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INFLUENCE OF THE SOLVENT ON THE STABILITY OF METAL ION COMPLEXES

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EXPECTED DIFFERENCES IN COMPLEX FORMATION BETWEEN APROTIC AND PROTIC SOLVENTS

The formation of a complex between a metal ion and a ligand in solution involves not only competition between the ligand and the solvent for the coordination sites of the metal ion but also competition for the ligand between the metal ion and the solvent. Though the ratio of charge to radius is generally higher and consequently the solvation stronger for metal ions than for ligands, the solvation of the latter is by no means negligible. The solvation may become quite strong, especially for ionic ligands able to form hydrogen bonds in protic solvents, the most important of these being water. This is clearly demonstrated by the high hydration enthalpies of typically hydrogen bonding ligands. Thus the hydration enthalpy of the fluoride ion exceeds that of most monovalent metal ions [1, 2].

Complexes of ligands prone to form hydrogen bonds should be much more stable in an aprotic solvent, where no such bonds can be formed, than in water, or any other protic solvent, provided of course that the solvation of the metal ion is not much stronger in the aprotic solvent. In any case, complexes of such ligands should be relatively more stable in the aprotic solvent than complexes of ligands forming only weak hydrogen bonds, or none at all.

CHOICE OF SOLVENTS, LIGANDS AND METAL IONS FOR COMPARISON

The halide ions, ranging from the strongly hydrogen bonding F^- to the weakly, if at all, hydrogen bonding I^-, provide a suitable series of ligands for the intended comparison, especially as many metal halide systems have been thoroughly investigated in water, the obvious reference protic solvent. A good aprotic solvent for many of these halide systems has been found in dimethylsulfoxide (DMSO) though fluorides are generally not soluble. Many pseudohalides such as thiocyanates are, on the other hand, soluble. DMSO also dissolves several "inert" salts, such as lithium, ammonium and tetraalkylammonium perchlorates, in fair amounts so that an ionic medium can be maintained [3–6]. Further, its dielectric constant, 46.4 at 25° C, is high enough to prevent purely electrostatic interactions becoming predominant though these of course will be stronger than in water. The convenient liquid range of DMSO, between 18.5° and 189.0° C under normal pressure, is a great advantage in practice [3].

The metal ions should be chosen so that ions of very different affinities to halide ions in aqueous solution are represented. This means that they should range from typical (a)- to typical (b)-acceptors, characterized by the affinity sequences $F^- \gg Cl^- > Br^- > I^-$ and $F^- \ll Cl^- < Br^- < I^-$, respectively [7]. A suitable series of acceptors of the same charge and outer electron configuration are the divalent d^{10} ions of the zinc group, ranging from the (a)-acceptor Zn^{2+} via Cd^{2+}, of mild (b)-character, to the very marked (b)-acceptor Hg^{2+}. Of these, the present authors have chosen Zn^{2+} and Cd^{2+}, determining the stability of their chloride, bromide, iodide and thiocyanate complexes potentiometrically, by means of zinc and cadmium amalgam electrodes [8]. The results can be compared with two sets of data for Hg^{2+} determined by others [9, 10].

The comparison can also be extended to the monovalent d^{10} acceptors, Cu^+, Ag^+ and Au^+, all of very marked (b)-character. The silver systems, including the cyanide have been rather extensively investigated [6, 11, 12]. A comparison between the conditions in DMSO and water is also possible for copper(I) for several systems [13, 14]. Like copper(I), the low oxidation state gold(I) is very much stabilized in DMSO so that interesting results can be obtained concerning the stability of the chloride and bromide complexes which, of course, have no counterpart in aqueous solution [15].

Besides the d^{10} acceptors mentioned, data for halide and thiocyanate complexes in DMSO also exist [13, 14] for the d^9 acceptor Cu^{2+}, and to some extent also [16] for the d^8 acceptor Ni^{2+} which both display a marked (a)-character in water [7].

