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Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide Solution. I. Dimethyl Sulfoxide Solvates of Silver(I), Zinc(II), Cadmium(II). and Mercury(II)

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Solid dimethyl sulfoxide solvates of silver(I), zinc(II), cadmium(II), and mercury(II) have been prepared. Their infrared spectra indicate that in all the solvates studied DMSO is coordinated *via* oxygen. The solvates have also been characterized by thermogravimetric measurements. The paper also contains an introduction to the investigations of solution equlibria in DMSO which are presently in progress.

The nature of the solvent has a great influence upon the formation of complexes between chemical species in solution. The solvent acts in two ways. First, it provides a medium of which the dielectric constant, D, determines the electrostatic forces of interaction between ions and dipoles present. Second, it forms solvates, thus competing with other coordination reactions which may take place in the solution.

The aim of the present series of investigations is to study the effect of a drastic change of solvent upon a number of complex formation reactions involving acceptors and donors of different bonding characteristics. As the large majority of existing data refers to aqueous solutions, water should evidently be chosen as the solvent of reference and the other solvent should thus have properties very different from those of water. This is certainly achieved if an aprotic solvent is chosen. In such a solvent the solvation of all ligands forming strong hydrogen bonds with water must be much weaker than in aqueous solution. This inference is supported by evidence gathered from very diverse experimental approaches, *viz.* from solvent activity coefficients, mainly determined by solubility measurements,[1–4] from Stokes ionic radii, calculated from ionic mobilities,[5] and from infrared spectra.[6] On the other hand, large and strongly polarizable ligands may well be more strongly solvated in an aprotic solvent.[1–4] Complexes formed by ligands able to form strong hydrogen bonds should therefore be much more stable in aprotic solvents than in water relative to complexes formed by ligands not able to form such bonds. Further, if the solvation of the metal ion is not much stronger in the aprotic solvent, the complexes formed by hydrogen bonding ligands must be not only relatively but also absolutely much stronger in aprotic solvents than in water. This tendency is further strengthened if, as is usually the case, the aprotic solvent has a lower D than water, resulting in a stronger electrostatic interaction.

Once it is recognized that hydrogen bonding ligands form stronger complexes in aprotic than in protic solvents, mainly because of the decrease of the desolvation energies, it is evident that the complex formation reactions should generally be rather more exothermic in the aprotic solvents. Also the increase in electrostatic interaction due to the lower D should act in the same direction. On the other hand, the desolvation accompanying the complex formation should involve a much smaller increase of the entropy in the aprotic than in the protic solvents. The decrease of $\Delta G°$ foreseen for the formation of complexes of hydrogen bonding ligands in aprotic solvents relative to protic ones should thus generally be brought about by a large decrease of $\Delta H°$, while a

simultaneous decrease of $\Delta S°$ will to some extent act in the opposite direction.

For ligands forming no hydrogen bonds the desolvation energy may, on the other hand, be much the same in protic and aprotic solvents. Again provided that the solvation energies of the metal ions are not of very different strength in the various solvents, no large difference in the values of $\Delta H°$ and $\Delta S°$, and consequently in the stability of the complexes, are to be expected. It is possible, however, that the ligand and/or the metal ion are selectively solvated by, *e.g.*, the aprotic solvent. In such case, great differences between the strengths of the complexes formed in the two solvents are of course bound to occur.

A thorough analysis of the various influences exerted by the solvent obviously demands the determination of both the stepwise stability constants, K_n, which directly yield values of $\Delta G°_n$, and the enthalpy changes, $\Delta H°_n$, for the formation of each consecutive complex. The present investigations will thus include equilibrium measurements as well as calorimetric determinations of the corresponding enthalpies of reaction.

