32, 2.50, 2.52, 2.55, 2.68, 2.75, 3.07 Ag(2) 2.38, 2.27, 2.57, 2.66, 2.68, 2.99	2.64 2.71	32
Ag[(CH ₃) ₂ SO] ₂ ClO ₄	2.362, 2.504, 2.354, 2.489, 2.411, 2.741	2.477	43
Ag ₂ (C ₂ H ₂ O ₄) ₂	2.373, 2.213, 2.225, 2.668, 2.851	2.466	44
BaAgP ₃ O ₉ ·4H ₂ O	2.370, 2.445, 2.531, 2.634, 2.629, 2.706	2.493	45

were carried out and the results supported a coordination number of four for Ag⁺, we have chosen an alternative way of analyzing the data.

The RDFs can be corrected for contributions from the known intramolecular interactions within NO₃⁻ and ClO₄⁻. The 2.4 Å peak will then contain contributions only from Ag–O bonding distances. The peaks are not, however, well resolved from the longer hydrogen bond distances O–H₂O and H₂O–H₂O, which are ex-

pected to occur around 2.8 Å. The 2.4 Å peak is especially poorly resolved in the nitrate solutions, where the complex formation between Ag⁺ and NO₃⁻ is expected to occur with resulting Ag⁺–NO₃⁻ distances (Ag–N and Ag–O) in the region around 3 Å. An approximate elimination of contributions from O–O contact distances (H₂O–H₂O and anion–H₂O) extending into the region of the 2.4 Å peaks can be achieved by calculating differences between the RDFs of the

Table 3. Parameters used for calculation of the theoretical curves in Figs. 1–3. r =distance in Å, b =temperature coefficient in Å² and n =number of interactions. n refers to one Ag atom in cases where nothing else is stated in the Table. R is the radius in Å of the spherical hole in the continuum assumed to be occupied by a discrete complex. B is the corresponding temperature coefficient.

Solution		A 3 M	B 9 M	C 9 M–1 M AgI
a. Silver perchlorate solutions				
Ag–H ₂ O(O)	r	2.38(1)	2.43(1)	2.48(1)
	b	0.013(1)	0.013(1)	0.012(1)
	n^a	4	4	4
ClO ₄ [–]	$r_{\text{Cl-O}}$	1.439(5)	1.460(3)	1.446(4)
	$b_{\text{Cl-O}^a}$	0.0008	0.0008	0.0008
	$b_{\text{O-O}^a}$	0.0012	0.0012	0.0012
Ag–I	r			2.81(1)
	b			0.0064
	n^b			3.8(1)
O...O	r	2.85	2.99	2.99
	b	0.01	0.015	0.01
	n^c	3.0	3.0	2.8
Cl...O	r	3.75	3.7	3.6
	b	0.05	0.04	0.05
	n^d	7.5	7.9	8.0
Ag...O	r	4.4	4.4	4.3
	b	0.04	0.06	0.06
	n	8.0	9.0	6.6
Ag ⁺	R	4.9	5.1	4.9
	B	0.37	0.1	0.6
ClO ₄ [–]	R	3.1	3.3	3.2
	B	0.05	0.06	0.05
H ₂ O	R	3.1	2.9	2.9
	B	0.02	0.03	0.03
Ag–O–ClO ₃	$r_{\text{Ag-Cl}^a}$		3.52	3.52
	$b_{\text{Ag-Cl}^a}$		0.02	0.02
	$n_{\text{Ag-Cl}^a}$		1	1
<hr/>				
Solution:		D 3 M	E 9 M	F 11 M–1 M AgI
b. Silver nitrate solutions				
Ag–H ₂ O(O)	r	2.42(1)	2.43(1)	2.46
	b	0.010(1)	0.010(1)	0.01
	n^a	4	4	4
NO ₃ [–]	$r_{\text{N-O}^a}$	1.26	1.26	1.26
	$b_{\text{N-O}^a}$	0.00085	0.00085	0.00085
	$b_{\text{O-O}^a}$	0.0010	0.0010	0.0010
Ag–I	r			2.82(2)
	b			0.004(1)
	n^b			4.3(2)
O...O	r	2.86	2.89	3.00
	b	0.005	0.01	0.01
	n^c	1.7	2.7	3.2