COMPARISON BETWEEN DMSO AND WATER FOR THE SYSTEMS CHOSEN

Zinc(II)

In water, the halide complexes of zinc are extremely weak and the thiocyanate complexes are not very strong, Table 1. In DMSO the chloride complexes are very much stronger. Also the bromide complexes are much stronger than in water though the increase is less. For the iodide and also for the thiocyanate, the increase is relatively small. The pattern is thus the one expected from the lack of hydrogen bonding in DMSO, resulting in an even more marked (a)-sequence in DMSO than in water. As the complexes are nevertheless more stable in DMSO for all the systems, it may be concluded that Zn^{2+} is certainly not much more strongly solvated by DMSO than by water.

In DMSO, the second complex is favored relative to its neighbours in all the

TABLE 1

Stability of zinc halide and pseudohalide complexes in DMSO and water, at 25°C

	DMSO				Water				
	NH_4ClO_4 (1 *M*)				$NaClO_4$ (1 *M*)	$NaClO_4$ (3 *M*)			
	Cl^-	Br^-	I^-	SCN^-	SCN^-	Cl^-	Br^-	I^-	CN^-
$\log K_1$	1.93	0.84	−0.70	1.38	0.71	−0.19	−0.57	−1.5	5.34
$\log K_2$	3.90	2.89	1.41	1.41	0.34	−0.40	−0.8		5.68
$\log K_3$	2.26	1.34	0.15	2.40	0.15	0.75	0.5		5.65
$\log K_4$	< 1.0	0.15		1.65	0.32				4.90
K_1/K_2	0.011	0.0088	0.0077	0.9	2.3	1.6	2		0.46
K_2/K_3	44	35	18	0.10	1.6	0.07	0.05		1.1
K_3/K_4	>18	~7		5.6	0.7				5.6
Ref.	8				17	18			19

halide systems, as seen from the small values of the ratios K_1/K_2 and the high values of the ratios K_2/K_3. These are outside the ordinary range, approximately between 1 and 10, found for systems of consecutive complexes of the same coordination [20—22]. The very narrow range of existence of the first complex, narrowing in the order $Cl^- > Br^- > I^-$, is especially remarkable. Such a narrow range is also observed for the second complex in the cadmium halide systems. Table 2. As will be further discussed there, the most likely interpretation of these phenomena is that a switch from the octahedral coordination of the initial solvate to the tetrahedral coordination of the fourth halide complex takes place mainly at the step of the poorly favored complex, i.e., at the first step in the case of the zinc halides [23]. In the thiocyanate system, no step is poorly favored to such a degree though the second has a fairly narrow range of existence, as is evident from the low value of K_2/K_3.

Cadmium(II)

Also in the case of cadmium, a switch from water to DMSO means, as expected, a very large increase in stability for the chloride complexes, a considerable, though smaller, increase for the bromide and a very modest one for the iodide and thiocyanate complexes. As a consequence, the mild (b)-sequence characterizing Cd^{2+} in water turns into an (a)-sequence, Table 2. A remarkable feature is that the stability of the chloride complexes in DMSO is much more dependent upon the medium than is usually found in water. A change of medium from 1 *M* to 0.1 *M* NH_4ClO_4 increases K_1 by a factor $\simeq 15$ while in water [24] the corresponding factor would presumably be $\simeq 2$. A plausible interpretation would be that NH_4^+ interacts with Cl^- via hydrogen bonds. This would explain both the strong increase of K_n as the concentration of NH_4^+ decreases and also the fact that markedly higher values of K_n are found in 1 *M* $LiClO_4$ containing 3 *M* H_2O* than in anhydrous 1 *M* NH_4ClO_4. In the former case, H_2O is evidently tied to Li^+, and no hydrogen bonding species will thus be available for Cl^-.

In the halide systems the second complex has, as mentioned, a narrow range of existence in DMSO, narrowing in the sequence $Cl^- > Br^- > I^-$. This is also observed to a less degree in aqueous solution, especially in the more concentrated medium of 3 *M* $NaClO_4$, Table 2. For most of these aqueous systems, all the thermodynamic functions are known [27, 28]. It turns out that the formation of the third complex is accompanied by an abnormally large entropy gain. Also the enthalpy change is abnormally positive, but generally not to such an extent that it fully compensates the increase of entropy. As a result, the third complex very much predominates over the second. The abnormally high values of ΔS_3^0 and ΔH_3^0 are most likely interpreted as due to a change

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* The water is added in order to prevent oxidation of the cadmium amalgam electrode which takes place in an anhydrous solution of 1 *M* $LiClO_4$ in DMSO.

