Inorganica Chimica Acta, *146* (1988) 233–241

On the Structure of Hg_2I^{3+} in Dimethylsulfoxide and Aqueous Solution. An X-ray Scattering and Raman Spectroscopic Study

LARS BENGTSSON, BERTIL HOLMBERG, INGMAR PERSSON

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

and ÅKE IVERFELDT*

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, S-412 96 Göteborg, Sweden

(Received October 8, 1987)

Abstract

Dimethylsulfoxide and aqueous solutions of mercury(II) in large excess over iodide have been investigated by X-ray scattering techniques supported by Raman spectroscopic measurements. The composition of the solutions has been selected to ensure that the cationic complex Hg_2I^{3+} is the predominant iodide species. The structure parameters of the solvated Hg_2I^{3+} ion have been refined by a least-squares procedure on the scattering data, using known structural parameters for the additional molecular entities present. The Hg_2I^{3+} entity is more or less identical in DMSO and water. The Hg–I bond distance is 2.613(12) and 2.632(5) Å and the Hg–Hg distance is 3.66(5) and 3.70(1) Å in DMSO and water, respectively. This yields a Hg–I–Hg angle of 89° in both solvents. The mercury(II) atom in this complex is most probably solvated in a tetrahedral fashion by three DMSO or H_2O molecules. The structure of Hg_2I^{3+} is discussed in the light of recent results for the Ag_4I^{3+} complex in solution and relevant crystal structures.

Introduction

The stepwise formation of mercury(II) iodide complexes HgI_j^{2-j} has been thoroughly investigated by thermodynamic methods in aqueous [1] and dimethylsulfoxide (DMSO) [2, 3] solution. Four mononuclear complexes are formed in DMSO and in aqueous solution, and each complex, including HgI^+, has a distinct predominance range in dilute DMSO solution [2]. This fact has initiated a number of studies aiming at a detailed structural characterization of the solvated halide complexes $Hg(DMSO)_iX_j^{2-j}$ in DMSO by means of X-ray scattering, Raman spectroscopy and EXAFS [4–9]. Recent attempts at a structural investigation of HgI^+ by X-ray scattering and Raman spectroscopy revealed, however, that this complex is stable only in dilute DMSO solutions [6]. At higher concentrations (>50 mM) the first mercury(II) chloride and bromide complexes disproportionate according to

$$2HgX^+ \rightleftharpoons Hg^{2+} + HgX_2 \tag{1}$$

For HgI^+ it has been concluded that the prevailing reaction is

$$3HgI^+ \rightleftharpoons HgI_2 + Hg_2I^{3+} \tag{2}$$

This conclusion is based on the absence of Raman bands characteristic of $Hg(DMSO)_6^{2+}$ and the presence of a new band at 173 cm^{-1}, assigned to the symmetric stretching of $[Hg–I–Hg]^{3+}$, in concentrated solutions with $C_{Hg} \geqslant C_I$ [6, 9].

The coordination of metal ions M^{n+} to halide ions yielding complexes of the type M_mX^{mn-1} in solution is well known to occur in systems of soft–soft donor-acceptor pairs in water, organic solvents and molten salts. The silver(I) halide systems appear to be most extensively studied, and the tendency to formation of Ag_mX^{m-1} species apparently increases with increasing softness of the halide ion—the iodide complexes being formed most readily [10–14]. Hence, one might expect that iodide would be a good coordinating central anion for mercury(II) too, and some thermodynamic data for aqueous solutions indicate that this is indeed the case. In systems with a large excess of mercury(II) over iodide the following equilibrium has been proposed to explain the solubility data [15]

$$2Hg^{2+} + I^- \rightleftharpoons Hg_2I^{3+} \tag{3}$$

An alternative interpretation of the data has later been given by Gyunner and Yakhkind, claiming that $Hg_2I_2^{2+}$ is formed [16]. These authors also ascribed the increased solubility of AgI in $Hg(NO_3)_2$ solutions to the formation of $AgHgI^{2+}$ [17]. Apart from HgX^+ no thermodynamic studies on mercury(II) complexation with halide ions in DMSO seem to

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*Present address: Swedish Environmental Research Institute (IVL), P.O. Box 47086, S-402 58 Göteborg, Sweden.

0020-1693/88/$3.50

include any cationic species. Still, the presence of a Hg_2Cl^{3+} complex has been revealed by kinetic studies of the Hg/Hg(II) electrode in DMSO solutions of chloride ions [18].

