Acta Chemica Scandinavica A 32 (1978) 607–625

On the Coordination around Mercury(II), Cadmium(II) and Zinc(II) in Dimethyl Sulfoxide and Aqueous Solutions. An X-Ray Diffraction, Raman and Infrared Investigation

MAGNUS SANDSTRÖM,[a] INGMAR PERSSON[b] and STEN AHRLAND[b]

[a] Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden and
[b] Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden

The structures of the solvated metal ions in dimethyl sulfoxide (DMSO) solutions of mercury(II) and cadmium perchlorates have been determined by X-ray diffraction measurements. In both cases, regularly octahedral hexasolvates are formed, with DMSO coordinated *via* the oxygen atom. The bond lengths are: Hg–O 2.393(5), Cd–O 2.292(4) Å. The value of Hg–O is significantly longer than in the solid hexasolvate, while that of Cd–O is virtually the same in both phases. The bond angles Hg–O–S, 120.2(1.0)° and Cd–O–S, 125.7(1.0)°, are not significantly different from the average angles found in the solid solvates. A recalculation of earlier X-ray diffraction data pertaining to mercury(II) perchlorate in aqueous solution confirms that the hydrate formed is indeed regularly octahedral. The bond length Hg–O is 2.41(1) Å, *i.e.* close to the value found in DMSO solution. These bond lengths correspond to octahedral ionic radii of Cd^{2+} and Hg^{2+} of 0.94 and 1.05 Å, respectively.

The Raman spectra of perchlorate solutions of mercury(II), cadmium and zinc in DMSO confirm that the metal ions are all coordinated *via* oxygen. The spectra also reflect the change in character of the M–O bond from mercury(II) to zinc. Both the decreasing covalency and the increasing electrostatic interaction are clearly indicated.

In the aprotic solvent dimethyl sulfoxide (DMSO), the neutral mercury halides $HgCl_2$, $HgBr_2$ and HgI_2 are all easily soluble.[1,2a] In the solvated HgX_2 molecules, the angles X–Hg–X (X=Cl, Br, I) deviate significantly[2] from the value 180° found in the gaseous and solid halides (except for red HgI_2).[3,4] On the addition of excess halide further ligands are taken up, resulting in the formation of HgX_3^- and finally, HgX_4^{2-}. The HgI_3^- and $HgBr_3^-$ ions are pyramidal, slightly flattened relative to a regularly tetrahedral arrangement.[1] In all the systems the fourth complex is a regular tetrahedron.[1,2]

In aqueous solution, the complexes HgX_2 should be less bent than in DMSO, on account of the weaker interaction with the solvent,[4,5] but the solubilities in this protic solvent are too low for a structure determination by X-ray diffraction. The complexes $HgBr_3^-$ and HgI_3^- are again slightly flattened pyramids, derived from tetrahedra.[6] As in DMSO, the mononuclear complexes HgX_4^{2-} finally formed are all regular tetrahedra.[6,7]

In the numerous solid compounds where linear HgX_2 units exist, four longer contacts usually complete a distorted octahedral coordination around Hg.[2b,3,8–15] Planar HgX_3^-, with two long contacts forming a trigonal bipyramid,[16–21] pyramidal HgX_3^-, with a bridging X atom completing a distorted tetrahedral coordination,[22–24] and tetrahedral HgX_4^{2-},[25–29] also exist in solid state. Even discrete bipyramids $HgCl_5^{3-}$ have been found.[30]

Both in water and in DMSO, the formation of the third complex thus involves a drastic change of the digonal coordination characteristic of the second complex. In the case of bromide and iodide, the new arrangements very probably are approximately tetrahedral, while the picture is less clear for the chloride complexes.

Another drastic change of coordination very probably occurs in both solvents, as the digonal second complex is formed when halide is added to a solution of the solvated mercury(II) ion. The solvated perchlorates $[Hg(H_2O)_6](ClO_4)_2$ and $[Hg(DMSO)_6](ClO_4)_2$ have been crystallized, the structures of which contain octahedrally coordinated solvate ions as discrete entities.[31,32] It is therefore very plausible that such species exist also in solution. In aqueous perchlorate solution, the existence of the hexahydrate has in fact been proved by X-ray diffraction measurements.[33]

In aqueous solution, the switch from digonal to tetrahedral coordination at the formation of the third complex is also clearly indicated by abrupt changes of the magnitude of the enthalpy changes ΔH_j° of the consecutive formation reactions. These become much less exothermic for the two later steps.[34]

Changes of ΔS_j° also occur, but they are not clear-cut enough to yield further evidence.[34] As to the postulated change from an initial octahedral coordination to an intermediate digonal one, relatively little can be learned from the thermodynamic data. Neither ΔH_j°, nor ΔS_j° differ very drastically between the first and second step. This must mean that water molecules are expelled from the close vicinity of the mercury atoms at both stages. The first ligand displaces one water molecule and loosens the bonds of the others except the one in *trans* position to the ligand which might be held even more tightly than before.[33] This is supported by the high acidities of the HgX^+ and $HgOH^+$ species compared with the acidity of the Hg^{2+} ion.[35] The second ligand replaces this water molecule and relegates the remaining ones to even more distant positions. Under such conditions, the thermodynamic functions of the first two steps need not be very different. The hydration of the HgX_2 complexes is indeed quite weak as is shown by their low heats of solvation.[36]

In DMSO, the thermodynamics of the formation of mercury(II) halide complexes follows a pattern which is quite different from that found in water. The values of ΔH_j° do not vary much between the different halides or, perhaps even more remarkable, between the consecutive steps.[37,38] This levelling of the ΔH_j° values is brought about by a combination of several causes.[38] Firstly, the heat of solvation of the mercury(II) ion is considerably larger in DMSO than in water,[36] which tends to decrease the values of $-\Delta H_j^\circ$, and preferentially for the first steps. Secondly, the differences between the heats of solvation of the halide ions are much smaller in DMSO than in water.[36,39] Evidently, it so happens that the sum of these changes rather nicely counterbalances the change of ΔH_j° due to the switch from digonal to tetrahedral coordination. The switch will therefore not be marked by any drastic change of ΔH_j°. The values of ΔS_j° found in DMSO are, on the other hand, very informative.[38] For all the halide systems, extremely large positive values of ΔS_1° clearly show that a very extensive desolvation takes place when the first complex is formed. Smaller, though still quite large values of ΔS_2° indicate a less extensive, though still quite substantial desolvation in the second step. The values of ΔS_3° are quite small which means that already the HgX_2 complexes are relatively weakly solvated. This has also been confirmed by a determination of their heats of solvation which are indeed low compared to those of the presumably tetrahedral solvated CdX_2 and ZnX_2 molecules.[36]

In analogy with the mercury(II) ion, the cadmium ion finally forms four-coordinated halide complexes CdX_4^{2-} in DMSO as the ligand ion concentration is increased.[40] The same is most probably true also in water, although in this solvent the chloride complexes are fairly unstable.[41-43] The complex CdI_4^{2-} has been found by X-ray diffraction measurements to be a regular tetrahedron in both solvents.[44,45] There is every reason to believe that $CdBr_4^{2-}$ and $CdCl_4^{2-}$ have the same structure.

Also in analogy with Hg(II), both DMSO and aqueous solutions of Cd(II) and Zn(II) perchlorates very probably contain hexacoordinated metal ions solvates. This is strongly indicated already by the existence of the crystalline solvates $[M(DMSO)_6](ClO_4)_2$,[46] and $[M(H_2O)_6](ClO_4)_2$,[47] where M = Zn or Cd. Several crystal structure determinations[48-52] confirm the existence of discrete octahedrally coordinated solvate cations. By means of X-ray diffraction measurements,[44,53] the hexahydrates have been found to exist also in aqueous solution, while no such direct proof of the existence of the hexasolvates in DMSO has so far been produced.

Contrary to mercury(II), cadmium(II) does not form any linear complexes. Therefore, only a change from the initial octahedral coordination to the final tetrahedral one is to be expected as halide is added to a solution of a cadmium(II) hexasolvate. The thermodynamic functions of the consecutive formation reactions also indicate that the change mainly occurs at a certain step of the complex formation. This step is characterized by values of ΔH_j° and ΔS_j° which are abnormally positive relative to the values of the neighbouring steps. The switch takes place at different steps in the two solvents, *viz.* at the formation of the third complex in water but at the formation of the second one in DMSO.[40]

In the solids $[Hg(DMSO)_6](ClO_4)_2$, $Hg(ClO_4)_2 \cdot 4DMSO$, and $[Cd(DMSO)_6](ClO_4)_2$, the solvent molecules are coordinated *via* oxygen.[32,46,48,54] For the very soft acceptor mercury(II), a coordination *via* the soft sulfur atom would perhaps rather have been expected. The most important reason why this does not occur is presumably that the donor properties of the sulfur atom are very considerably reduced by its bonding to the electronegative oxygen. Also sterically, the oxygen coordination is certainly much more favourable. Rather as expected, the infrared spectra also indicate[46,55] that the hard acceptor zinc(II) is oxygen coordinated in the solids $[Zn(DMSO)_6](ClO_4)_2$ and $Zn(ClO_4)_2 . 5DMSO$. It might be presumed that, for all three acceptors, oxygen coordination prevails also in solution but this has so far not been proved.