The halide ions provide a suitable series of ligands for the test of the conclusions drawn above as their hydrogen bonding properties strongly decrease from the fluoride to the iodide ion as is also clearly reflected by the decrease of the hydration enthalpies along the series.[7]

In order to ensure the intended comparison, a number of complex systems already investigated in aqueous solution must be sufficiently soluble also in the aprotic solvent to be chosen, *i.e.* the species involved must be so strongly solvated that the formation of solid phases does not become the predominating feature. Further, as an ionic medium must be provided in order to keep the activity conditions at least reasonably constant, the solvent must also be able to dissolve suitable "inert" salts in fairly large amounts.

As an aprotic solvent fulfilling these conditions, dimethyl sulfoxide (DMSO) has been chosen.* This solvent has the further interesting feature that it might coordinate either *via* oxygen or *via* sulfur though the latter mode of coordination is sterically less favoured. In spite of this, very soft acceptors do in fact coordinate *via* the sulfur atom, evidently forming a bond of markedly covalent character.[8] This kind of selective solvation has of course no counterpart in aqueous solutions.

The dielectric constant of DMSO is 46.4, as against 78.5 for water, at 25 °C.[8] The electrostatic interactions are thus stronger in DMSO, implying *per se* a stronger complex formation. The increase will of course be more marked the higher the charges and the smaller the radii of the interacting species.

DMSO is also a suitable solvent from some essential practical points of view. The wide and conveniently situated liquid range, between 18.5 °C and 189.0 °C under normal pressure, very much facilitates its use.[8] It is also fairly easy to obtain and keep in a sufficiently pure and dry state though its hygroscopic properties require that precautions are taken to avoid contamination with water during storage and use. Also the marked ability of DMSO to dissolve or penetrate the most diverse organic substances, such as many plastics, rubber and living tissues, poses some practical problems. Chemically, DMSO is fairly inert, though it reacts with strong reducing and oxidizing agents. Often such reactions stop at the corresponding sulfide and sulfone, respectively,[9,10] but very strong oxidizing agents, such as perchloric acid and perchlorates, may bring about a rapid complete oxidation, resulting in an often very violent explosion.[8] Also solid metal perchlorate solvates of DMSO are sometimes highly explosive as will be further discussed below.

As to the choice of complex systems to be investigated, halides of zinc(II), cadmium(II), and mercury(II) seem to be very suitable, for several reasons.

First, these halides are all fairly soluble in DMSO, with the exception of the fluorides. Equally important, the corresponding perchlorates are not difficult to prepare water-free as well-defined and fairly stable DMSO-solvates which are readily soluble in DMSO. These solvates can thus serve as convenient sources for the metal ions. The halide ions, agian with the exception of the fluoride ion, also fulfil the necessary conditions that they form salts easily soluble in DMSO with several cations (Li^+,

* A very informative survey of the physical and chemical properties of DMSO, and particularly of its interaction with inorganic compounds, has recently been compiled by Reynolds.[8]

NH_4^+, tetraalkylammonium ions) which may conceivably be used in order to make up the ionic medium.[6,11]

Second, the acceptors as well as the donors involved show a wide variation in their preferences for coordination partners. The metal ions range from the fairly hard zinc(II) *via* cadmium(II), of a typical border-line behaviour, to the markedly soft mercury(II) while the properties of the ligands change considerably from the mildly soft chloride to the very soft iodide ion.[12,13]

Third, the complex formation in aqueous solution is well known for all these halide systems from a large number of reliable investigations.

The zinc and cadmium systems have not previously been systematically studied in DMSO. On the other hand, the chloride, bromide, and iodide systems of mercury(II), and also of silver(I) and copper(I) have been rather extensively investigated.[2,14-18] In all these systems except copper(I) iodide, more stable complexes are formed in DMSO than in water, but the increase of stability becomes, as expected, much smaller in the sequence $Cl^- > Br^- > I^-$. Especially interesting comparisons should be possible between the monovalent d^{10} acceptors silver(I), and copper(I), of very soft behaviour, and the divalent d^{10} acceptors of the zinc group once the results of the presently planned measurements have emerged. In view of the special interest attached to this comparison, it might even be worthwhile to redetermine *e.g.* the silver halide systems in one or more of the media employed in the present investigation. Anhydrous silver perchlorate and nitrate can easily be prepared and used as sources of silver ions in such a study. In order to make the picture complete, however, the formerly unknown DMSO-solvates of these salts have also been prepared.