The previous reported observations of Hg_2I^{3+} in DMSO are based on the assignment of a Raman band in the region 173–175 cm^{-1} to the symmetric stretching of the Hg_2I^{3+} ion [5, 6, 9]. This assignment is based on the original registration of a Raman line at 168 cm^{-1} from an aqueous solution of $Hg(NO_3)_2$ (2–4 M) and KI (0.2 M) [19]. The 168 cm^{-1} peak has tentatively been assigned by Clarke and Woodward to ν_1 for the bent Hg_2I^{3+} complex, and the Hg–I–Hg angle has roughly been estimated to 112°. Geske later confirmed this assignment [20], although ν_1 was determined to 162 cm^{-1}. A weak low-frequency band at 142 cm^{-1}, appearing for $Hg(ClO_4)_2$–HgI_2 solutions saturated in HgI_2, has been assigned to the Hg–I stretching in chain fragments $(HgI^+)_n$. Raman spectra of solid $(HgI)_2MF_6$ (M = Sn, Ti, Zr) and HgIA (A = NO_3, BF_4, benzene sulfonate, *p*-toluene sulfonate) with $(HgI^+)_\infty$ chains show sharp peaks at 130–140 cm^{-1}, thus supporting the interpretation of the low-frequency spectral features for aqueous solutions with high concentrations of both mercury(II) and iodide [21, 22].

Although the cationic complexes M_mX^{mn-1} have been proposed to account for a large number of thermodynamic and vibrational spectroscopy data, the nature of these complexes is still rather unclear. The structure is known for a number of solid iodide compounds like $Ag_3I(ClO_4)_2 \cdot 2H_2O$, $Ag_3I(NO_3)_2$, Ag_2INO_3, $Ag_2IF \cdot H_2O$, $Ag_7I_2F_5 \cdot 2.5H_2O$, $Ag_2HgI_2(NO_3)_2 \cdot H_2O$, $HgINO_3$ and $(HgI)_2TiF_6$ [23–31]. None of these contain discrete cationic complexes. Efforts at a structural characterization of cationic complexes in solution by scattering techniques have so far been directed towards the silver(I) iodide systems [32, 33]. The results obtained in these studies are quite remarkable. In nitrate melts as well as in aqueous nitrate and perchlorate solutions the central iodide ion coordinates four silver atoms at a well defined distance of 2.81–2.82 Å, corresponding to the expected length of covalent Ag–I bonds. However, no Ag–Ag correlation could be observed in the coordination sphere of I^- in any system. The apparent lack of directional demands of the Ag–I bonds may either be characteristic of the central iodide ion in mononuclear cationic complexes in solution or a feature exhibited specifically by the I–Ag system. Hence, it is of great interest to determine the structure of Hg_2I^{3+} in solution, not only in order to confirm the original Raman assignment by Clarke and Woodward for aqueous solutions, but particularly to obtain detailed structural information on the ability of I^- to coordinate another d^{10} cation, Hg^{2+}. The present work is an X-ray scattering study of solutions of $Hg(ClO_4)_2$ and HgI_2 in DMSO and water, supported by Raman spectroscopic measurements. It is also of special interest to examine the effects on the structure of Hg_2I^{3+} exerted by the solvent molecules in the solvation sphere of mercury(II), since water and DMSO differ considerably in their respective solvating ability [34].

In previous X-ray scattering studies on DMSO solutions, originally aiming at a determination of the HgI^+ structure, solutions with $C_{Hg} = C_I$ were examined [5, 6]. HgI_2 and Hg_2I^{3+} were assumed to be present according to eqn. (2) but no least-squares refinement of the distances *d*(Hg–I) and *d*(Hg–Hg) in Hg_2I^{3+} could be made. Introduction of distances *d*(Hg–Hg) = 4.3 [5] and 3.7 [6] Å and rather large temperature coefficients $b = 0.03$–0.05 $Å^2$ were necessary in order to obtain an acceptable fit with the experimental data. In view of the results for the Ag_4I^{3+} complexes cited above, it seems highly desirable to decide if these proposed *b* values actually do reflect a considerable flexibility in the Hg–I–Hg angle. Therefore, the composition of the DMSO solution in the present study was chosen to make Hg_2I^{3+} the predominating iodide complex in order to assure the determination of the structure of this complex.