A direct structure determination of the solvates formed by these acceptors in DMSO would evidently decide whether the solvation number and mode of coordination inferred are indeed correct. While the mercury(II) and cadmium perchlorates are sufficiently soluble to allow a determination of the solvate structure by means of X-ray diffraction, this is unfortunately not the case for the zinc perchlorate. The concentrations of the solutions in equilibrium with the solid hexasolvates are 0.93, 0.70 and 0.29 M, respectively, at room temperature. On the other hand, recent improvements in the evaluation technique has allowed a considerable refinement of the parameters determined earlier for the hydrated mercury(II) ion in solution.[33]

In order to obtain further information about the nature and strength of the various acceptor to solvent bonds Raman spectra of the saturated solutions of the zinc, cadmium and mercury(II) perchlorates have been recorded. With the modern laser technique, all these solutions yield spectra of high resolution. The bands principally due to the M – O stretching modes are discerned in both solvents and, in DMSO, also bands due to the M – O bending vibrations. The solution spectra are compared to those obtained for solid hydrates and DMSO solvates. In order to facilitate the assignments, the infrared spectra of the solid solvates have also been recorded.

Table 1. Compositions of the DMSO solutions at 25 °C in mol l^{-1}. The linear absorption coefficient, μ, is calculated for Mo*K*α-radiation.

Hg(II)	Cd(II)	ClO_4^-	DMSO	μ/cm^{-1}
–	0.685	1.370	13.33	7.2
0.932	–	1.864	13.00	26.8
0.434	–	0.868	13.55	15.0

EXPERIMENTAL

Preparation and analysis of solvates and solutions. The DMSO solutions investigated were prepared by dissolving DMSO solvates of the metal perchlorates in DMSO. The solvent had been purified as described earlier.[46] The water content, determined by Karl Fischer titration,[56] was <0.08 %. The composition of the solutions, checked by EDTA titration,[57] is given in Table 1. Their densities were determined pycnometrically.

The solvates $[Zn(DMSO)_6](ClO_4)_2$ and $[Cd(DMSO)_6](ClO_4)_2$ were prepared as described previously.[46] The mercury(II) hexasolvate prepared previously[46] was, on the other hand, not pure and stable enough to meet the demands of the present investigations, or of the potentiometric and calorimetric measurements also in progress.[36,38] Its mercury(II) content was generally somewhat too low and varied significantly between different preparations. Moreover, the compound, as well as the DMSO solutions prepared from it, decomposed appreciably in a few weeks even at ordinary temperature. In a few months, the solutions might even turn dark yellow, with a very sizable reduction of the mercury(II) concentration. Instant decomposition of the solid solvate also took place at a much lower temperature (Table 2) than for the pure $[Hg(DMSO)_6](ClO_4)_2$ that has now been prepared by another route.[32] While the impure solvate decomposed violently immediately upon melting, the pure one survives its melting by ≃80 °C. Remarkably enough, the melting point of the pure compound is only slightly higher than that of the impure one. By a modified method of preparation, described below, a pure tetrasolvate was first obtained. From a saturated DMSO solution of the tetrasolvate, the pure hexasolvate crystallized.[32]

The solid solvates were analysed for metal and sulfur as described before.[46,57] Especially for the mercury compounds, the results are very close to the theoretical values, Table 2. As mentioned, this was not the case for the mercury hexasolvate prepared previously, whose values have also been entered.

Melting and decomposition points were determined using a Bücki apparatus. Measured densities,

Table 2. The crystalline DMSO solvates.

Compound	M.p./°C	Dec.p./°C	Metal/% Calc.	Metal/% Found	Sulfur/% Calc.	Sulfur/% Found	D_m/g cm^{-3}	D_x/g cm^{-3}
$[Zn(DMSO)_6](ClO_4)_2$	168 – 174	195 – 205	8.92	8.98	27.43	27.04	1.52(2)	1.54
$[Cd(DMSO)_6](ClO_4)_2$	188 – 190	200 – 210	14.41	14.14	24.66	24.49	1.58(1)	1.60
$[Hg(DMSO)_6](ClO_4)_2$	126 – 129	204 – 207	23.10	23.12	22.15	22.20	1.96(2)	1.99
$[Hg(DMSO)_6](ClO_4)_2$[46]	125 – 128	125 – 128	23.10	22.57	22.15	22.05	–	–
$Hg(ClO_4)_2.4DMSO$	167 – 168	170 – 174	28.17	28.19	18.02	18.00	1.76(3)	1.82

D_m, were obtained from the apparent loss of weight in benzene. They are compared to calculated densities, D_x, from unit cell dimensions found in the structure determinations.[32,48,54] The unit cell for $[Zn(DMSO)_6](ClO_4)_2$ was found to be trigonal with $a=b=20.818(1)$ and $c=12.659(2)$ Å, by X-ray diffraction methods.

Preparation of $Hg(ClO_4)_2.4DMSO$. Mercury(II) perchlorate trihydrate[46] (0.01 mol) was dissolved in a minimum amount of methanol (100 ml). A few drops of concentrated perchloric acid had previously been added to the methanol in order to minimize the hydrolysis of mercury(II). Still it was sometimes necessary to decant the solution in order to remove a slight solid residue. About 0.06 mol DMSO was then added and the solution cooled to about −78 °C. Very small white crystals precipitated which were filtered in dry air at the low temperature and then dried in vacuum over silica gel at room temperature, in order to remove the methanol. This resulted in a recrystallization of the phase obtained originally into the tetrasolvate. Larger crystals, suitable for investigation by single X-ray diffraction technique,[54] were obtained by recrystallization at lower temperature, ~5 °C. The compound seems to be stable for years when stored over silica gel at room temperature.

Warning. Metal perchlorates and nitrates solvated by DMSO are generally powerful explosives and under certain conditions a violent reaction is easily triggered.[46,58,59] During one of the earlier attempts to prepare a mercury(II) solvate, the compound obtained at room temperature from a methanol solution exploded with extreme violence, after having been kept for about two weeks in a desiccator over sulfuric acid. The explosion seemingly occurred without outer provocation. On the other hand, the solvates described above explode only when subjected to very unmild mechanical treatment and stand fairly high temperatures before a rapid decomposition occurs, Table 2. Generally, the sensitivity seems to decrease with increasing purity. This does not exclude that even pure DMSO solvates might be very explosive as is no doubt the case[46] with $Ag(ClO_4)_2.2DMSO$.

Great caution must also be exercised when handling DMSO solutions of poisonous substances, such as mercury and cadmium salts, since these are easily carried through the skin by the DMSO which penetrates lipid tissues at an astonishing rate.[59] DMSO dissolves many natural and synthetic polymers.[59] The unusual solvent properties must of course be taken into account in the design of the apparatus, and also in order to ensure good personal protection.

X-RAY DATA

Data collection

The X-ray scattering of Mo$K\alpha$-radiation $\lambda=0.71069$ Å) was measured from the free surface of the DMSO solutions, as described in previous papers.[33,60] The solutions were enclosed in an airtight shield, with a cylindrical beryllium window for the X-rays. The scattered intensity was repeatedly measured at discrete points between the θ values 1.5 and 70°, where 2θ is the scattering angle. Intervals of 0.1° for $1.5° < \theta < 15°$ and 0.25° for $15 < \theta < 70°$ were used. At least 100 000 counts were accumulated for each point which corresponds to a statistical error of about 0.3 %. All measurements were performed at 25±1 °C.

Data reduction and corrections

All calculations were carried out by means of the KURVLR and PUTSLR programs.[61] The measured intensities were corrected for background, polarization, and double scattering, and normalized to a stoichiometric unit of volume, V, corresponding to the average volume per metal atom in the solutions. The normalization was done by comparing the high angle region of the corrected intensities to the calculated sum of the independent coherent scattering and the fraction of the incoherent scattering reaching the counter. The correction for double scattering did not exceed 3 % for any of the three DMSO solutions. A few points clearly outside estimated statistical error limits were removed.

Only the low-absorbing cadmium solution (Table 1) had to be corrected for absorption effects.[62] The largest correction of the intensity curve (at $\theta = 45°$) was 3.3 %.