N...O	<i>r</i>	3.5	3.4	3.3
	<i>b</i>	0.016	0.013	0.013
	<i>n</i> ^c	11.0	7.2	8.0
Ag...O	<i>r</i>	4.30	4.36	4.30
	<i>b</i>	0.10	0.05	0.05
	<i>n</i>	5.0	4.9	6.5
Ag...Ag	<i>r</i>		3.78	3.67
	<i>b</i>		0.055	0.062
	<i>n</i> ^f		0.52	0.59
Ag ⁺	<i>R</i>	4.9	4.8	4.8
	<i>B</i>	0.37	0.13	0.2
NO ₃ ⁻	<i>R</i>	2.7	3.0	3.0
	<i>B</i>	0.01	0.01	0.01
H ₂ O	<i>R</i>	3.0	3.1	3.1
	<i>B</i>	0.1	0.05	0.05
Ag-O-NO ₂	<i>r</i> _{Ag-N^a}	3.13	3.13	3.13
	<i>b</i> _{Ag-N^a}	0.022	0.022	0.022
	<i>n</i> _{Ag-N^a}	1	1	1

^a Not varied. ^b Per I atom. ^c Number of O neighbours around each O atom. ^d Per Cl atom. ^e Per N atom. ^f Number of Ag atoms around each Ag.

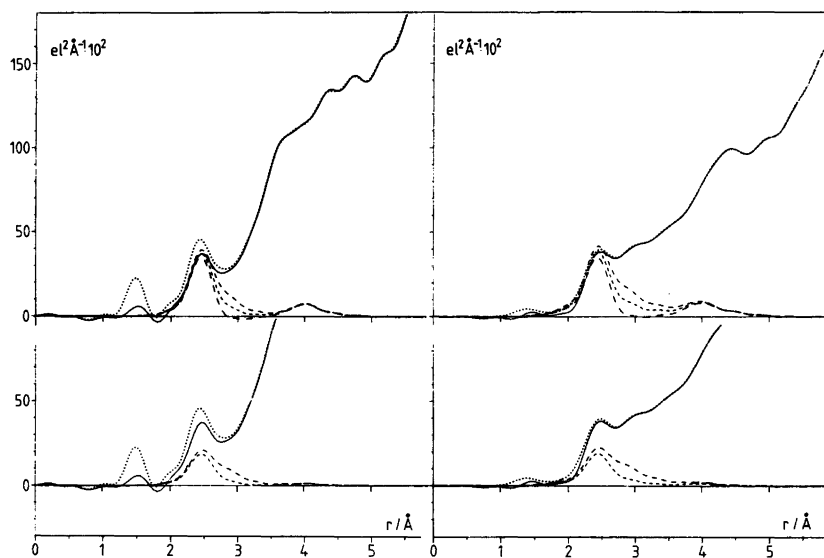


Fig. 4. Differences between $D(r)$ functions for the 9 M and the 3 M perchlorate solutions (left) and nitrate solutions (right). For each solution the measured data have been normalized to stoichiometric volumes containing equal numbers of oxygen atoms. Dotted lines give differences obtained without, and solid lines with, corrections for intramolecular anion interactions. In the upper drawings comparisons are made with peaks (short dashes) calculated for a coordination number of four for Ag⁺ ($r=2.43$ Å, $b=0.008$ Å², $n=4$). The effect that would be expected if the number of oxygen neighbours at ~ 2.8 Å around each oxygen differed by one between the two solutions is shown (long dashes). In the lower drawings corresponding peak shapes are given for a coordination number of two for Ag⁺.