Experimental

Preparation of Solutions

The chemicals used were HgI_2 (Merck, p a), $Hg(NO_3)_2 \cdot H_2O$ (Merck, p a), $Hg(ClO_4)_2 \cdot 3H_2O$ (GFS, hydrated reagent) and $HClO_4$ (BDH, analytical

TABLE I. The Composition of Solutions Studied by X-ray Scattering (M)

Solution	$Hg(ClO_4)_2$/ $Hg(NO_3)_2$	HgI_2	$HClO_4$	H_2O/ DMSO	V ($Å^3$)	ρ (g cm^{-3})	μ (cm^{-1})
DMSO1 (ClO_4)	0.775	0.225		12.39	1660	1.38	30.6
DMSO2 (NO_3)	0.875	0.225		12.59	1509	1.38	32.4
AQ1 (ClO_4)	1.916	0.240	1.17	41.52	770.2	1.740	56.2
AQ2 (ClO_4)	3.991	0.500	1.12	33.22	369.8	2.532	115

V is the stoichiometric unit volume per Hg atom, ρ the mass density and μ the linear absorption coefficient.

reagent). HgI_2 and $Hg(NO_3)_2 \cdot H_2O$ were dried in vacuum prior to use. The solvate $Hg(ClO_4)_2 \cdot 4DMSO$ was prepared and analyzed according to Sandström *et al.* [7]. The DMSO solutions were prepared from weighed amounts of HgI_2 and $Hg(NO_3)_2 \cdot H_2O$ or $Hg(ClO_4)_2 \cdot 4DMSO$, dissolved in DMSO, which had been purified by distillation as described elsewhere [35]. For the aqueous solutions approximate amounts of $Hg(ClO_4)_2 \cdot 3H_2O$ were dissolved in doubly distilled water with 1 M $HClO_4$ to prevent hydrolysis. Weighed amounts of HgI_2 were then dissolved in the $Hg(ClO_4)_2$ solutions. The mercury(II) concentrations were determined by a standard EDTA procedure [36]. The composition of the solutions is given in Table I.

X-ray Scattering Measurements

A large angle $\theta - \theta$ diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å) was used to measure the scattered intensities from the surface of the solutions [37].

The DMSO solutions were studied in a diffractometer of the type previously used by Johansson [38] with a curved LiF monochromator. The sample holder was a teflon container in an air-tight shield. The scattered intensity was measured at discrete points, using intervals of 0.1° in the range $1° < \theta < 30°$ and intervals of 0.25° in the range $30° < \theta < 63°$. 40 000 counts were collected twice at each point. The aqueous solutions were investigated by a diffractometer of Seifert GDS type with a curved graphite monochromator. The sample was kept in an open teflon vessel in a shield with a mylar window. No significant evaporation was observed during the experiment. Scattered intensities were collected in the range $0.65° \leqslant \theta \leqslant 64.90°$ with steps of $s = 0.0335$ ($s = 4\pi\lambda^{-1} \sin \theta$). The reproducibility was checked by repeated scans, where 40 000 counts were collected at each point in the scans.

Data Treatment

Experimental data were corrected for background and polarization effects [37]. No corrections were made for multiple scattering due to the high absorption coefficients (Table I). The corrected intensity data were normalized to a stoichiometric unit volume V containing one mercury atom. The normalization factor K was derived by comparison of the measured and total independent scattering in the high angle region $s > 13.5$ Å^{-1}. This normalization factor was almost identical to a K value calculated according to Krogh-Moe [39] and Norman [40].

The reduced intensity functions $i(s)$ and the differential electronic radial distribution functions $D(r) - 4\pi r^2 \rho_0$ were derived by standard procedures [41, 42]. Spurious peaks below 1.0 Å, which could not be identified with interatomic distances in the solutions, were removed by a Fourier transformation procedure [37]. All calculations were performed using the program KURVLR [43]. The theoretical interaction parameters were refined by use of the reduced intensities $i_{obs}(s)$ and $i_{calc}(s)$ in a least-squares program, STEPLR [44], minimizing

$$U = \sum_{s_{min}}^{s_{max}} w(s)[i_{obs}(s) - i_{calc}(s)]^2 \tag{4}$$

The weighting function $w(s)$ is proportional to $(I(s))^{-2} \cos \theta$, where $I(s)$ represents the scaled and corrected intensity data.

Raman Spectroscopic Measurements

Raman spectra of the DMSO solutions were recorded as described previously [6]. Spectra for the aqueous solutions were obtained using d c amplification from a D.I.L.O.R. RTI 30 triple monochromator with 4 cm^{-1} spectral bandwidth. The light source was the 514.5 nm line of a Coherent Radiation Laboratories Innova 90-5 Ar-ion laser.