RHF scattering factors, f, for the neutral atoms[63,64] were used, except for H, where the spherical form factors proposed by Stewart *et al.* were employed.[65] For the recalculation of the aqueous mercury(II) perchlorate solution *A*1 of Ref. 33, spherical form factors for the H_2O molecule were used.[66] Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were applied for all atoms.[64] The incoherent scattering factors, I_{incoh}, were taken from the same sources as before.[6] Correction for the Breit-Dirac factor[67,68] in the appropriate form for a radiation counter, $(\lambda/\lambda')^2$, were applied.[69]

The reduced intensity curves, $i(s)$, were calculated for each experimental point from:

$$i_{\text{obs}}(s) = I_{\text{obs}}(s) - \sum_m \{(f_m(s) + \Delta f_m')^2 + (\Delta f_m'')^2 + \\ + del(s)\ (\lambda/\lambda')^2 I_{m,\text{incoh}}(s)\}$$

Here $I_{\text{obs}}(s)$ are the corrected and normalized intensities and $s = 4\pi\lambda^{-1}\sin\theta$. The summations are performed over all the atoms m in a stoichiometric unit of volume, V. The function $del(s)$, describing the fraction of the incoherent radiation which passes the monochromator, was determined as follows. The apparent shape of the spectrum of the Mo-tube was measured after reflection by the (200) lattice planes in the LiF-monochromator used. For radiation scattered incoherently, the wavelength (in Å) is increased: $\lambda' = \lambda + 0.02426(1 - \cos 2\theta)$.[64] The relative intensity at the wavelength λ' from the measured spectrum compared to the peak intensity at $\lambda(K\alpha)$ then gives $del(s)$ for the scattering angle 2θ.

An independent check of this function at high angles ($2\theta > 135°$) was obtained by measurements with a Zr-filter.[70]

The electronic radial distribution functions, $D(r)$, were calculated as $D(r) = 4\pi r^2\rho_0 + (2r/\pi)\int_0^{s_{\max}} si(s) \times Mod(s)\sin(rs)\mathrm{d}s$ where the modification function, $Mod(s)$, was $\{f_{\mathrm{M}}^2(0)/f_{\mathrm{M}}^2(s)\}\exp(-0.01s^2)$, (M = Cd or Hg) and $\rho_0 = \{(\sum_m(f_m + \Delta f_m'))^2 + (\sum_m \Delta f_m'')^2\}/V$.

Finally, a correction was made for errors giving low-frequency additions to the $i(s)$ curves. Small spurious peaks below 1 Å in the $D(r)$ functions, which could not be related to interatomic distances, were removed by a Fourier transformation procedure.[70]

The calculations of intramolecular intensity contributions and peak shapes were carried out as described previously.[6,61]

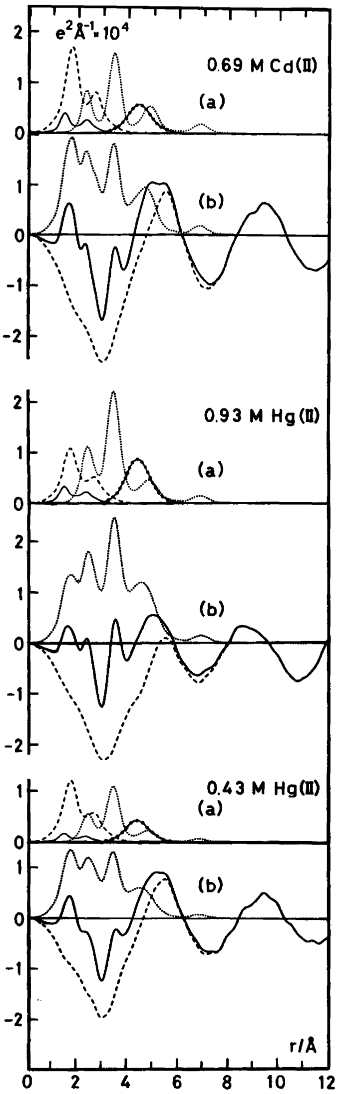

Fig. 1. (a) Peak shapes calculated for the refined models of the DMSO solutions, using the parameter values in Table 3, columns *B*. Dotted lines refer to M – O, M – S, S – S and O – O interactions, solid lines with large dots to M – C interactions within the complex $[M(DMSO)_6]^{2+}$. Dashed lines refer to S – O, S – C, O – C and C – C interactions within DMSO, and solid lines to Cl – O and O – O interactions within ClO_4^-. (b) $D(r) - 4\pi r^2\rho_0$ functions (solid lines) compared with sums of calculated peak shapes (dotted lines). The differences are shown by the dashed lines.

Results

Intensity curves and radial distribution functions (RDF). The experimental distribution functions, $D(r)-4\pi r^2\rho_0$, are shown in Fig. 1. The peaks found at about 2.3 and 3.4 Å in the RDF's fit in with the M−O and M−S distances expected for an octahedral complex and are close to corresponding values found in the crystal structures of the hexasolvates.[32,48]

Intramolecular DMSO-distances should occur at about 1.52 (S−O), 1.78 (S−C) and 2.7 Å (O−C and C−C).[10,32,48,71,72] The S−O and S−C interactions explain the observed peak at 1.6−1.7 Å (Fig. 1). Expected Cl−O and O−O distances within the tetrahedral ClO_4^- ion are 1.43 and 2.33 Å, respectively.[73] Two broad peaks at about 5−6 and 9−10 Å also occur in the RDF's. They are, as well as the sharp intensity peak at $s \sim 1.5$ Å^{-1} (Fig. 2), features also found in an X-ray diffraction study of liquid DMSO,[2a] and are very probably mainly caused by intermolecular interactions between DMSO molecules.

For the 0.93 M mercury(II) perchlorate solution, a separation of the intensity contributions from the various interactions can be performed with fair accuracy. This has been done in Fig. 3, where the functions $si(s)$ have been plotted separately for the various types of intramolecular interaction taking place in the solution, *viz.* those due to the complex formation, and those originating from the DMSO molecules and the perchlorate ions. The interactions due to the complex formation have been further divided so that the contributions from Hg−O, Hg−S, O−O and S−S have been combined, while the contribution from Hg−C has been separated.

For all three solutions investigated, the sum of

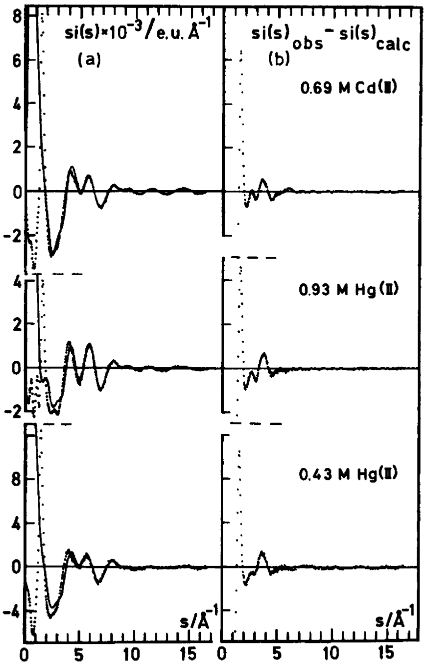

Fig. 2. (a) Reduced intensities multiplied by s for the DMSO solutions investigated. Experimental values are denoted by dots, values calculated for the refined model (with the parameter values in Table 3, columns *B*) by solid lines. (b) Differences between experimental and calculated values.

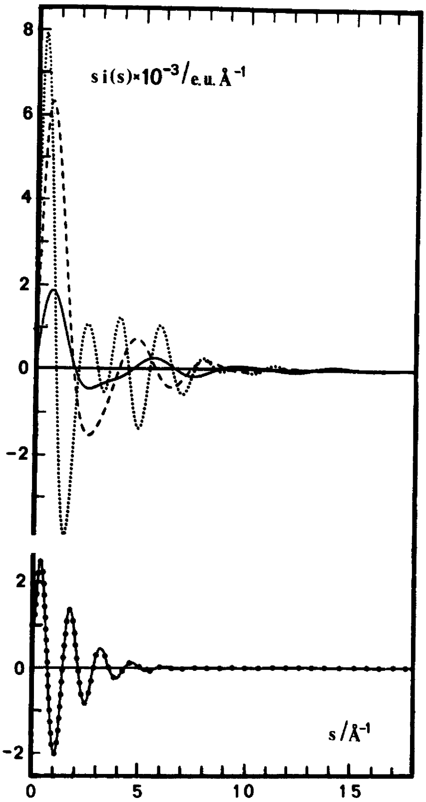

Fig. 3. Separation of the reduced intensities between various interactions for 0.93 M mercury(II) perchlorate in DMSO. The various lines refer to the same interactions as in Fig. 1a. For clarity, the highly damped curve of the Hg−C interactions is shown separately in the lower part of the figure.