TABLE 2

Stability of cadmium halide and pseudohalide complexes in DMSO [8] and water, at 25°C

	DMSO								
	NH_4ClO_4 (1 *M*)				NH_4ClO_4 (0.1 *M*)	$LiClO_4.3H_2O$ (1 *M*)			
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Cl^-			
log K_1	3.20	2.93	2.19	1.81	4.40	3.62			
log K_2	1.88	1.77	1.41	0.91	2.96	2.56			
log K_3	2.63	2.86	2.90	0.20	3.51	3.11			
log K_4	1.72	1.64	1.18		2.43	2.36			
K_1/K_2	21	14	6	7.9	27	12			
K_2/K_3	0.17	0.08	0.03	5	0.29	0.28			
K_3/K_4	8	16	53		12	5.7			
	Water								
	$NaClO_4$ (1 *M*)				$NaClO_4$ (3 *M*)				
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-	CN^-
log K_1	1.35	1.56	1.88	1.32	1.59	1.76	2.08	1.39	5.62
log K_2	0.43	0.46	0.78	0.67	0.64	0.59	0.70	0.59	5.20
log K_3	−0.37	0.23	1.69	0.04	0.18	0.98	2.14	0.60	4.90
log K_4		0.41	1.28	−0.15		0.38	1.60		3.48
K_1/K_2	8.3	12	13	4.4	8.8	15	24	6.3	2.6
K_2/K_3	6	1.7	0.12	4.3	2.9	0.41	0.04	1.0	2.0
K_3/K_4		0.7	2.6	1.6		4.0	3.4		27
Ref.	24	25	26	26		21,27			19

from octahedral to tetrahedral coordination taking place mainly at the third step [23]. Such a change would involve an unusually extensive liberation of water and also an unusually large heat of dehydration at this very step which would account for the abnormal values of ΔS_3^0 and ΔH_3^0 actually observed. In DMSO values of ΔS_n^0 and ΔH_n^0 are in the course of determination. Surprisingly enough it seems as if here values of ΔS_2^0 and ΔH_2^0 are abnormally large implying that the change mainly takes place at the second step. In the thiocyanate system of Cd^{2+} no step is particularly unfavored, nor was this the case in the corresponding Zn^{2+} system.

The octahedral solvates postulated for Zn^{2+} and Cd^{2+} in water and DMSO are certainly strongly indicated already by the preponderance of hexasolvates in salts of non-complexing anions crystallized from these solvents [29—31]. In those cases where the structures have been determined a regular octahedral coordination has been found. As the rate of exchange between the hydrate shell and the bulk of the solution is very fast for these ions most of the methods used for the determination of the number of water molecules in the shell are not applicable [32]. Recently, however, the existence of octahedral hexahydrates $Zn(H_2O)_6^{2+}$ and $Cd(H_2O)_6^{2+}$ in solution has been confirmed by means of X-ray diffraction [33]. As to the halide complexes ML_4^{2-}, finally formed in the solutions, it has long been argued that they presumably possess a tetrahedral structure [21]. This view has also been supported by spectral evidence [34]. In the case of CdI_4^{2-} in aqueous solution, it has recently been fully confirmed by X-ray diffraction studies [35].

In DMSO, Cd^{2+} complexes beyond the fourth seem to be formed at very high concentrations of chloride and bromide (but not iodide), viz. the dinuclear complex $Cd_2L_9^{5-}$ and the mononuclear ML_6^{4-} (but not ML_5^{3-}). As seen from Tables 2 and 3, these complexes are fairly weak compared with

TABLE 3

Formation of cadmium chloride and bromide complexes beyond CdL_4^{2-} in dimethylsulfoxide

	NH_4ClO_4 (1 M)		$LiClO_4.3H_2O$ (1 M)	
	Cl^-	Br^-	Cl^-	
$\beta_4\ M^{-4}$	2.7×10^9	1.6×10^9	4.5×10^{11}	
$\beta_5\ M^{-5}$	0	0	0	
$\beta_6\ M^{-6}$	2.8×10^{10}	3.7×10^9	6×10^{12}	
$K_5K_6\ M^{-2}$	10	2.3	13	(1)
$\beta_{92}\ M^{-10}$	6×10^{21}	3.7×10^{20}	10^{26}	
$\beta_{92}/\beta_4^2\ M^{-2}$	800	140	500	(2)