Results and Discussion

The basic idea of investigating solutions having mercury(II) in large excess over iodide is of course to make Hg_2I^{3+} be the dominating complex. However, other structural entities are also present and they certainly interfere in the determination of the Hg_2I^{3+} structure. It is thus of great importance to establish the complex distribution, *i.e.* the speciation of mercury and iodide, as precisely as possible. This was achieved by analysis of Raman spectra of a number of aqueous and DMSO solutions with reference to the assignments which have been discussed above [5, 6, 9, 19–22]. For DMSO solutions with $C = C_{Hg} = C_I$, it was recently concluded from Raman measurements that the disproportionation according to reaction (2) was practically complete for $C = 0.2$ M [6]. The Raman spectra were reinvestigated with respect to the bands at 173 and 145 cm^{-1}, ascribed to Hg_2I^{3+} and HgI_2, respectively. Spectra were obtained for $C = 0.66$, 0.85 and 1.27 M. The ratios between the integrated intensities of these bands were found to be constant, *i.e.* $I_{145}/I_{173} = 1.5$ for $[HgI_2] = [Hg_2I^{3+}]$, and independent of C. A new spectrum was recorded for a solution S with $C_{Hg} = 1.00$ M and $C_I = 0.40$ M. In addition to a weaker band at 145 cm^{-1} and a distinct peak at 173 cm^{-1}, some weak bands were observed in the region 200–250 cm^{-1}. These bands most probably emerge from Hg–O bending modes of the solvated Hg^{2+} ion [7]. The dominating equilibrium is thus

$$3Hg^{2+} + HgI_2 \rightleftharpoons 2Hg_2I^{3+} \tag{5}$$

with a ratio I_{145}/I_{173} at 0.57. On the assumption that the intensity is proportional to the concentration of the Raman active species in all solutions, a combination with the observation for the solutions with $[HgI_2] = [Hg_2I^{3+}]$ yields $[HgI_2] = 0.39[Hg_2I^{3+}]$ in the solution S. A conditional equilibrium constant K for process (5) in this concentrated solution may be defined as

$$K = [Hg_2I^{3+}]^2[Hg^{2+}]^{-3}[HgI_2]^{-1} \qquad (6)$$

From the results for solution S we may estimate K to 5.9 M^{-2}. A direct application of eqn. (6) to the rather similar solution DMSO1 gives the equilibrium concentrations $[Hg^{2+}] = 0.43$, $[HgI_2] = 0.11$ and $[Hg_2I^{3+}] = 0.23$ M.

Raman spectra were recorded for a number of aqueous solutions with different molar ratios of mercury(II) to iodide. The results are briefly summarized in Table II. Frequencies around 192, 164 and 137 cm^{-1} are attributed to the Hg–I stretching vibrations of HgI^+, Hg_2I^{3+} and $(HgI^+)_n$, respectively [19, 20]. It is concluded that an increase in the ratio C_{Hg}/C_I causes a diminishing influence of polymer species. At molar ratios $C_{Hg}/C_I > 5$ the weak line at 137 cm^{-1} cannot be observed at all. The very weak peak from HgI^+ at 192 cm^{-1} was observable only at the lowest mercury(II) concentration. Hence, HgI^+ gives negligible contributions to C_I in the solutions studied by X-ray scattering. A Raman spectrum of the AQ2 sample, used in the X-ray scattering study, displayed a strong peak at 164 cm^{-1} and a weak peak at 137 cm^{-1}. In general, Raman spectroscopic measurements are very sensitive to the presence of polymer chains since their vibration modes give rise to sharp peaks of high intensity in the spectrum [20–22]. It is thus concluded that both AQ1 and AQ2 may contain some chain fragments like $(HgI^+)_n$ besides Hg_2I^{3+}, although no quantitative estimates of the amount can be made. The weak Raman intensities that we observed, however, suggest that $(HgI^+)_n$ chains are of minor importance in the studied aqueous solutions. Furthermore, no chain fragments can be identified from the X-ray scattering data (basically, no significant I–I interactions are observed), and hence the final analysis of the scattering data was based on Hg_2I^{3+}(aq) as the only cationic species besides Hg^{2+}(aq). No tendency to polymerization could be observed in the DMSO solutions. Obviously, the strong solvating power of DMSO effectively prevents aggregation to $(HgI^+)_n$.

TABLE II. The Composition and Vibration Frequencies for the Aqueous Solutions[a]

C_{Hg} (M)	C_I (M)	$\nu(HgI^+)$ (cm^{-1})	$\nu(Hg_2I^{3+})$ (cm^{-1})	$\nu((HgI^+)_n)$ (cm^{-1})
4.50	1.51		164	137
4.32	1.04		165	138
4.30	0.49		164	
4.29	0.21		164	
3.34	0.58		162	137
2.35	0.59	192	162	137

[a] The concentration of $HClO_4$ was 0.85 M in all solutions.