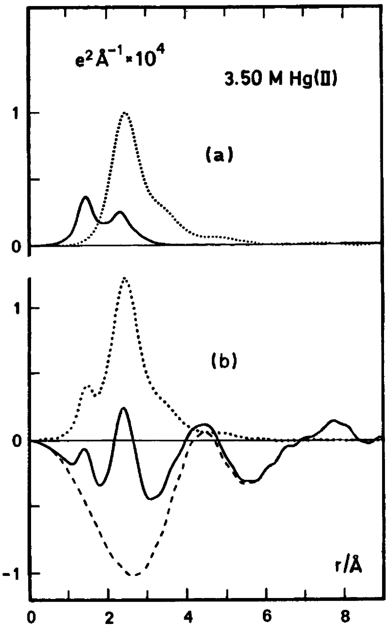

Fig. 4. (a) Peak shapes calculated for intramolecular interactions within the $[Hg(H_2O)_6]^{2+}$ complex (dotted line) and the ClO_4^- ion (solid line), using the parameter values in Table 4, column *B*. (b) $D(r)-4\pi r^2\rho_0$ function for the acidic aqueous 3.50 M $Hg(ClO_4)_2$ solution (solid line), the sum of the calculated peak shapes (dotted line), and the difference between them (dashed line).

all the calculated intramolecular reduced intensity contributions, $i_{calc}(s)$, are compared with the experimental $i_{obs}(s)$ curves of Fig. 2*a*, after multiplication by *s*. As can be seen from the differences $si_{obs}-si_{calc}$ in Fig. 2*b*, these intramolecular intensities are the dominant contributors to the high angle regions of the observed intensity curves, where the effect of the highly damped intermolecular contributions become negligible.[6]

A recalculation of the aqueous mercury(II) perchlorate solution *A*1 in Ref. 33 (3.50 M $Hg(ClO_4)_2$ + 0.64 M $HClO_4$) was performed, since it was felt that, with the better scattering factors now available and the efficient data treatment now possible,[61] a more precise value of the Hg–O bond length could be obtained, to be compared with the present data. The $D(r)-4\pi r^2\rho_0$ curve obtained is shown in Fig. 4. Distinct peaks are found at 1.4 and 2.4 Å. The shorter distance can be identified with Cl–O in the perchlorate ion[73] and the longer one with Hg–O in the hydrated Hg^{2+} ion.[31] A contribution to the peak at 2.4 Å also comes from the O–O interactions in ClO_4^-. These assignments are founded on the distances determined in crystal structures. The broad peak at about 4.5 Å is mainly caused by intermolecular interactions in the solutions as is discussed later.

Least-squares refinements. The parameter values of the models used for calculations of intramolecular intensity contributions can be refined using the high angle regions of the intensity curves. A series of refinements were performed where a minimum was sought[6,61] for the weighted error-square-sum $\sum_{s_{min}}^{s_{max}} w(s)\{i_{obs}(s)-i_{calc}(s)\}^2$. The weighting function, $w(s)$, was proportional to $I_{obs}^{-2}\cos\theta$, which gives each part of the refined $i(s)$ curve a weight corresponding approximately to its statistical precision and also compensates for the unequal spacing between the points caused by the constant $\Delta\theta$ interval used during the intensity measurements.

To check for correlations between the parameters of the refined models, different combinations of parameters were refined. Those held constant were systematically given different values within their probable limits of variation.[74] The influence of systematic errors in different parts of the intensity curves were estimated by using different *s* ranges in the refinements. Especially the lower *s* limit was varied.[6]

For the DMSO solutions, the model selected in the final refinements consisted of the following parts.

1. Oxygen coordinated $M(DMSO)_6^{2+}$ complexes, where the distances *d* of the M–O and M–S interactions, the coefficients *b* of their temperature factors $\exp(-bs^2)$ and, in some cases, the number of distances, *n*, were refined. The contributions from the O–O and S–S interactions, assuming octahedral arrangements around the metal atoms as in the crystal structure of $[Hg(DMSO)_6](ClO_4)_2$,[32] were also introduced.

2. Pyramidal DMSO molecules, where in some cases the S–O and S–C distances and a *b* value, common to S–O and S–C, were refined. The O–C and C–C distances were taken from the crystal structure of pure DMSO at 5 °C.[71] The *b* values of these interactions were assumed to be twice as large as the refined one for the S–O and S–C interactions. The C–H distance 1.08 Å and $b_{C-H}=0.0030$ Å^2 were used.[75] All DMSO molecules,

Table 3. Results of the least-squares refinements of the DMSO solutions. The refined parameters, d = distance (Å), b = temperature factor coefficient (Å^2) and n = number of distances per metal atom, are obtained for the range $6 < s < 16$ Å^{-1} of the reduced intensity curves. Estimated standard deviations are given within parentheses for refined parameters. In columns *A* all parameters in the table have been independently refined, in columns *B* a few are held constant.

Complex	Interaction	Parameter	0.69 M $Cd(ClO_4)_2$		0.93 M $Hg(ClO_4)_2$		0.44 M $Hg(ClO_4)_2$
			A	*B*	*A*	*B*	*B*
$M(DMSO)_n^{2+}$	M−O	d	2.290(3)	2.294(2)	2.394(3)	2.392(3)	2.39(1)
		b	0.0041(5)	0.0044(3)	0.010(1)	0.0098(3)	0.013(1)
	M−S	d	3.417(3)	3.422(3)	3.426(3)	3.427(3)	3.437(5)
		b	0.016(1)	0.0154(4)	0.018(1)	0.0190(3)	0.016(1)
	M−O and M−S	n	6.5(4)	6	5.6(2)	6	6
ClO_4^-	Cl−O	d	1.425(3)	1.426	1.447(5)	1.426	1.426
DMSO	S−O	d	1.559(3)	1.53	1.51(1)	1.53	1.53
	S−C	d	1.814(3)	1.80	1.78(1)	1.80	1.80
		b	0.0032(2)	0.0031(2)	0.0036(3)	0.0036(2)	0.0034(4)

Table 4. Results of least-squares refinements of an aqueous 3.5 M $Hg(ClO_4)_2$ solution in 0.64 M $HClO_4$. The refined parameters with the estimated standard deviation within parentheses are obtained for the range $4 < s < 16$ Å^{-1} of the reduced intensity curve. In column *A* only $Hg-H_2O$ and $Cl-O$ interactions are taken into account, while in column *B* also H_2O-H_2O interactions along the edges of a regular octahedron are included. Spherical formfactors are used for the water molecules.[66]

Complex	Interaction	Parameter	*A*	*B*
$Hg(H_2O)_n^{2+}$	$Hg-H_2O$	d	2.40(1)	2.41(1)
		b	0.022(3)	0.026(1)
		n	5.4(4)	6.0(4)
	H_2O-H_2O	d		$2.41\times\sqrt{2}$
		b		0.022(7)
		n		12
ClO_4^-	Cl−O	d	1.423(4)	1.420(4)

bonded or non-bonded, were accounted for in this way.

3. Regular tetrahedral ClO_4^- ions, for which only one parameter, determining all distances, was independently refined. The b values were taken from mean-square amplitudes of vibration calculated from spectroscopic data.[76] The values $b_{Cl-O} = 0.00074$ and $b_{O-O} = 0.0016$ Å^2 were used.

For the aqueous solution the model used in the final refinements was the hydrated Hg(II) ion, where the three parameters d, b and n, describing the $Hg-H_2O$ interactions, were refined. H_2O-H_2O interactions, assuming octahedral coordination around mercury, were introduced. A regular ClO_4^- tetrahedron was included as described above.

The parameter values of the DMSO solutions, from refinements in the range $6 < s < 16$ Å^{-1}, are summarized in Table 3, and the ones of the aqueous solution, in the range $4 < s < 16$ Å^{-1}, in Table 4. Significant deviations occurred in the values when the lower s limit was $\lesssim 5$ for DMSO and $\lesssim 3$ for water. This is also indicated by the differences between experimental and calculated $si(s)$ curves for the DMSO solutions in Fig. 2*b*.

The standard deviations given in Tables 3 and 4 are those calculated in the least-squares process. From the variation of the results with different ranges of s, it seems that the inherent systematic errors may be of the same order of magnitude and the estimated standard deviations given in the text have been accordingly increased to give a more realistic error estimate.[74]

Discussion

The solvated Cd^{2+} and Hg^{2+} ions in DMSO. If assumed to be the same, the number of M – O and M – S distances obtained in the least-squares refinements (columns *A* in Table 3) is six, within the estimated limits of error. Also when the number is allowed to vary independently for the two interactions, the same result emerges, though the error becomes larger. This of course further confirms that the lower peaks at 2.3 Å are due to M – O and the higher ones at 3.4 Å to M – S interactions, *i.e.* that both Cd^{2+} and Hg^{2+} are in fact coordinated *via* oxygen.

When the constant contributions from O – O and S – S interactions within the same complex, assuming octahedral configurations, were included in the refinements, the error-square-sum decreased 3 – 4 %. A coefficient *b* corresponds to a root-mean-square variation, $l=\sqrt{2b}$, in the average distance. This *l* value includes both mean-square amplitudes from thermal vibrations[75] and more permanent variations of the distance for a specific type of interaction. The b_{S-S} was therefore given a rather large value, 0.04 Å^2 ($l=0.28$ Å), corresponding to the expected large variation in the individual S – S distances.[32,48]

An inclusion in the refinements of the M – C interactions, which vary considerably around an average of 4.4 Å[32,48] in the crystal structures did not reduce the error-square-sum for the refined high angle regions of the intensity curves ($s>6$ Å^{-1}). This indicates that large variations in the M – C distances occur also in the solutions, corresponding to the estimated large *b* value $\simeq 0.07$ Å^2.