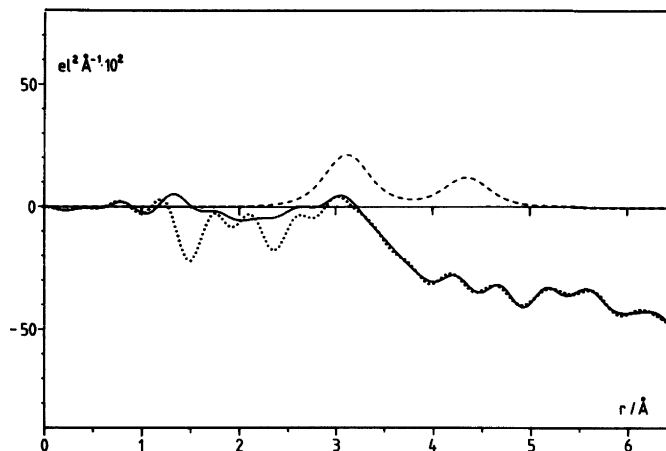


Fig. 5. The difference between the $D(r)$ functions for the 3 M AgNO_3 and the 3 M AgClO_4 solutions, normalized as in Table 1, before (dotted line) and after (solid line) corrections for intramolecular anion interactions. The calculated peak (dashed line) corresponds to interactions (Ag-N , Ag-O_2 , Ag-O_3) in an ion pair Ag^+NO_3^- as illustrated in Fig. 6.

9 M and the 3 M solutions, choosing the stoichiometric units of volume to contain equal numbers of oxygen atoms. If the average surrounding of an oxygen atom is unchanged when the concentration is increased from 3 M to 9 M the contributions from O–O contact distances will cancel in the difference curves. Since the increase in concentration leads to a replacement of water oxygens by anion oxygens some changes are likely to occur, but the effects of these that extend into the region of the 2.4 Å peak should be much less than in the original RDFs.

The results of the calculations are shown in Fig. 4. The 2.4 Å peaks are now, as expected, better resolved towards longer distances. They are compared with calculated peaks for an assumed fourfold or twofold coordination around Ag^+ . In order to estimate the effect of possible differences in the average number of oxygen neighbours surrounding each oxygen in the two solutions corresponding peak shapes are included in the drawings in Fig. 4. The results show that a coordination number of four is in excellent agreement with the difference curves. Also, it seems obvious that no reasonable assumptions about differences in oxygen surroundings in the two solutions can bring the experimental curves into agreement with curves calculated for a coordination number of two.

Ion-pair Formation

A similar difference curve (Fig. 5) between the 3 M nitrate and the 3 M perchlorate solutions brings out more clearly the difference in the number of interactions for the two solutions in the region around 3 Å. It is already apparent from the $D(r)$ functions for the nitrate solutions (Figs. 2 and 3) and the difference curve in Fig. 4, when compared to the corresponding curves for the perchlorate solutions, that the number of contributions in the 3 Å region is larger in the nitrate solutions.

In Fig. 5 this difference is compared with a peak calculated for an assumed Ag-NO_3 pair formation as illustrated in Fig. 6 and including the Ag-N , Ag-O_2 and Ag-O_3 interactions. The comparison shows that the observed differences between the nitrate and the perchlorate

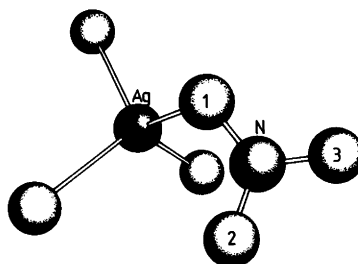


Fig. 6. Assumed model for the Ag^+NO_3^- ion pair.