The experimental part of this first paper describes the preparation, analysis and characterization of a number of solid metal DMSO solvates of interest for the intended measurements. In all, six well-defined compounds have been prepared, *viz.* perchlorates of zinc (two solvates), cadmium, mercury, and silver, and a nitrate of silver. Of these only two have been identified beyond doubt with compounds described previously, *viz.* $Zn(DMSO)_5(ClO_4)_2$ and $Hg(DMSO)_6(Cl_4)_2$.[19,20]

EXPERIMENTAL

Chemicals. The *metal perchlorates* (G. F. Smith Chemical Co) and the *silver nitrate* (Baker & Adamson) were used for the preparations without further purification. The *DMSO* (BDH laboratory reagent) was distilled in vacuum over calcium hydride and kept in a dark bottle over Union Carbide molecular sieves 3A (diameter of pores ≈3 Å). The product thus obtained had a melting point of 18.55 °C (*cf.* Ref. 8, p. 4) and a water content of 0.02 %. The *hexadeuterio-DMSO*, used in order to confirm IR-assignments, was obtained from Merck.

Preparations. *$Ag(DMSO)NO_3$* was prepared by addition of silver nitrate to DMSO and evaporation of excess DMSO in vacuum. The oil obtained crystallized on rubbing with a glass rod.

$Ag(DMSO)_2ClO_4$. Anhydrous silver perchlorate (0.05 mol) was dissolved in acetone (10 ml) and DMSO (0.20 mol) was added. Acetone and excess DMSO were evaporated in vacuum. On cooling the oily liquid solidified to a glass which was dissolved in dry acetone. On slow evaporation of the solvent, crystals precipitated. *Extreme caution must be exercised when these crystals are handled.* On rubbing or scratching, they explode with extreme violence. This compound is by far the most unstable of the solvates described in this paper.

$Zn(DMSO)_5(ClO_4)_2$ was prepared according to Currier and Weber,[19] with the modification that a temperature of 25 °C was used instead of 40 °C.

$Zn(DMSO)_6(ClO_4)_2$. The zinc perchlorate hexahydrate (0.02 mol) was dissolved in a minimum amount of acetone and DMSO (0.12 mol) was added. On cooling to −20 °C crystals were obtained. The crystals were recrystallized at least twice from dry acetone. Attempts to prepare this compound according to Cotton and Francis [21] always resulted in crystals containing more than 6 DMSO per Zn. The method used here is almost identical with that reported by Selbin *et al.*[22] to yield $Zn(DMSO)_4(ClO_4)_2$.

$Cd(DMSO)_6(ClO_4)_2$. The cadmium perchlorate (0.02 mol) hexahydrate was dissolved in a minimum amount (12 ml) of acetone. After addition of 2,2-dimethoxypropane [23] (0.12 mol) the solution was shaken for 2 h. DMSO (0.12 mol) was then added and the resulting mixture shaken for another 0.5 h. On cooling to −20 °C crystals were formed which were recrystallized from acetone.

$Hg(DMSO)_6(ClO_4)_2$. The mercury(II) perchlorate trihydrate (0.01 mol) was dissolved in ethanol (17 ml). Sometimes, it was necessary to decant the solution in order to remove a slight residue of insoluble matter. When DMSO (0.06 mol) was added, precipitation occurred immediately. The crystals were filtered in a dry nitrogen atmosphere and dried in vacuum over night. On standing, mercury(I) was formed in the ethanol solution with production of acetal-

dehyde. The addition of DMSO should therefore be done without delay.

Chemical analyses. Zinc, cadmium, and *mercury* were titrated with EDTA. *Silver* was titrated according to Volhard.