Especially for M – O, the number of distances, *n*, is strongly correlated to the *b* value. Therefore, calculations have also been performed with a constant coordination number of six. This results in more precise *b* values, but the other parameters do not change significantly, Table 3.

The b_{Cd-O} value corresponds to $l=0.085(4)$ Å. This is not much larger than the expected vibrational amplitude. The spread of the Cd – O distances is thus small, confirming that the coordination is regularly octahedral.

The b_{Hg-O} is significantly larger, corresponding to $l=0.15(1)$ Å. This probably does not reflect any permanent deviation from regular octahedral symmetry, however, since the Hg – O peak (Fig. 1) seems too symmetrical to contain Hg – O interactions from a markedly distorted octahedral configuration. If any of the bonds were markedly shorter and stronger, they also ought to have small *b* values and therefore be prominent in the outermost parts of the intensity curves. No sign of such an influence has been detected, however.

Comparisons between the RDF's and the calculated peak shapes for the refined model (see above) using the parameter values in Table 3, columns *B*, are made in Fig. 1. The M – C interactions are also included, with the average distance 4.4 Å and the estimated $b_{M-C}=0.07$ Å^2 ($l=0.37$ Å). Smooth difference curves are obtained showing that the refined model accounts for all distinct intramolecular interactions.

The hydrated Hg^{2+} ion. Within the estimated limits of error six oxygen atoms are found to be coordinated to Hg (Table 4). The parameters obtained, when only the $Hg-H_2O$ and the intramolecular interactions in ClO_4^- are taken into account, are listed in column *A*, Table 4. There is, however, a small shoulder at 3.4 Å in the RDF (Fig. 4) corresponding to O – O distances along the edges of a regular octahedral complex. Such expected O – O interactions were therefore included in the refinements, adjusting only the b_{O-O} independently (column *B*, Table 4). The error-square-sum then decreased by 5 %.

The *b* value of the Hg – O distances is rather large, corresponding to a root-mean-square variation $l=0.23(1)$ Å. For the same reasons as discussed for $Hg(DMSO)_6^{2+}$, however, the average symmetry seems to be regularly octahedral (*cf.* Fig. 5, Ref. 33). This is also supported by the relatively small average $l=0.21(3)$ Å obtained for the non-bonded O – O distances along the octahedral edges.

Peak shapes, calculated from the parameter values in column *B*, Table 4, have been subtracted from the RDF of the aqueous solution. A smooth difference curve was obtained (Fig. 4), which supports the assumption of a regular octahedral coordination around mercury.

Comparison of the structures of the DMSO solvates of Hg^{2+} and Cd^{2+} in solution and in crystals. In the octahedrally oxygen coordinated solid compounds $[M(DMSO)_6](ClO_4)_2$, the orientation of the DMSO ligands differ for Cd^{2+} and Hg^{2+}.[48] For the Cd complex even alternative orientations are found. In solution, the DMSO ligands certainly have a considerable freedom of movement. As the methyl groups have a rather large free volume available,[32,48] rotations around the M – O and S – O bonds should be possible. This would give

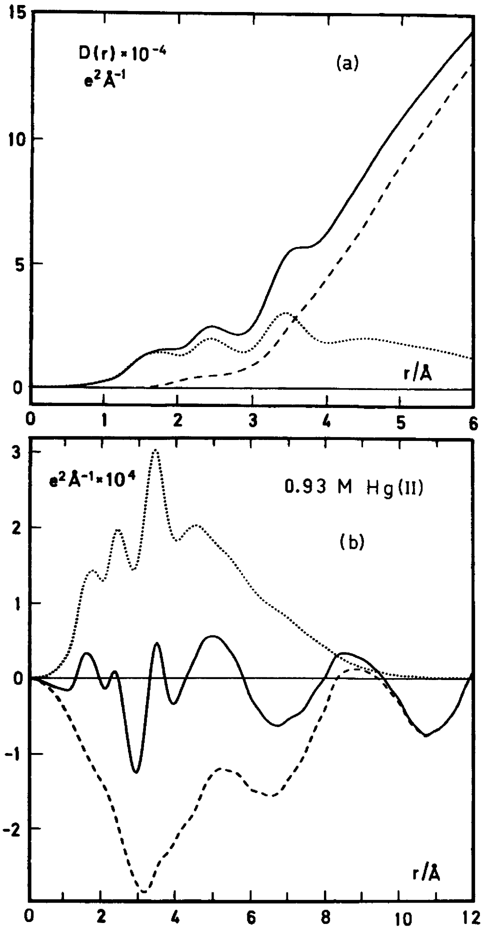

Fig. 5. (a) $D(r)$ curve (solid line) for the 0.93 M $Hg(ClO_4)_2$ solution in DMSO, compared with the sum of the calculated peak shapes (dotted line) for all intramolecular interactions within $[Hg(DMSO)_6]^{2+}$, free DMSO and ClO_4^-. For $[Hg(DMSO)_6]^{2+}$ the positional parameters from the crystal structure determination in Ref. 32 were used, except for the Hg–O distances which were lengthened to 2.393 Å. The dashed line gives the difference between the functions. (b) $D(r)-4\pi r^2\rho_0$ function (solid line), the sum of the calculated peaks (dotted line), and the difference between them (dashed line).

constant M–O and M–S, but varying M–C distances, as is in fact found. There are therefore no reasons to believe that the different shapes found in the crystals would persist in solution.

Discrete dinuclear complexes with a double DMSO oxygen bridge are found in the structure of $Hg(ClO_4)_2.4DMSO$.[54] The Hg–Hg distance is 3.913(4) Å. Also in the structure of $3HgCl_2.2DMSO$ such a double bridge exists. In this case, the Hg–Hg distance is 4.01_6 Å.[10] Therefore, the RDF's were checked for signs of bridge-formation. No trace of such Hg–Hg distances could be found, however.

The complex $Hg(DMSO)_6^{2+}$ in the crystals of $[Hg(DMSO)_6](ClO_4)_2$ has been used to calculate peak shapes for a comparison with the RDF of the 0.93 M $Hg(ClO_4)_2$ solution (Fig. 5). The positional parameters obtained in the structure determination were used,[32] except for the Hg–O distance which was lengthened to 2.39 Å. The freedom of rotation of the DMSO ligands was accounted for by giving the appropriate interactions rather large b values. The intramolecular interactions of ClO_4^- and non-bonded DMSO were also included in the same way as described before. The main difference between this model and the previously refined one is that all intramolecular interactions within $Hg(DMSO)_6^{2+}$ are now taken into account. Subtraction of peak shapes, calculated with this model, from the RDF's give smooth background curves with fairly low electron pair densities up to 4–5 Å (dashed curves in Fig. 5). This indicates that intermolecular interactions from the heavy metal atoms to the ClO_4^- ion and to free DMSO molecules are not frequently occurring within a radius of about 5 Å from the metal atoms. This is consistent with an approximately octahedral arrangement of the S atoms, just as in the solid compound. The remaining broad peaks at about 5.5 and 9 Å in the back-ground curve, agree with peaks found for intermolecular interactions in liquid DMSO.[2] In the solution, non-coordinated DMSO molecules, as well as ClO_4^- ions, are evidently kept away from the mercury rather efficiently by the movements of the DMSO ligands attached to the mercury atoms.

Comparison of the structure of the hydrated Hg^{2+} in solution and in crystal. The very concentrated solution used, 3.5 M $Hg(ClO_4)_2$ in 0.64 M $HClO_4$, contains less than five non-bonded H_2O molecules per $Hg(H_2O)_6^{2+}$ complex. A comparison with intermolecular interactions involving Hg atoms in the structure of the solid hydrate, $[Hg(H_2O)_6](ClO_4)_2$ is therefore of immediate interest. In this compound a slight deviation from a regular octahedral O_h symmetry for the $Hg(H_2O)_6^{2+}$ complexes is observed.[31] This is probably an effect of H-bonds between the complexes leading to Hg–Hg distances of 5.34 Å. There are no indications of such Hg – Hg interactions in the RDF (Fig. 4), and H-bonds between the complexes are evidently not formed in the solution.

In the solid hydrate each Hg is surrounded by six equidistant ClO_4^-. There are therefore six Hg – Cl distances at 4.75 Å, 12 Hg – O distances at 4.39 Å, and another six at 4.64 Å. They correspond very well to the large and broad peak from about 4 to 5 Å which remains in the "back-ground" curve discussed above (dashed curve in Fig. 4). This strongly indicates that in this concentrated solution the complex $Hg(H_2O)_6^{2+}$ is surrounded by ClO_4^- ions at much the same distance as in the solid (*cf.* the results of the refinements in Table 3, Ref. 33).