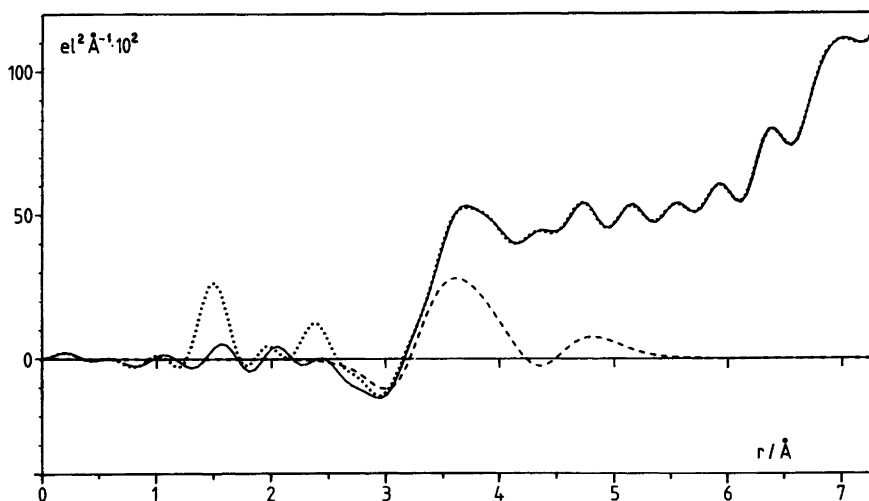


Fig. 7. The difference between the $D(r)$ functions for the 9 M AgClO_4 and the 9 M AgNO_3 solutions, normalized as in Table 1, before (dotted line) and after (solid line) corrections for intramolecular anion interactions. The calculated peak (dashed line) corresponds to interactions ($\text{Ag}-\text{Cl}$, $\text{Ag}-\text{O}_2$, $\text{Ag}-\text{O}_3$, $\text{Ag}-\text{O}_4$) in an ion pair $\text{Ag}^+\text{ClO}_4^-$ as illustrated in Fig. 8.

solutions is of a magnitude expected for a complex formation in which about one NO_3^- is bonded to each Ag^+ as a monodentate ligand.

The RDFs for the AgClO_4 solutions show a pronounced change, not observed for the nitrate solution, in the region around 3.6 Å, when the concentration is increased from 3 M to 9 M. In the 9 M perchlorate solution the total number of water molecules per Ag^+ is only 3.3 (Table 1), which is not sufficient to give Ag^+ a coordination number of four. For stoichiometric reasons, therefore, the perchlorate ion would be expected to enter the coordination sphere of Ag^+ . In Fig. 7 the difference between the RDFs for the 9 M perchlorate and the 9 M nitrate solutions is given, after corrections for intramolecular anion in-

teractions. It is compared to a theoretical curve calculated for a monodentate perchlorate bonding to Ag^+ similar to that found in the crystal structure of AgClO_4 ³⁴ and illustrated in Fig. 8. The $\text{Ag}-\text{Cl}$, $\text{Ag}-\text{O}_2$, $\text{Ag}-\text{O}_3$, and $\text{Ag}-\text{O}_4$ interactions are included in the calculated peak as are the $\text{Ag}-\text{N}$ and $\text{Ag}-\text{O}$ interactions for an Ag^+NO_3^- pair formation in the nitrate solution as discussed above. The comparison shows the effects in the experimental curve to occur at a distance and to be of a magnitude expected for a $\text{Ag}^+\text{ClO}_4^-$ ion pair.

The Iodide Containing Solutions

The effect of dissolving AgI into the concentrated aqueous AgNO_3 and AgClO_4 solutions is best brought out by the curves in Fig. 9, which give differences between the overall radial distribution functions for iodide-containing and iodide-free solutions, each referred to a stoichiometric volume containing equal numbers of oxygen atoms and corrected for the known intramolecular interactions. Each difference curve shows only one significant peak, which occurs at 2.8 Å and is obviously due to $\text{Ag}-\text{I}$ interactions. Comparison with calculated $\text{Ag}-\text{I}$

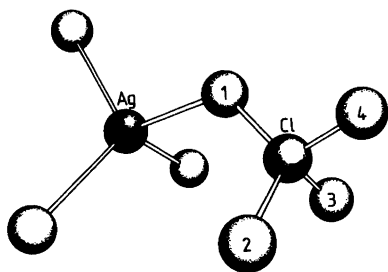


Fig. 8. Assumed model for the $\text{Ag}^+\text{ClO}_4^-$ ion pair.