(1) Refers to the equilibrium $CdL_4^{2-} + 2L^- \rightleftharpoons CdL_6^{4-}$. (2) Refers to the equilibrium $2CdL_4^{2-} + L^- \rightleftharpoons Cd_2L_9^{5-}$.

the preceding ones, especially in the bromide system. The complex formation functions have in fact very marked stops at $n = 4$. The formation of these complexes would involve a switch back to an octahedral coordination at very high ligand concentrations, as might also probably be the case for the thallium(III) chloride system in aqueous solution [36].

Mercury(II)

Much the same trend is also found for the halides of Hg^{2+}, Table 4. A very large increase of stability from water to DMSO occurs for the chloride system, a somewhat smaller increase for the bromide and almost none at all for the iodide. This last circumstance, together with the fact that the thiocyanate complexes even become somewhat weaker, probably means that the solvation of Hg^{2+} is stronger in DMSO than in water. This conclusion is strengthened by the fact that the neutral complex HgI_2 which is very slightly soluble in water has quite a high solubility in DMSO (4.25 *M* at 25°C) [5]. The change of complex stability between water and DMSO is not quite enough to switch the very marked (b)-sequence found for Hg^{2+} in water into an (a)-sequence in DMSO though the differences in stability between the various ligands are very much evened out, Table 4.

The data available for DMSO do not allow the calculation of any other K_n/K_{n+1} ratios than K_3/K_4. In both the media employed the values of K_3/K_4 are quite high. The third•complex is thus remarkably stable relative to the fourth one, and more so in the iodide than in the bromide system. This is in contrast to the conditions in water where the value of K_3/K_4 is not very large, though also increasing in this solvent in the order $Cl^- < Br^- < I^-$. The fourth complex is tetrahedral both in DMSO [42] and in water [43] while the third complex has a pyramidal structure in DMSO and the second complex, as expected, a linear one [42].

Copper(I), silver(I) and gold(I)

In aqueous solution, the monovalent d^{10} acceptors, Cu^+ and Ag^+, display very marked (b)-sequences, most marked in the case of Ag^+, Table 5. Their halide complexes are much more stable than those of their isoelectronic neighbours Zn^{2+} and Cd^{2+}, though not as stable as those of Hg^{2+}, of the highest period. The changes taking place between water and DMSO are very similar to those found for Hg^{2+}. For Cu^+, having the less marked (b)-sequence in water, an (a)-sequence is found in DMSO, for Ag^+ the (b)-sequence found in water is very much evened out. The thiocyanate complexes of Ag^+ have much the same strength in both solvents. Also for the cyanide complexes, the difference in strength is small.

The neutral halide and thiocyanate complexes CuL are all at least fairly soluble in DMSO [13, 14]. This circumstance, and even more the fact that Cu^+

TABLE 4

Stability of mercury(II) halide and pseudohalide complexes in DMSO and water, at 25°C

DMSO

	Et_4NClO_4 (0.1 *M*)				$NaClO_4$ (1 *M*)	
	Cl^-	Br^-	I^-	SCN	Br^-	I^-
log β_2	21.2	22.2	24.2	16.1		
log K_1						
log K_2						
log K_3	5.7	5.8	6.2	3.0	5.58	6.08
log K_4		2.4	2.2	2.1	2.65	2.58
K_1/K_2						
K_2/K_3						
K_3/K_4		2500	10^4	8	850	3200
Ref.	9	9	9	9	10	10

Water

	$NaClO_4$ (0.5 *M*)			(1 *M*)		(3 *M*)		0
	Cl^-	Br^-	I^-	Cl^-	SCN^-	Cl^-	Br^-	CN^-
log β_2	13.22	17.33	23.82	12.23	16.86	13.98	17.98	32.75
log K_1	6.74	9.05	12.87	6.72	9.08	7.07	9.40	17.00
log K_2	6.48	8.28	10.95	6.51	7.78	6.91	8.58	15.75
log K_3	0.85	2.41	3.78	1.00	2.84	0.75	2.76	3.56
log K_4	1.00	1.26	2.23	0.97	1.97	1.38	1.49	2.66
K_1/K_2	1.8	5.9	83	1.6	20	1.4	6.6	18
K_2/K_3	4×10^5	7×10^5	1.5×10^7	3×10^5	9×10^4	1.4×10^6	7×10^{-5}	1.5×10^{12}
K_3/K_4	0.7	14	35	1.1	7	0.23	19	8
Ref.	37	37	37	38	39	40	40	41