Bond lengths, bond angles and ionic radii. The Cd – O bond length 2.292(4) Å, found in DMSO solution of $Cd(DMSO)_6^{2+}$, does not differ significantly from the well-defined Cd – O1 bond length, 2.278(7) [2.291]* Å, in the crystalline solvate $[Cd(DMSO)_6](ClO_4)_2$.[48] Also in aqueous solution, much the same bond lengths have been found, *viz.* 2.289 ± 0.013 and 2.31 ± 0.02 Å,[53,44] and these are not significantly different from the average Cd – O bond length in the crystalline hydrate $[Cd(H_2O)_6](NH_4)_2(SO_4)_2$, *viz.* 2.28 Å.[49]

On the other hand, the average Hg – O bond length is significantly longer in the solutions studied than in the crystalline solvates. In aqueous and DMSO solutions (Tables 3 and 4) the values found are 2.41(1) and 2.393(5) Å, respectively, while 2.341(6) [2.349]* Å is found in $[Hg(H_2O)_6](ClO_4)_2$ and 2.338 [2.350]* in $[Hg(DMSO)_6](ClO_4)_2$.[31,32]

In solution, the average values of the angle M – O – S are 120.2(1.0) and 125.7(1.0)° for the Hg and Cd solvates, respectively. This is not significantly different from the corresponding values 123 and 125° in the crystalline solvates.[32,48]

Nor do the intramolecular S – O and S – C distances obtained in the refinements (Table 3) in the DMSO molecules in solution differ significantly from the values found in crystals of DMSO[71] or oxygen coordinated solvates,[32,48] see also surveys in Refs. 10 and 72.

The Cl – O bond length in ClO_4^- found in the least squares refinements agrees very well with that found in crystal structures, especially where only weak hydrogen bonding occurs.[73]

From the average bond lengths obtained, the ionic radii of Cd^{2+} and Hg^{2+} in octahedral coordination can be derived. If the radii of oxygen are taken as 1.35 Å in the two-coordination of the DMSO solvates and as 1.36 Å in the three-coordination of the hydrates,[77] virtually the same radii, $r(Cd^{2+}) = 0.94$ Å and $r(Hg^{2+}) = 1.05$ Å, are found for both DMSO and aqueous solutions. From the crystalline DMSO solvates, $r(Cd^{2+}) = 0.92$ Å and $r(Hg^{2+}) = 0.99$ Å are calculated, from the hydrates 0.92 Å and 0.98 Å. The radii found for the solids are thus somewhat shorter than found for the solutions, and in the case of Hg^{2+} the difference is certainly significant. The radii derived from crystal structures by Shannon and Prewitt[77] are somewhat longer than the present ones, however, *viz.* $r(Cd^{2+}) = 0.95$ Å and $r(Hg^{2+}) = 1.02$ Å, *i.e.* rather close to the values presently found in solution.

While the octahedral bond length relative to oxygen is ≃0.1 Å longer for Hg(II) than for Cd(II), the bond lengths do not differ significantly in the tetrahedral tetraiodo complexes. The Cd – I bonds are 2.79 Å both in DMSO[45] and in aqueous solution[44] and the Hg – I bonds are 2.80 and 2.785(3) Å, respectively.[1,6] In the tetrachloro complexes, on the other hand, the bond length of Hg(II) seems again to be slightly longer than of Cd(II). Admittedly, only one reliable determination has so far been performed in solution, *viz.* for $HgCl_4^{2-}$ in water,[7] where the distance Hg – Cl is 2.47(1) Å. This result agrees well with those found for solids,[26,25] *viz.* 2.46_4 and 2.50 Å. Thus, in the case of this complex, the distance seems to be the same in solution and in crystalline compounds. For $CdCl_4^{2-}$, the average distance Cd – Cl in two recently investigated solid compounds[78] is 2.45_4 Å, *i.e.* most probably shorter than the mean of the values found for Hg – Cl.

The bond distance Hg – L thus becomes shorter relative to Cd – L as the ligand atom L becomes softer, and the bonding hence more covalent, in the sequence O < Cl < I. As might be expected, the softer acceptor Hg^{2+} is able to utilize the covalent bonding capacities of the softer ligands more efficiently than Cd^{2+}, with the result that the bonds Hg – L are strengthened, and consequently also markedly shortened relative to the bonds Cd – L. For the very soft iodide ion, the effect becomes so considerable that the bond lengths, and hence the radii of Hg^{2+} and Cd^{2+}, become virtually equal. For even softer ligands, $r(Hg^{2+})$ might well be even shorter than $r(Cd^{2+})$. Such an inversion has in fact been observed between the neighbour acceptors

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* Corrected for thermal motion assuming oxygen to ride on the metal atom.

gold(I) and silver(I). In the bidentate complexes MCl(PP),[79] the bonds Au–P are 0.1 and 0.15 Å shorter than the corresponding bonds Ag–P while Au–Cl is 0.3 Å longer than Ag–Cl.

RAMAN AND INFRARED SPECTRA

Data collection

The Raman spectra were recorded in the range 1550 to 150 cm^{-1}, with a Cary 82 argon ion laser spectrophotometer using the 4880 Å line. Glass tubes of 1 mm diameter were used both for the solids and the solutions. The infrared spectra were recorded in the range 4000 to 230 cm^{-1}, with a Perkin-Elmer 221 or a Beckman IR-9 spectrometer. In the low-frequency range, 400 to 150 cm^{-1}, the measurements were carried out on an RIIC FS-720 Fourier spectrometer at liquid nitrogen temperature. All other measurements were carried out at room temperature. Depending upon substance and frequency, various techniques had to be used (polyethene or KRS-5 windows; KBr pellets).

Results and discussion

DMSO solvates of Zn^{2+}, Cd^{2+} and Hg^{2+} in solids and solutions. The Raman and infrared spectra recorded display a large number of bands. These can be divided into three distinct groups, *viz.* bands

Table 5. Raman bands (cm^{-1}) of pure DMSO(l), of solid solvates $[M(DMSO)_6](ClO_4)_2$, M = Zn, Cd, Hg and $Hg(ClO_4)_2.4DMSO$ (= Hg 4), and of the saturated DMSO solutions of the hexasolvates. Intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

	Hexasolvates				Solutions[a]			
DMSO(l)	Zn	Cd	Hg	Hg 4	Zn	Cd	Hg	Vibration
	~416 w	~412 w	422 m	~420 m	415 vw	~411 vw	425 w	M–O str, sym
	176 w	197 m	221 m		175 vw	195 w	202 m	M–O bend
1420 m	1425 vs	1425 s	1405 s			1422 s	1420 s	C–H def, asym
1310 w	1325 vw	1305 vw	1320 w			1312 w	1313 w	C–H def, sym
1045 vs	1042 m				1047 s	1047 s	1048 s	S–O str
	1021 s	1028 s	1028 s	1029 w			1025 m[b]	S–O str
997 vw	1003 m	1007 m	1001 m	998 w	1000 vw	1005 vw	996 vw	C–H rock
995 m	954 m	962 m	960 vw		955 m	955 w	950 ww	C–H rock
928 vw	912 m	912 m	909 m		912 w	912 w	911 w	C–H rock
	717 s	717 s	717 s	718 s		~712 m[b]	713 m[b]	C–S str, asym
699 s					698 m	700 m	700 m	C–S str, asym
	683 vs	681 vs	683 vs	683 vs				C–S str, sym
670 vs					668 vs	672 vs	674 vs	C–S str, sym
			399 m	402 m			397 w[b]	C–S–O def, sym
382 m					383 m	384 m	384 m	C–S–O def, sym
	345 s	343 s	342 s	341 s				C–S–O def, asym
332 s					334 s	338 s	336 s	C–S–O def, asym
	317 s	315 s	316 s	314 m				C–S–C def
308 m					308 m	311 m	310 m	C–S–C def
	1102 m	1100 m	1100 m	1093 m				Cl–O
	935 vs	932 vs	932 vs	932 s	932 s	933 s	933 s	Cl–O
	626 m	626 m	625 w	621 w	[c]	625 w	626 w	Cl–O
	460 m	460 m	459 w	463 w	457 w	458 w	460 w	Cl–O

[a] Concentrations: Zn, 0.29 M; Cd, 0.71 M; Hg, 0.93 M. [b] Shoulders. [c] Covered by the very strong C–S stretch at 668 cm^{-1}.

Table 6. Infrared bands (cm^{-1}) of pure DMSO(l), and of solid solvates$[M(DMSO)]_6(ClO_4)_2$, M = Zn, Cd, Hg, and $Hg(ClO_4)_2.4DMSO$ (= Hg 4).

	Hexasolvates				
DMSO(l)	Zn	Cd	Hg	Hg 4	Vibration
	431 m	418 m	445 s		M – O str, asym
	192, 178 w	191, 195 w			M – O bend
2985 s	2978 vw	2970 vw	2980 vw	2985 vw	C – H str
2902 s	2900 vw	2899 vw	2900 vw	2900 vw	C – H str
1432 s		1418 m	1425 vw	1429 w	C – H def, asym
1401 s	1412 vw	1395 m	1397 vw	1397 w	C – H def, asym
1305 m	1303 vw	1304 w		1305 w	C – H def, sym
1048 vs	1015 m	1019 m	1025 m	1015 s	S – O stretch
949 m	948 m	947 m	948 m	945 s	C – H rock
690 m	694 w	695 w	692 w	697 w	C – S stretch, asym
660 w	660 vw	665 vw	666 vw	665 vw	C – S stretch, sym
378 m	368 w	370 w	370 w	371 m	C – S – O def, sym
327 m	321 w	320 w	322 w	340 m	C – S – O def, asym
	1100 w	1088 m	1100 w	1088 s	Cl – O
	621 vs	621 vs	621 vw	621 vw	Cl – O

due to the coordinate bond, to the bonds within DMSO, and to the bonds within ClO_4^-.