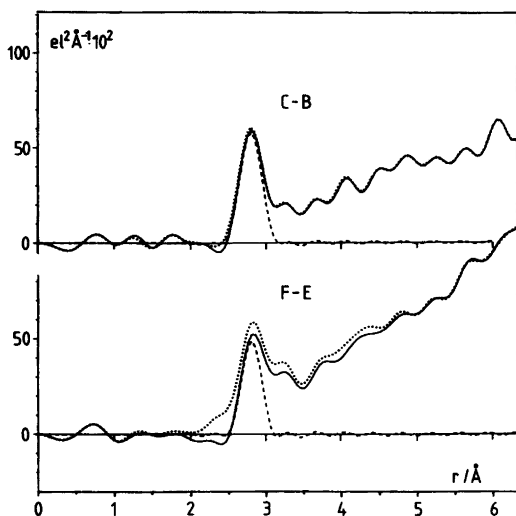


Fig. 9. Differences between $D(r)$ functions for the solutions with and without dissolved silver iodide. The measured data are normalized to stoichiometric volumes containing equal numbers of oxygen atoms. Dotted lines give differences obtained without, and solid lines with, corrections for intramolecular anion interactions, Ag-O interactions at 2.4 Å and interactions from Ag^+NO_3 ion pair formation. The calculated peak (dashed line) represents I-4Ag interactions ($r=2.79$ Å, $b=0.005$ Å²). Upper drawing perchlorate, lower drawing nitrate solutions.

peak shapes shows the number of Ag-I bonds per I atom to be close to four with an average distance of 2.79 Å. The peak shapes indicate well-defined distances, which correspond to those expected for covalent Ag-I bonds, and the results are in accordance with the complex formation model suggested by Leden and Parck⁷ for perchlorate solutions. A preliminary Raman spectroscopic investigation of the 9 M AgClO_4 and the AgClO_4 -AgI solutions shows the presence of a polarized band at about 130 cm^{-1} in the iodide containing solutions, which is not observed for the pure AgClO_4 solution. (A similar result has been obtained by Geske⁴⁷ for a 6 M AgClO_4 -AgI solution.) The observed frequency agrees with Ag-I stretching frequencies in AgI-KI melts⁴⁸ and in the AgI_2 ion.⁴⁹ It thus seems likely that the interatomic distance of 2.8 Å in the RDF is indeed due to well-defined covalent Ag-I bonds in the iodide containing solutions.

The apparent lack of well-defined Ag-Ag distances within the coordination sphere of Γ^- is remarkable. A tetrahedral Ag_4I^{3+} ion would, for instance, lead to six equivalent Ag-Ag distances at 4.6 Å, which should have been clearly observable. These structural characteristics are similar to those observed for (K,Na) NO_3 based molten salt mixtures containing AgNO_3 and AgI.¹³ The observed average of four Ag-I bonds per I can of course also be explained by a wide distribution of various species like Ag_3I^{2+} , Ag_4I^{3+} and Ag_5I^{4+} with the same Ag-I bond length (2.8 Å) but different Ag-Ag distances. The distribution of Ag-Ag distances in such complexes with different stoichiometries might be large enough to obscure any clearcut contribution to the RDF in *e.g.* the 4-5 Å region. However, an average number, \bar{m} , of 4 Ag^+ ligands per Γ^- was deduced already in 1 M AgClO_4 solutions from thermodynamic measurements.⁷ In (K,Na) NO_3 melts $\bar{m}=4$ was reached for the Ag(I) cation fraction $X_{\text{Ag}}=0.1$ (thermodynamic data)¹⁴ and this number was found by X-ray diffraction techniques¹³ to persist for $X_{\text{Ag}}=0.38$ and $X_{\text{Ag}}=0.75$. Hence, the maximum number of Ag^+ ligands bonded to Γ^- is most likely 4. It thus seems that the occurrence of four covalent Ag-I bonds to Γ^- without corresponding Ag-Ag interactions is characteristic for the so-called cationic complex Ag_4I^{3+} and is not the result of an effect imposed by the purely ionic environment in the molten salt. If so, the observations can be explained either by a model consisting of a number of different Ag_4I^{3+} species, all with Ag-I distances of 2.8 Å but with different coordination geometries, or by a dynamic model with the silver ions moving randomly on the surface of the Γ^- ion.

Final Models

An attempt to make a complete explanation of each scattering curve was based on the following starting model.

The Ag^+ ion was assumed to be tetrahedrally coordinated by four water molecules or anion oxygens. Interatomic distances of the anions, NO_3^- and ClO_4^- , were taken from crystal structure determinations and the corresponding temperature coefficients from values calculated from spectroscopic data.¹ In the nitrate solutions each Ag^+ was assumed to be associated with one NO_3^-

according to the model given in Fig. 6. A similar ion pair formation (Fig. 8) was assumed for the concentrated perchlorate solution. An O—O intermolecular interaction (hydrogen bonding distance) at about 2.8 Å was introduced to account for the packing of oxygen atoms around each O atom in the solution. For the iodide containing solutions an Ag—I interaction at 2.8 Å was also included.