TABLE 5

Stability of copper(I) and silver(I) halide and pseudohalide complexes in DMSO and water, and of gold(I) complexes in DMSO, at 25°C. To maintain the medium at an ionic strength I, tetraethylammonium perchlorate has been used in the DMSO, and sodium perchlorate in the aqueous solutions

		Cl^-	Br^-	I^-	SCN^-	CN^-	Ref.
Copper(I), DMSO							
$\log \beta_2$	0.1*	11.95	9.6	8.2	9.3		13
$\log K_1$	0.1	6	5.0	5.5	4.3		13
$\log K_2$	0.1	6	4.6	2.7	5.0		13
K_1/K_2	0.1	1	2.5	600	0.2		13
Copper(I), water							
pK_{so}	5	7.38	8.89	12.72	14.78		44, 45
$\log \beta_2$	0	5.31	5.89	8.76			46
	5	6.00	6.23	8.69			44, 45
Silver(I), DMSO							
pK_{so}	0.1	10.4	10.6	12.0			6
		10.4	10.9	12.1	7.6	14.9	12
$\log \beta_2$	0.1	11.9	11.7	13.1			6
		11.7	12.0	13.0	8.4	23.4	12
Silver(I), water							
pK_{so}	0	9.75	12.30	16.08	12.00		47, 48
	5^a	10.10	12.62	16.35	12.11		49–52
$\log \beta_2$	0	5.04	7.34	11.74^b	8.23	20.85^c	53, 54
	5^a	5.40	7.23	10.95	8.29		49–52
$\log K_1$	5^a	3.08	4.2		4.59		
$\log K_2$	5^a	2.32	3.0		3.70		
K_1/K_2	5^a	5.7	16		7.8		
Gold(I), DMSO							
$\log \beta_2$	0.1	18.0	16.6				15
$\log K_1$	0.1	12.6	10.6				
$\log K_2$	0.1	5.4	6.0				
K_1/K_2	0.1	1.6×10^7	4×10^4				

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* Ionic strength, I, (M).

[a] For the iodide and thiocyanate systems $I = 4\ M$.

[b] At 18°C.

[c] At 20°C.

is strongly stabilized relative to Cu^{2+} in DMSO* certainly shows that Cu^{+} is very strongly solvated in this solvent [13]. This is also in keeping with the fact that the stability of the iodide complexes of Cu^{+} seem to decrease from water to DMSO.

The solubility of the neutral copper(I) complexes makes the determination of β_1 comparatively simple in DMSO. The first complex has a rather wide range of existence in the iodide system, where $K_1/K_2 = 600$, but not in the other systems investigated.

The solubilities of the neutral complexes AgL are still fairly low in DMSO though certainly much higher than in water. From the values of K_{SO} given and from values of K_1 either given or estimated, the solubilities $S_1 = K_1 \times K_{\mathrm{SO}}$ of AgL can be calculated. Values between 10^{-4} and 10^{-5} are found for DMSO and between 10^{-7} and 10^{-10} M for water, implying about the same relative increase between water and DMSO for AgL as CuL.

Remarkably enough, no complexes beyond the second have so far been found for any of these systems in DMSO. This is in marked contrast to water where the third and/or the fourth complexes are well-established in all the systems discussed [44, 45]. The question certainly merits further investigation.