The well-known frequencies[80] of the Cl – O bands are, as expected, not shifted in the present solids or solutions, Tables 5 and 6.

On the other hand, the frequencies found in pure DMSO[81] are shifted considerably when the solvent molecules are coordinated to a metal atom. As might be expected, the shifts are larger, the closer the bond associated with the vibration is to the site of coordination. As will be further discussed below, the direction of the shifts depends upon whether the metal ion is coordinated *via* oxygen or *via* sulfur. Especially the S – O stretching frequency, strongly active in both Raman and infrared, exhibits very characteristic shifts. Those found in the infrared spectra have repeatedly been used to discern between different modes of coordination in solid solvates.[82–85,46]

In addition to the ClO_4^- and DMSO bands, the solvates display two new bands of low energy, with wavenumbers just above 400 cm^{-1} and just below 200 cm^{-1}, Tables 5 and 6. The bands observed are of weak to medium intensity. The higher frequency band has been found earlier[55] in the infrared spectra of DMSO hexasolvates of several divalent metal ions, including Zn^{2+}. It has been assigned to the M – O stretching mode.[55] It seems natural to assign the band of lower frequency now discovered to M – O bending modes. Evidence supporting this assignment will be presented below.

A coordination of a metal ion to the O-atom in DMSO should bring about a lowering of the S – O bond order and hence a decrease of the S – O stretching frequency relative to free DMSO. Conversely, a coordination to the S-atom should bring about an increase of the S – O bond order, and hence of the S – O stretching frequency.[83,84] These inferences have later been amply confirmed by complete structure determinations of several of those solids which were used in the previous studies of infrared spectra.[32,48,72,86]

The present Raman spectra of the solid hexasolvates show, as expected, shifts in the S – O stretching frequency very similar to those found in the infrared spectra, Table 5. The latter have moreover been checked, Table 6, with results that agree very well with those previously found.[46] The wavenumbers found in the pure solvent, 1045 cm^{-1} in Raman and 1048 cm^{-1} in infrared, are in all the solvates lowered by 20 to 30 cm^{-1} as expected for O-coordination. The same applies to the actually dimeric[54] $Hg(ClO_4)_2.4DMSO$.

In solutions of these solvates, free DMSO predominates over coordinated DMSO, even if the solutions are saturated. It might be hoped, however, that the bands due to free and coordinated DMSO are resolved in the laser Raman spectra. Unfortunately, the shifts are not large enough for such a resolution. Especially for Zn^{2+}, but also for Cd^{2+}, the solubility is so low that the bands due to coordinated DMSO only appear as rather insignificant shoulders on the low frequency side of the intense band due to free DMSO. For Hg^{2+}, however, where the solubility is higher, a well-developed shoulder is observed, consistent with a downward shift of the S – O stretching band in coordinated DMSO to ≃1025 cm^{-1}, *i.e.* to the value found for the solid hexasolvate, Table 5. This is of course in line with the result of the structure determination reported above for $Hg(DMSO)_6^{2+}$ in solution.

The decrease of the S – O bond order brought about by a coordination of a metal ion via the O atom should induce a compensatory increase in the C – S bond order. Consequently the wavenumbers of the C – S stretching modes, both the symmetric and the antisymmetric ones, should increase. Such shifts, ranging from 10 to 30 cm^{-1}, have in fact been observed in infrared for the antisymmetric mode.[84,85] For the solvates studied here, corresponding shifts have been found for both modes, though smaller, only ≃5 cm^{-1}, Table 6. Especially the bands due to the symmetric vibrations are of low intensity, however, so the determinations are not very precise. For the pure solvent, these bands are found at 660 and 690 cm^{-1} for the symmetric and antisymmetric mode, respectively. The values agree very well with those originally found by Cotton *et al.*[82] and differ only slightly from later determinations which generally record wavenumbers ≃10 cm^{-1} higher.[84,85] Also in the present Raman measurements, somewhat higher wavenumbers are found for these vibrations, *viz.* 670 and 699 cm^{-1}, in accord with earlier determinations,[81] Table 5. For the solid solvates, upward shifts are again found, somewhat larger than in infrared, *viz.* 10 to 13 cm^{-1} for the symmetric and 16 to 17 cm^{-1} for the antisymmetric mode, Table 5. Most probably, the differences found between the infrared and Raman shifts are mainly due to the relatively low precision of the infrared measurements. There is no doubt, however, that the wavenumbers of the C – S stretching modes increase on the coordination of a metal ion to the O-atom, just as expected.

In saturated solutions of the mercury and cadmium solvates, these shifts appear as shoulders on the high frequency side of the bands due to free DMSO. The shoulders are especially marked for the bands due to the antisymmetric stretching, where the shifts are larger. For the less soluble zinc solvate, on the other hand, the concentration of coordinated DMSO is too low to bring about any perceptible shoulders of the DMSO bands.

In contrast to earlier work,[55] we have found that also other vibrations involving the C – S bond, *viz.* the symmetric C – S – C deformation, and the symmetric and antisymmetric C – S – O deformations, increase their wavenumbers perceptibly in the solid solvates, Table 5. This is borne out beyond doubt by the Raman spectrum of the mercury(II) hexasolvate where all three modes are represented by bands of medium to strong intensity. For zinc and cadmium, the symmetric C – S – O bands presumably overlap with the M – O stretching bands which would imply upward shifts of ≃30 cm^{-1}. Considering that shifts of more than 40 cm^{-1} have been found for lanthanide DMSO solvates,[87] this seems quite plausible. Moreover, at least the cadmium band has a deformed shape indicating a composite absorption.

Generally, the complex formation does not bring about large shifts of the vibrations involving the C – H bonds, Tables 5 and 6. Evidently, these are too far from the site of coordination to be much affected by the new bond. The C – H rocking band at 928 cm^{-1} has moved markedly downwards, however. Virtually the same shift is observed when liquid DMSO is vaporized, or diluted by carbon tetrachloride.[81b] Most likely, therefore, this shift is due to the disappearance of the molecular packing preferred by the pure solvent.

Not surprisingly, the most direct information about the M – O coordinate bonds is provided by their own vibrations. The antisymmetrical stretching modes are displayed by the infrared spectra of the solid hexasolvates, Table 6. For zinc, the band is in exactly the same position as found in an earlier study.[55] In the Raman spectra, bands assigned to the symmetrical M – O stretching modes are found for all the hexasolvates, Table 5. For zinc and cadmium, the intensities are fairly low while the mercury band is well-developed. The frequencies are markedly lower than for the anti-symmetric stretching bands recorded in infrared. As the Raman data are more complete, and certainly are more precise, they will serve as the main basis for the following discussion.

Also the Raman spectra of the saturated solutions yield both the M – O bending and the M – O stretching bands, Table 5. In the case of zinc and cadmium, however, the concentrations are so low that the bands are barely perceptible. For mercury they are stronger and, for some unknown reason, the wavenumber of the bending mode is lower than for the solid solvate.

The wavenumber of the stretching modes decreases from zinc to cadmium and then increases again the mercury, Tables 5 and 6. The latter value is even higher than that of zinc. This certainly holds even if, as postulated above, the zinc and cadmium bands in the Raman spectra are somewhat affected by the overlap with the C–S–O deformation frequency. For regularly octahedral complexes like the present ones, the stretching force constants are approximately proportional to the square of the wavenumbers for a symmetric stretching (*cf.* below) which means that they vary in a similar manner, with a marked minimum at cadmium, Table 8. The force constants of course do not measure the total strength of the M–O bonds but rather their resistance to a small disturbance.[88] Nevertheless, the minimum indicates that the Cd–O bond is most probably weaker than both Zn–O and Hg–O. The conclusion is moreover convincingly vindicated by the similar trend found for the heats of solvation, as will be further discussed below. The reason for the remarkable minimum of bond strength at Cd^{2+} must be the rapid change of bond character along the series Zn^{2+}, Cd^{2+}, Hg^{2+}. The small and hard acceptor Zn^{2+} forms a strong bond of a markedly electrostatic character. The very soft and much larger acceptor Hg^{2+} forms a strong bond of a rather covalent character. The intermediate Cd^{2+} is evidently handicapped by being on one hand much larger than Zn^{2+}, on the other much less soft than Hg^{2+}. The outcome is a bond of a lower overall strength than developed by either Zn^{2+} or Hg^{2+}.

This topic will be further discussed later on when the comparison can be extended to stretching force constants for bonds in other complexes of the three metal ions considered, and also to quantities connected with the total strength of these bonds.