Since the molecular structure of all species except Hg_2I^{3+} is *a priori* known, the general strategy for evaluating the structure of Hg_2I^{3+} in DMSO and

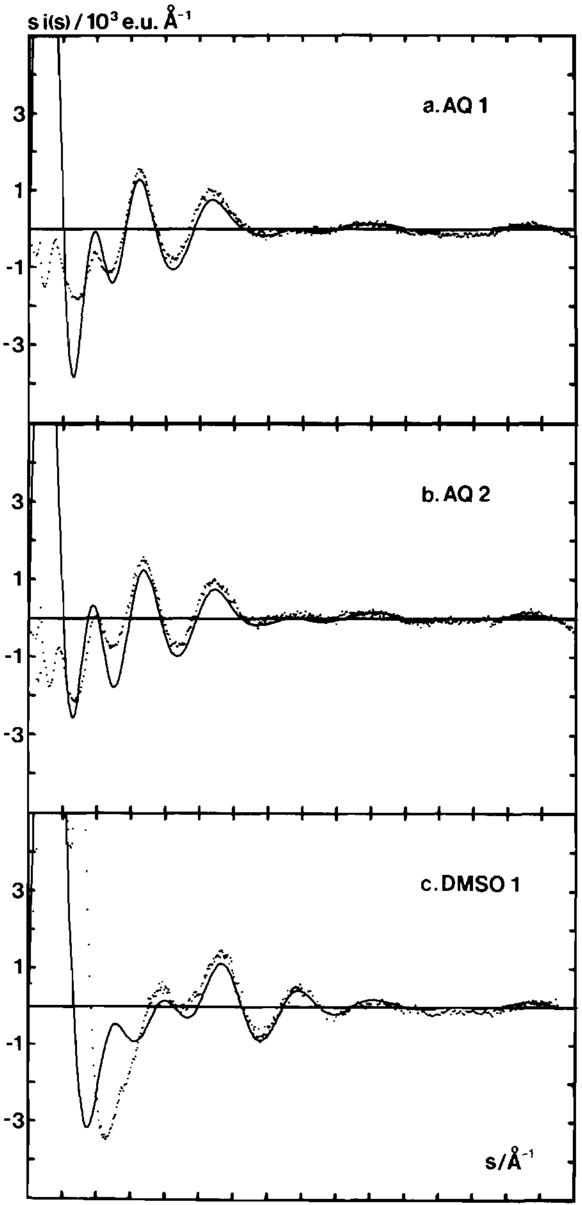

Fig. 1. Reduced intensities $i(s)$ multiplied by s as a function of s for the solutions (a) AQ1, (b) AQ2 and (c) DMSO1. Dots are experimental values and the full-drawn curve represents values calculated from the final structural model given in Table III.

water has been to introduce fixed structural parameters for all species but Hg_2I^{3+}. Least-squares refinements of interatomic distances d, corresponding temperature coefficients b and number of distances n in Hg_2I^{3+} were made. For the aqueous solutions the structural parameters pertaining to the second hydration sphere of uncomplexed Hg^{2+}, ClO_4^- and the bulk H_2O structure were also included in the least-squares refinements.

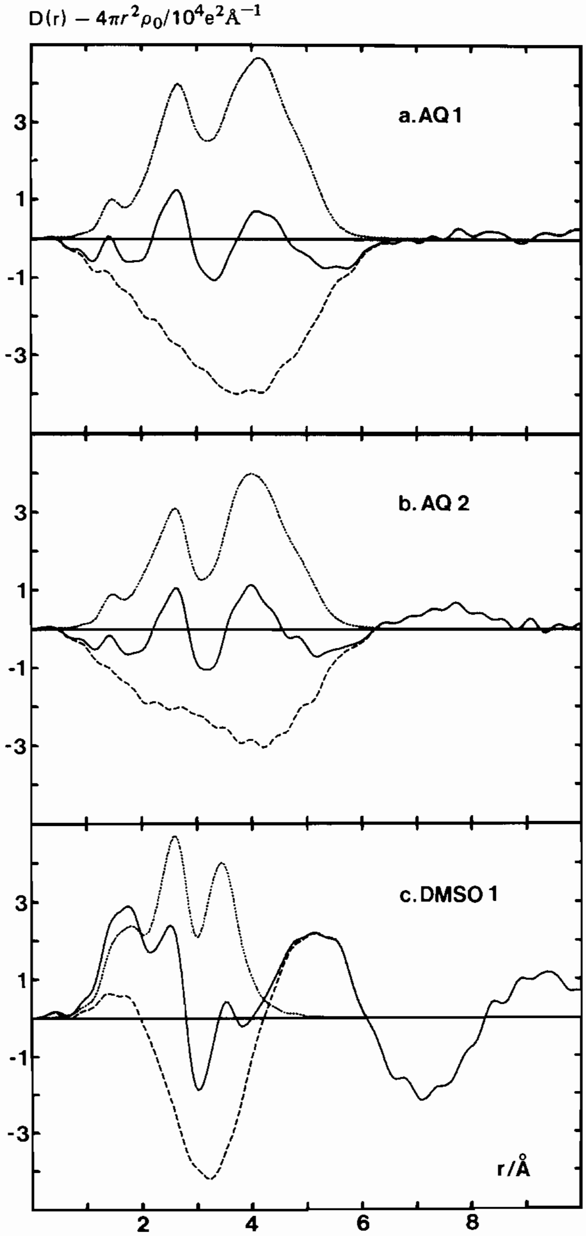

Fig. 2. The differential electronic radial distribution function $D(r) - 4\pi r^2\rho_0$ for solutions (a) AQ1, (b) AQ2 and (c) DMSO1 (solid line). The dotted curve represents the sum of calculated peak shapes and the difference is drawn with dashed line.