DMSO was analyzed by a procedure described by Douglas[10] and the *water* content determined by a modified Karl Fischer method.[24] The water determinations, as well as the conventional carbon, hydrogen, and sulfur analyses were performed by the Dept. of Analytical Chemistry of this Chemical Center.

Melting points were determined with a Büchi melting point apparatus.

Infrared spectra were recorded on a Perkin-Elmer Model 221. All spectra were obtained using KBr pellets.

Thermogravimetric analyses were performed by means of a Mettler thermogravimetric balance, at the Dept. of Inorganic Chemistry, University of Gothenburg.

RESULTS AND DISCUSSION

Analytical data, water contents, and melting points of the solvates prepared are presented in Table 1. Zinc and cadmium both form hexasolvates of fairly high melting points. Mercury also forms a hexasolvate that decomposes at a considerably lower temperature. In the case of zinc, a pentasolvate is also easily prepared. The silver perchlorate is a disolvate, the nitrate a monosolvate, both melting considerably lower than the zinc group solvates. Especially the nitrate has quite a low melting point, 50 – 51 °C.

For the mercury compound the thermogravimetric measurements showed no weight loss and no reliable melting point before the decomposition at 130 °C. None of the other solvates lost solvate molecules before melting, except the zinc hexasolvate which lost 1 DMSO. The melting point found thermogravimetrically for the resulting compound is identical with that of the directly prepared zinc pentasolvate.* All compounds, except the mercury one, disintegrated around 200 °C.

For steric reasons, the hexasolvates are most certainly oxygen coordinated, even in the case of mercury(II) which has *per se* a high affinity for sulfur. In the case of the di- and monosolvates of silver(I) no such steric hindrance occurs.

The mode of coordination may be inferred from infrared spectra, as the bond order, and hence the stretching frequency of the sulfur to oxygen bond, is affected very differently depending upon whether the metal ion is coordinated to the oxygen or to the sulfur atom. In the case of oxygen coordination, a lowering of the bond order and hence a decrease of the stretching frequency should occur. Conversely, coordination to the sulfur atom should result in a higher bond order and hence in an increase of the stretching frequency. This effect has been intensively studied especially for the DMSO complexes of the first row transition metals.[19–22,25–29] The deductions drawn have later also been verified by determinations of the structures of several of the complexes, *e.g.* the sulfur coordinated *trans*-$Pd(DMSO)_2Cl_2$[30] and the oxygen coordinated $La(DMSO)_4(NO_3)_3$.[31]

The interpretation of the infrared spectra of oxygen bonded DMSO-complexes has been somewhat in doubt because of the coupling that most probably exists between the SO stretching and the methyl rocking frequencies.[27,32] Some authors [22,25] assign the bands near 1000 and 930 cm^{-1} to the SO stretching

* In the Büchi apparatus, on the other hand, the hexasolvate seemed to keep practically all DMSO until its admittedly not very sharp melting point (Table 1).

Table 1. Analytical data (%).

	Mp °C	DMSO Calc.	DMSO Found	Metal Calc.	Metal Found	Water
$Ag(DMSO)NO_3$	50 – 51	31.50	29.14	43.50	44.11	–
$Ag(DMSO)_2ClO_4$	91 – 92	42.98	43.87	29.67	29.01	–
$Zn(DMSO)_5(ClO_4)_2$	182 – 184	59.65	60.10	9.98	9.95	1.2
$Zn(DMSO)_6(ClO_4)_2$	165 – 175	63.95	63.02	8.92	8.96	0.2
$Cd(DMSO)_6(ClO_4)_2$[a]	188 – 190			14.41	14.45	< 0.1
$Hg(DMSO)_6(ClO_4)_2$[b]	125 – 128 dec.			23.10	22.57	0.25

[a] Calc.: S 24.66; C 18.47, H 4.65. Found: S 23.0, C 18.6, H 4.75. [b] Calc.: S 22.15. Found: S 22.05.