The wavenumber of the vibration assigned to the M–O bending mode increases monotonously from zinc to mercury, Table 5. The resistance to this deformation thus increases as the bond becomes more covalent, and hence the directional forces stronger. This is evidently just what to expect for a bending mode and strongly confirms the assignment done for this vibration.

Hydrates of Zn^{2+}, Cd^{2+} and Hg^{2+} in solids and solutions. In the spectral studies of the hydrates, the interest has been focussed on the M–O bonds. In Raman, the symmetric stretching frequencies are found for all the solid solvates, and also for all the saturated solutions, Table 7. The wavenumbers are throughout lower than in DMSO. As in DMSO, a minimum is found at cadmium. In water, the wavenumber for mercury is lower than for zinc, however. The implications of these differences will be discussed below.

The wavenumbers found agree fairly well with those reported previously[89,90] for near-saturated aqueous nitrate and perchlorate solutions (385–390 cm^{-1} for zinc, *ca.* 356 cm^{-1} for cadmium and 380 cm^{-1} for mercury).

For the solid hydrates, faint bands presumably due to the M–O bending mode are observed at $\simeq 175$ cm^{-1}. These bands are too poorly developed, however, to allow a reliable determination of the shifts between the various hydrates.

Force constants and bond strengths. For the present octahedral solvates, a valence force field approach allows a simple calculation of the primary

Table 7. Raman bands (cm^{-1}) of the solid hydrates $[M(H_2O)_6](ClO_4)_2$, M = Zn, Cd, Hg, and of their saturated aqueous solutions.[a]

Solvates			Solutions[b]			
Zn	Cd	Hg	Zn	Cd	Hg	Vibration
385 w	352 m	360 s	~380 m	352 m	370 m	M–O stretch
933 vs	933 vs	933 vs	933 s	933 s	933 s	Cl–O
631 s	630 s	627 s	630 m	627 m	629 m	Cl–O
463 s	465 s	466 s	464 m	461 m	462 m	Cl–O

[a] No measurements at wavenumber >1000 cm^{-1}. [b] Concentrations: Zn, 3.26 M; Cd, 3.23 M; Hg, 3.50 M (+0.64 M $HClO_4$).

stretching force constants F_r. If it is assumed that the frequency is determined solely by the interaction between the metal ion and the oxygen ligand atom and if the secondary interaction constants are neglected, the following relation holds for the symmetric mode[91]

$$F_r = 4\pi^2 c^2 \bar{\nu}^2 N^{-1} A_L$$

where c = the velocity of light, $\bar{\nu}$ = the wavenumber, N = the Avogadro number and A_L = the atomic weight of the ligand atom.

Especially for the DMSO solvates, this approach is a considerable simplification of the actual conditions, as the vibrations of the ligand atom are influenced by the bond joining it to the rest of the DMSO molecule. The values of F_r calculated in this manner, listed in Table 8, will evidently represent the lower limits of the force constants in the present approximation. The other extreme, *viz.* insertion of the total mass of DMSO, would certainly yield values of F_r much further from the truth. However, the influence of the mixing with the bending modes is probably larger for the DMSO solvates than for the hydrates and would counteract the effect of a too small effective ligand mass in the calculations.

This is also borne out by a comparison with the corresponding values of F_r found for the hydrates (Table 8), where insertion of the mass of the whole ligand H_2O certainly is the best approximation. The values of F_r found are not very different from the lower limits calculated for the DMSO solvates. As there is no reason to believe, that the M–O bond strength differs radically between the hydrates and the DMSO solvates, the true values of F_r for the DMSO solvates should be fairly close to those calculated by insertion of the mass of the oxygen atom. Even when this minimum mass is applied, the values for the DMSO solvates are higher, and the M–O bonds, therefore, presumably stronger than for the hydrates. Comparisons between complexes of different acceptors with the same ligand are of course not influenced by this uncertainty.

Table 8. Stretching force constants of the M–O bonds in solid hexasolvates and of the M–X bonds in gaseous dihalides (10^5 dyn cm^{-1}).

	M–O			M–X		
	H_2O^a	H_2O^b	DMSO^a	Cl^-	Br^-	I^-
Zn^{2+}	1.40	1.57	1.63	2.67	2.33	1.77
Cd^{2+}	1.17	1.32	1.60	2.34^c	1.93	1.61
Hg^{2+}	1.22	1.38	1.68	2.63	2.25	1.85

^{a} Force constants calculated with A_L = atomic weight of oxygen atom. ^{b} with A_L = molecular weight of water. ^{c} Corrected value, calculated from ν_3 of Ref. 92.

It is also of interest to compare stretching force constants of these solvates with those found for other complexes of the acceptors studied. As to the gaseous linear[3,92,93] halides MX_2, the symmetric stretching frequencies are so far known only in the case of mercury. The antisymmetric stretching frequencies are, on the other hand, known for all the halides. Again assuming that the secondary interaction constant is negligible, the primary stretching force constant F_r can be calculated from[94]

$$F_r = 4\pi^2 c^2 \bar{\nu}^2 N^{-1} \frac{A_L}{1 + 2A_L A_M^{-1}}$$

where A_M = the atomic weight of the metal. The values of F_r thus found are listed in Table 8. For the mercury systems, they differ somewhat from the set published previously[92] which was calculated as the mean between the values of F_r found from the symmetric and antisymmetric stretching frequencies. It seems better, however, to compare data calculated on the same basis. It is nevertheless reassuring that the values calculated from the symmetric and antisymmetric stretching frequencies do not differ very much.

For all the dihalides, the value of F_r displays that minimum at cadmium which has already been noticed for the solvates, coordinated via oxygen. The lower bond strength of Cd^{2+} relative to both Zn^{2+} and Hg^{2+} thus persists even if the character of the coordinating ligand varies greatly. Moreover, Hg^{2+} is favoured relative to Zn^{2+} by a typically soft ligand as I^- (and also by DMSO!) while the reverse is true for a typically hard ligand as H_2O. The ligands Cl^- and Br^- are intermediate, as might be expected.

The heats of solvation measure the total strength of the M–O bonds while, as already pointed out, the stretching force constants measure their resistance to a limited deformation. As the potential curves of different M–O bonds generally do not conform, the two quantities cannot be expected to vary according to quite the same pattern between different systems. The minimum at Cd^{2+} nevertheless persists also in the heats of solvation, both for

Table 9. Solvation enthalpies,[36] ΔH°_{sv}, and coordination bond energies,[95] CBE, of Zn^{2+}, Cd^{2+} and Hg^{2+} (kJ mol^{-1}).

	$-\Delta H^\circ_{sv}$		CBE		
	H_2O	DMSO	Cl^-	Br^-	I^-
Zn^{2+}	2063	2123	2590	2530	2460
Cd^{2+}	1831	1898	2360	2340	2290
Hg^{2+}	1845	1921	2570	2540	2520

DMSO and water,[36] Table 9. As expected, it is more marked for the softer ligand DMSO. The total bond strength is considerably higher for Zn^{2+} than for Hg^{2+} in both cases.

For the gaseous halides, the coordinate bond energies,[95] *i.e.* the enthalpy changes for the reactions $MX_2(g)\rightarrow M^{2+}(g)+2X^-$, provide a measure of the total strength of the M–X bonds. For all three ligands, the minimum at Cd^{2+} is again evident, Table 9. For the complexes of the very soft ligand I^-, the total bond strength is even higher for Hg^{2+} than for Zn^{2+}, while for the less soft Br^- they are practically equal. For the least soft halide Cl^-, the bond strength is again higher for Zn^{2+} than for Hg^{2+}. This ligand thus reverts to a pattern similar to that found for DMSO and water. As might be expected, however, the difference between Zn^{2+} and Hg^{2+} is much smaller for Cl^- than for the considerably harder oxygen donors.

Conclusion

The Raman spectra confirm that the acceptors Zn^{2+}, Cd^{2+} and Hg^{2+} form DMSO solvates coordinated *via* oxygen not only in solids but also in solutions. They clearly indicate an increase of the covalency of the M–O interaction in the order $Zn^{2+} < Cd^{2+} < Hg^{2+}$, and also a simultaneous decrease of its electrostatic character. These variations thus counteract each other which results in a minimum of M–O bond strength at Cd^{2+}, as is also found from other evidence. The M–O bonds are more covalent in the DMSO solvates than in the hydrates, but the bond strength minimum at Cd^{2+} nevertheless persists also for the harder water ligand.

Acknowledgements. We have been fortunate to have the advice of Dr. Georg Johansson, Stockholm, on the X-ray measurements, and of Dr. Ragnar Larsson, Lund, on the Raman and infrared spectra. We are most grateful for their valuable and generous help.

Our thanks are also due to Professor Kåre Larsson who made the Raman spectrophotometer available. The infrared spectra have been recorded by Dr. Jan Lindgren, Uppsala and Mrs. Karin Trankell, Lund.

We gratefully acknowledge the support given to these investigations by "Naturvetenskapliga forskningsrådet" (The Swedish Natural Science Research Council).

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Received March 29, 1978.