The reduced intensity curves and the differential radial distribution functions are shown in Figs. 1 and 2. Interactions at distances larger than 5 Å were not considered in the data analysis because of the difficulty of making correct assignments. In fact, the aqueous solutions exhibit very little structure at distances $r > 5$ Å whereas the two main peaks around 5.5 and 9 Å in the DMSO solution may be identified as intermolecular interactions in the bulk DMSO [5]. For the intramolecular structure of DMSO the parameters of refs. 5 and 6 were used in the data fit. The structure of ClO_4^- was taken from ref. 7 for both DMSO and aqueous solutions. For the solvated Hg^{2+} ion it has been shown that regularly octahedral hexasolvates are formed in DMSO and water, and that the DMSO molecules are coordinated via the oxygen atom [7]. The dimensions of the solvates have been taken from refs. 6 and 7. Finally, the structural parameters for HgI_2, occurring in the DMSO1 solution, were adopted from the thorough investigation of Sandström [5]; the distance d(Hg–I) being 2.63 Å.

The bulk water structure had to be taken in account in the least-squares refinements of AQ1 and AQ2, and the intermolecular water interactions were found at 2.9 and 4.4 Å as expected. Furthermore, interactions in the second coordination sphere of mercury(II) make significant contributions to the radial distribution function for the aqueous samples. A peak at 4.1 Å was assigned to the second shell Hg–O interactions of hydrated mercury(II) ions. The peak at 4.9 Å, which is more distinct for the more concentrated solution AQ2 (*cf.* Fig. 2a and b) was assigned to the Hg–Cl(ClO_4^-) distance in the second coordination sphere, supported by distances found in the solid $[Hg(H_2O)_6](ClO_4)_2$ [45]. At approximately 3.6 Å a minor peak is also observed. It is assumed to arise from interactions between perchlorate ions and adjacent water molecules or other perchlorate ions. These contributions are very similar to those proposed for aqueous silver perchlorate solutions [33].

For the Hg_2I^{3+} complex the Hg–I and Hg–Hg distances appear at 2.6 and 3.7 Å respectively in all solutions. The refined parameter values are summarized in Table III. From the interatomic distances the Hg–I–Hg angle is calculated to 89° in both aqueous and DMSO solution. It is also anticipated that mercury(II) in Hg_2I^{3+} is solvated by H_2O or DMSO molecules. The presence of significant amounts of free mercury(II) ions coordinated by six solvent molecules causes difficulties in the evaluation of a reliable coordination number and geometry for the mercury(II) atoms in Hg_2I^{3+}. Calculations carried out at different fixed values of n for Hg–O and Hg–S indicate a significantly lower coordination number than six. The short Hg–O distances, especially in water (*cf.* d(Hg–O) = 2.41 Å

TABLE III. Results of Least-squares Refinements

Parameter			AQ1	AQ2	DMSO1
Hg_2I^{3+}:	Hg–I	*d*	2.629(5)	2.635(4)	2.613(12)
		b	0.0084(8)	0.0057(6)	0.0086(11)
		n^a	1.70(4)	1.71(4)	1.74(13)
	Hg–Hg	*d*	3.690(11)	3.718(9)	3.664(54)
		b	0.0185(20)	0.0159(5)	0.0427(135)
		n^a	0.97(5)	1.00(4)	0.96(30)
	Hg–O, 1st	*d*	2.146(20)	2.111(13)	2.267(23)
		b	0.0312(43)	0.0275(27)	0.0030(16)
		n^b	3.9(3)	4.4(2)	2.4(4)
	or				
		b	0.0034(31)	0.0018(16)	
		n^b	1.0(fixed)	1.0(fixed)	
	Hg–S	*d*			3.332(32)
		b			0.0221(44)
		n^b			3.4(5)
$Hg^{2+}(aq)$:	Hg–O, 2nd	*d*	4.131(7)	4.123(7)	
		b	0.0240(15)	0.0295(16)	
		n^b	12.5(3)	12.9(4)	
	Hg–Cl, 2nd	*d*	4.905(15)	4.895(20)	
		b	0.0405(36)	0.0361(47)	
		n^b	2.5(2)	1.6(1)	
Bulk:	H_2O-OH_2, 1st	*d*	2.864(8)	2.882(32)	
		b	0.0237(21)		
		n^c	3.74(14)	3.7(6)	
	H_2O-OH_2, 2nd	*d*	4.385(15)	4.415(27)	
		b	0.0330(36)	0.0421(58)	
		n^c	4.1(2)	14.2(1.1)	
ClO_4^-:	Cl–O, 2nd	*d*	3.594(35)	3.637(37)	
		b	0.0874(91)	0.0579(90)	
		n^d	7.7(9)	5.5(7)	