Gold(I) is so strongly stabilized in DMSO that even in the absence of complexing ligands no disproportionation takes place, at least not for concentrations of $[Au^{+}] < 10$ mM. It has been claimed that no gold(III) is formed in DMSO by anodic oxidation before the solvent is oxidized which would mean that the higher oxidation state is not at all stable in DMSO [15]. This revolution relative to water of the stability of the oxidation states allows the formation of chloride and bromide complexes of Au^{+} in DMSO, Table 5. They are, as expected, much stronger than the corresponding Ag^{+} and Cu^{+} complexes, in fact not much weaker than the Hg^{2+} complexes, in spite of the weaker electrostatic interaction. The neutral complexes AuCl and AuBr are soluble at least up to concentrations $\simeq 1$ mM. They also seem to be very stable relative to the consecutive complexes, the values of K_1/K_2 being very high. Remarkably enough, this ratio seems to be highest for the chloride complex which is certainly against the general rule for acceptors presumed to form a linear second complex, Tables 4 and 5. The iodide complexes cannot be investigated as Au^{+} is reduced by I^{-} in DMSO.

Copper(II) and nickel(II)

Like all other divalent ions of the first transition series, the d^9 acceptor Cu^{2+} and the d^8 acceptor Ni^{2+} form extremely weak halide complexes in aqueous solution. Also the thiocyanate complexes are quite weak, Table 6. As for all the acceptors discussed previously, the complexes become stronger in DMSO, the strengthening decreasing in the sequence $Cl^{-} > Br^{-} > SCN^{-}$.

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* The value of the disproportionation constant $K = [Cu^{2+}]/[Cu^{+}]^2$ in DMSO [13] is ca. 2 M^{-1}, as against ca. 10^6 M^{-1} in water [44].

TABLE 6

Stability of copper(II) and nickel(II) halide and thiocyanate complexes in DMSO and water

	DMSO				Water		
	Cl^-	Cl^-	Br^-	SCN^-	Cl^-	Br^-	SCN^-
Copper(II)[a]							
log K_1	4.4	4.5	3.4	3.2	~0	~0	1.9
log K_2	3.1[c]	3.0	0.9	2.1			1.1
log K_3	3[d]	1.6					
log K_4	2.0						
K_1/K_2	20	30	300	13			6
K_2/K_3	1	25					
K_3/K_4	10						
Ref.	14	13	13	13	22	22	55
Nickel(II)[b]							
log K_1	2.7			3.0	~0		1.8
Ref.		16			22		56

[a] At 25°C and $I = 0.1$ *M*, brought about by tetraethylammonium perchlorate in DMSO and by $NaClO_4$ in water.
[b] At 20°C and $I = 0$.
[c] Weighted mean between potentiometric and spectrophotometric measurements.
[d] Judged by the authors as most plausible value (values actually found by various methods range between 1.6 and 4.0).

It should be noted that the relative stability within the transition series follows the Irving—Williams order $Ni^{2+} < Cu^{2+} > Zn^{2+}$.

As rather different values of K_n are found by different methods and by various investigators, the ratios K_n/K_{n+1} listed in Table 6 for the copper(II) systems must be considered as very approximate. The coordination around Cu^{2+} is presumably square planar both in the solvate and in the complex CuL_4^{2-} finally formed, so no abnormal values of K_n/K_{n+1} due to changes of coordination are in fact expected in these systems.

CONCLUSIONS

The stabilities of all the halide complexes discussed evidently change from water to DMSO in the manner expected from the capacity of the various ligands for the formation of hydrogen bonds in the protic solvent. For ligands forming strong hydrogen bonds, the complexes are always very much stronger in DMSO than in water. But with ligands of fairly low capacity for hydrogen bonding, e.g. I^- and SCN^-, a modest increase of stability is often found. The stronger electrostatic interaction in DMSO should per se bring about a larger increase than actually found for such ligands, but the stronger solvation of the metal ion evidently counteracts so that the net change remains small. In case of the typically soft acceptors Hg^{2+}, Cu^+ and Ag^+ the latter term often becomes the larger so that the complexes formed with weakly hydrogen bonding ligands are somewhat stronger in water than in DMSO. The strong preference of these acceptors for DMSO is also evident from the increased solubilities of their neutral complexes. For the monovalent d^{10} acceptors, this preference is even more drastically shown by the marked increase relative to water of their stability towards disproportionation which results in the existence of solvated Cu^+ and even Au^+ ions in DMSO. It might be thought that this preferential stabilization of soft acceptors would be due to a coordination to the soft sulfur donor atom of DMSO. In some cases such coordination does occur [57], but on the other hand, many DMSO solvates of even very soft acceptors, e.g. Hg^{2+} and Ag^+ are, undoubtedly oxygen coordinated [31].

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