Table 2. Infrared spectra of the DMSO-complexes.[a]

	SO-stretch.	CH_3-rock.
$Ag(DMSO)NO_3$	1018 vs	949 s
$Ag(DMSO)_2ClO_4$	1020 vs	950 s
$Zn(DMSO)_5(ClO_4)_2$	1018 vs	950 s
$Zn(DMSO)_5(ClO_4)_2$	1018 vs	948 s
$Cd(DMSO)_6(ClO_4)_2$	1015 vs	948 s
$Hg(DMSO)_6(ClO_4)_2$	1018 vs	949 s

[a] In Tables 2 and 3, the intensities are indicated as follows: w = weak, m = medium, s = strong, sh = shoulder and v = very.

and the methyl rocking, respectively. Others [26,28] reverse these assignments.

In the pure solvent the band at about 950 cm^{-1} can be fairly safely identified by coordinate analysis as due to the methyl rocking.[26,32] The strong band at 1055 cm^{-1} can no doubt be assigned to the SO stretch. These assignments are in line with the band shifts observed on deuteration of the DMSO.[26,32] For the deuterated compound (DMSO-d_6) the wave number of the methyl rocking should be much lower, while that of the SO stretch should not be much affected. In fact the band at 950 cm^{-1} has moved down to 800 cm^{-1}, while the other band has moved only about 10 cm^{-1}, and moreover upwards.

All spectra in this investigation are very similar. The interesting parts of them are listed in Table 2. The very strong band around 1020 cm^{-1} has been assigned to the SO stretch involving a lowering from 1055 cm^{-1} as expected for oxygen bonded solvates. The wave number of the methyl rocking stays around 950 cm^{-1}, as is also to be expected. In all cases this band is less intense than the SO band.

To get further information two of the complexes have been synthesized with DMSO-d_6, *viz.* $Zn(DMSO\text{-}d_6)_5(ClO_4)_2$ and $Hg(DMSO\text{-}d_6)_6(ClO_4)_2$. Because of the marked similarity between the spectra, the results should be valid for all the complexes studied. The assignments follow Cotton,[26,32] except for the SO stretching where we prefer the alternative interpretation suggested by Drago and Meek.[27] The wave numbers of the principal bands are given in Table 3. Unfortunately, some bands presumably due to CD_3 deformations enter the region of interest, but the fact that all the bands between 900 and 1000 cm^{-1} are of low intensity shows that the SO stretch must give rise to one of the strong bands at 1020 and 1045 cm^{-1}. Most likely the strongest of them should be assigned to the SO stretch.

It is obvious (Table 2) that in all complexes prepared the SO stretching frequency is lower than in uncoordinated DMSO. The magnitude of this shift is $35-40$ cm^{-1}. In all the solvates prepared, DMSO is thus coordinated *via* oxygen. It may be inferred that this is the case also in DMSO solutions.

It is striking that the DMSO solvates of silver(I) and mercury(II) are coordinated *via* oxygen and not *via* sulfur which might have been expected since both are quite soft d^{10} acceptors. In order to investigate this further, complete structure determinations of $Ag(DMSO)_2ClO_4$ and $Hg(DMSO)_6(ClO_4)_2$ are now in progress. As to the silver compound the determination is so far advanced that the main features of the structure are evident, confirming

Table 3. Infrared spectra of $Zn(DMSO\text{-}d_6)_5(ClO_4)_2$ and $Hg(DMSO\text{-}d_6)_6(ClO_4)_2$.

$Zn(DMSO\text{-}d_6)_5(ClO_4)_2$	$Hg(DMSO\text{-}d_6)_6(ClO_4)_2$	Assignment
2240 m	2238 m	Asym CD stretch
–	2104 w	Sym CD stretch
1046 s	1043 s	Sym CD_3 def.
1019 vs	1015 vs	SO stretch
1002 w sh	998 w sh	
959 m	963 m	CD_3 def.
	948 m	
816 m	814 m	
755 m	752 m	CD_3 rocks

the oxygen coordination. The silver atoms are in fact joined to chains by double bridges of 2 DMSO. A detailed report will soon be published.[33]

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