The parameters are distance *d* (in Å), temperature coefficient *b* (in $Å^2$) and number of distances *n* per [a]iodide, [b]mercury, [c]water molecule or [d]perchlorate ion. Mean errors are given in parentheses. The intervals $3.0 \leq sÅ \leq 15.0$ and $3.0 \leq sÅ \leq 15.45$ were used for the aqueous and DMSO solutions, respectively.

in $Hg(OH_2)_6^{2+}$ [7]), also support this assumption. Table III shows two data sets for Hg–O(1st) in AQ1 and AQ2, yielding equally good fits, in order to illustrate the difficulties discussed here. The best fit for DMSO1 gives $n(Hg-O) = 2.4$ in Hg_2I^{3+}, which is in good agreement with the previous conclusion that not more than three DMSO can be coordinated to the bent Hg_2I^{3+} entity for steric reasons [6]. The decreased coordination number in DMSO is also reflected in the decrease in $d(Hg-O)$: 2.27 Å in the solvated Hg_2I^{3+} ion compared to 2.39 Å in $Hg(DMSO)_6^{2+}$ in DMSO solution [7]. Figure 3 shows the most probable structure for the solvated Hg_2I^{3+} ion in DMSO with a distorted tetrahedral over-all coordination geometry for mercury(II). With DMSO replaced for water this may obviously be a good model for the hydrated complex as well.

The natural choice of counterion is perchlorate, but DMSO2 was made with $Hg(NO_3)_2 \cdot H_2O$ in order to see if possible effects on the Hg_2I^{3+} structure emerging from the predominating anion might be traced. In a previous study, Sandström reports that the dominating complex in a 2 M solution of $HgBrNO_3$ in DMSO probably is Hg_2OBr_2, as a result of oxidation of DMSO to dimethylsulfone [5].

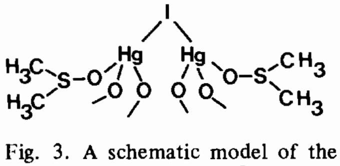

Fig. 3. A schematic model of the most probable structure of the solvated ion Hg_2I^{3+} in DMSO. The angle Hg–I–Hg is 89°.

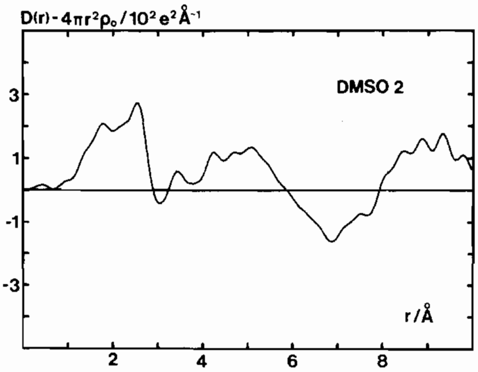

Fig. 4. The experimental function $D(r) - 4\pi r^2\rho_0$ for solution DMSO2.

It was therefore of interest to study if nitrate has a similar effect on a DMSO solution with mercury(II) in large excess over iodide. The differential radial distribution function for the solution DMSO2 is given in Fig. 4. This curve is significantly different from those of the solutions in this study, which contain the complex Hg_2I^{3+}, see Fig. 2. The large peaks at 3.2 and 4.0 Å indicate predominance of one or several polynuclear complexes, which are different from Hg_2I^{3+}. As the curve is complicated and the kind of complexes present in this solution is not known, it has not been possible with any certainty to determine the structure of the predominating complex in the solution DMSO2.

The present work is actually the first conclusive determination of a distinct structure of a M_mX^{mn-1} complex in solution. There is a fundamental difference between the results pertaining to Hg_2I^{3+} and those obtained for the equally charged complex Ag_4I^{3+} [32, 33], notably that the Hg–Hg distance and hence the Hg–I–Hg angle, has been determined while no Ag–Ag correlation within the Ag_4I^{3+} ions could be detected in aqueous solutions [33] and molten salts [32]. Still, it should be noted that the temperature coefficient b(Hg–Hg) is remarkably high for the DMSO solution. This is in agreement with previous assumptions [5, 6] and it may be taken as an indication of a rather high flexibility in the Hg–I–Hg angle.