The broad peaks in the region around 3–5 Å indicate a long-range structure in the solutions probably with contributions from many different types of interactions. They were approximated by Ag···O and anion···O interactions and, for the concentrated nitrate solutions, by Ag···Ag interactions analogous to what was used for molten AgNO₃.¹³

The corresponding parameters, distance, temperature coefficient, number of interactions, were refined in a least-squares procedure minimizing the expression given in eqn. (5). The final parameters for each solution are given in Table 3. Calculated intensities and distribution curves based on these values are in satisfactory agreement with experimental values as shown in Figs. 1–3.

The main value in these refinements is the demonstration that reasonable assumptions about intermolecular interactions lead to a reproduction of the experimental curves. Correlations between many of the different parameters introduced will occur, for example, between values assumed for the emergence of the continuum and long intermolecular interactions, which are greatly simplified in the model. Standard deviations obtained in the least-squares refinements are, therefore, of limited value and are not given in Table 3, except for some of the intramolecular interactions, which can be judged to be fairly independent of other parameters.

The final agreement between observed and calculated curves (Figs. 1–3) supports the previous conclusions about the coordination number of Ag⁺ and its complex formation. The calculations are not very sensitive to different degrees of complex formation with the oxoanions, which was, therefore, assumed to involve one nitrate (or perchlorate) ion for each Ag⁺.

Concluding Remarks

The comparison between scattering data for silver(I) nitrate and perchlorate solutions shows that the coordination number for Ag⁺ in aqueous solutions is four, with bonding distances in the hydrated ion of 2.4 Å.

In the perchlorate solutions ion pairs are formed only in very concentrated solutions, when the number of water molecules is not sufficient to fill out the inner coordination sphere of the Ag⁺ ion. In the nitrate solutions inner-sphere complexes are formed even in the dilute (3 M) solution with one oxygen of the nitrate group more closely bonded to Ag⁺ than the others (Fig. 6).

The coordination of four oxygen atoms persists in more concentrated nitrate solutions and in anhydrous liquid AgNO₃.¹³ The structural transition from pure molten salt via hydrous melt and highly concentrated aqueous solution to dilute water solution thus probably occurs via a gradual substitution of NO₃⁻ by H₂O in the coordination sphere of a 4-coordinated Ag⁺ ion.

Concentrated silver nitrate and perchlorate solutions can dissolve silver iodide to a considerable extent. Comparison of scattering data for such solutions with those of iodide free solutions, shows that the I⁻ ion surrounds itself with about four Ag⁺ ions at a distance of 2.8 Å, which corresponds to the expected length for a covalent Ag—I bond. The presence of I⁻ however, does not lead to any observable Ag—Ag interactions or any other significant structural changes as judged from the distribution curves. The very similar results obtained for different nitrate melts and aqueous nitrate and perchlorate solutions and the observation of the same average number of Ag(I) bonded to I⁻ irrespective of the composition of the investigated systems strongly indicates that Ag₄I³⁺ is indeed the maximum composition of these kind of complexes. It thus seems that the occurrence of an average of four distinct Ag—I interactions to every I⁻ and the lack of any observable Ag—Ag correlation in the iodide coordination sphere is a characteristic consequence of the coordination ability of I⁻ rather than a specific structural effect due to the introduction of iodide ions in an anion sublattice of ionic melts. Hence, it seems reasonable to use a complex ion model and the term "cationic complex", although the nature of the chemical

bond in these species is still unclear. The Ag_4I^{3+} complexes thus seem to have either several different types of coordination geometry or a high mobility of the Ag^+ ions on the surface of the large I^- ion, though the short $\text{Ag}-\text{I}$ distances indicate a considerable extent of orbital overlapping. Further studies with *e.g.* Raman spectroscopy may hopefully give a deeper insight into the coordination chemistry of the cationic complexes.

Note added in proof. Texter and co-workers⁵⁰ recently published UV absorption data for hydrated Ag^+ ions in aqueous solution, which give further strong evidence for a tetrahedral arrangement of four water molecules in the primary hydration sphere of $\text{Ag}(\text{I})$.

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