There is nevertheless a striking similarity in the structural parameters for Hg_2I^{3+} in aqueous and DMSO solutions, see Table III, although the results for Hg_2I^{3+}(aq) may to some minor extent comprise Hg–I and Hg–Hg distances in $(HgI^+)_n$ chain fragments. It is noticeable that the Hg–I distance, 2.61–2.63 Å in Hg_2I^{3+}, is practically identical with d(Hg–I) for the neutral complex HgI_2 in DMSO [5]. This indicates that the chemical bond in Hg_2I^{3+} may be of the same covalent character as in HgI_2. In this respect there is a good analogy with the corresponding Ag–I bond relations [32, 33]. The Hg–I–Hg angle of 89° observed for both water and DMSO solutions is most probably an effect of geometrical restrictions for orbital overlapping.

Relevant comparisons may be made with some solid compounds listed in Table IV. $(HgI)_2TiF_6$ and $HgINO_3$ are built up by infinite zigzag chains $(HgI^+)_\infty$ with the Hg–I–Hg angle around 90°. Some crystal structures have also been reported having discrete $Hg_2I_6{}^{2-}$ ions [46–48]. $Hg_2I_6{}^{2-}$ may be described as two edgesharing HgI_4-tetrahedra which are distorted in such a way that the Hg–I–Hg angles all fall in the range 85.7°–86.4°. A further comparison can be made with $Ag_2HgI_2(NO_3)_2 \cdot H_2O(s)$, with three-coordinated iodide in the top of an Ag_2HgI-pyramid, having Hg–I–Ag and Ag–I–Ag angles between 89.8° and 102.6°. These structures all indicate a preference for an angle around 90° for iodide. Another instructive comparison may be made with the chemically closely related gold(I) halides. AuCl, α-AuBr and AuI all crystallize to give infinite $(AuX)_\infty$ zigzag chains like $(HgI^+)_\infty$. In the chloride and bromide compounds the Au–X–Au angles are approximately 90° [49, 50], while a considerably smaller angle is found for AuI (*cf.* Table IV). This difference has been ascribed to a strong Au–Au interaction [50], and it is expected that tendencies to metal–metal bond formation may influence the structure and stability of M_mX^{mn-1} species in general. Another factor influencing the

TABLE IV. The Bond Angle –I– in some Compounds with Two- or Three-coordinated Iodine

Compound	Structure fragment	Angle –I– (°)	Reference
$(HgI)_2TiF_6(s)$	$(HgI^+)_\infty$	89.4, 97.2	31
$HgINO_3(s)$	$(HgI^+)_\infty$	90.2	30
$[P(C_6H_5)_4][HgI_3](s)$	$Hg_2I_6{}^{2-}$	85.7	48
$Ag_2HgI_2(NO_3)_2 \cdot H_2O(s)$	$[Ag_2I-Hg-IAg_2]^{4+}$	89.8–102.6	29
AuI(s)	$(AuI)_\infty$	72.6	51, 52
$ICl_3(s)$	$ICl_2{}^+$	94	53
$ISbCl_8(s)$	$ICl_2{}^+$	91.5	54
	Hg_2I^{3+}(aq)	89	this work
	Hg_2I^{3+}(DMSO)	89	this work

structure may be the actual electron density left located in the p-orbitals of iodine after an assumed electron donation to the metal cation ligands. Extreme structural comparisons of relevance in this aspect can be made with the compounds $ICl_3(s)$ and $ISbCl_8(s)$ with iodine in the formal oxidation state +III. These compounds both contain discrete ICl_2^+ ions with the Cl–I–Cl angle about 90°.

In summary, it is evident that our understanding of the nature of cationic complexes M_mX^{mn-1} is still very rudimentary and, in some aspects, contradictory. Further thermodynamic and structural research in this field at our laboratory will also include the $d^{10}s^2$-ions Tl^+ and Pb^{2+} as metal cation ligands.

Conclusion

The complex Hg_2I^{3+} has the very same structure in both aqueous and DMSO solutions. In DMSO the Hg–I bond distance in Hg_2I^{3+} is almost equal to what is found in the HgI_2 complex; in spite of that the geometry around mercury(II) is considerably different. The Hg–I–Hg angle in Hg_2I^{3+} is 89°, and angles close to 90° are indeed found in the most two-coordinated halide complexes.

Acknowledgements

The authors are indebted to Dr Magnus Sandström, Inorganic Chemistry, Royal Institute of Technology, Stockholm, for his assistance in recording the Raman spectra of aqueous solutions and for some enlightening discussions.

The support from the Swedish Natural Science Research Council, and Knut and Alice Wallenberg's Foundation is gratefully acknowledged.

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