Journal of Organometallic Chemistry, 181 (1979) 17—24
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THERMODYNAMICS OF COMPLEX FORMATION IN DIMETHYL SULFOXIDE WITH LIGANDS COORDINATING VIA N, P, As, Sb, OR Bi

III *. A COMPARISON BETWEEN AROMATIC AND ALIPHATIC AMINES AND PHOSPHINES **

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(Received June 6th, 1979)

Summary

The stabilities of the complexes formed by silver(I), cadmium(II) and zinc(II) with tri-n-butylamine and tri-n-butylphosphine have been determined in dimethyl sulfoxide (DMSO). For the two latter metal ions, it has also been found that complexes are not formed in appreciable amounts with the triphenyl compounds Ph_3X, X = N, P and, in the case of cadmium(II), also As.

From these and earlier measurements referring to DMSO as well as aqueous solutions, it was found that the stepwise stability constants increase by roughly one power of ten for each aromatic ring replaced by an aliphatic group, evidently as a consequence of the improved donor properties of the coordinating atoms. Further, for ligands of the same type, the stabilities are always markedly lower in DMSO than in aqueous solution. This is certainly due to the fact that the solvent molecules compete more strongly for the coordination sites in DMSO than in water, as reflected by the larger heats of solvation found in the former solvent for the metal ions concerned.

Introduction

The donor properties of a coordinating atom present in a non-monoatomic ligand depend upon its atomic environment. Firstly, the number and character

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* For parts I and II see refs. 4 and 5.

** Dedicated to Joseph Chatt on the occasion of his 65th birthday.

of the bonds to neighbouring atoms exert a strong influence upon the electron density on the prospective donor atom, and hence upon its ability to donate electrons, i.e. to form covalent bonds. Electrostatic interactions with ions and polar molecules are also influenced of course. Secondly, the groups adjacent to the donor atom cause serious steric hindrance to coordination. The sulfur atom in sulfoxides provides a good example of such influences. The S=O bond drastically reduces the electron density on the sulfur atom, as compared with the analogous sulfides, and its situation is also much less favourable sterically. As a consequence, the sulfur atom in sulfoxides has much weaker donor properties than that in sulfides. Even to soft metal ions, sulfoxides are therefore generally coordinated via the oxygen atom [1,2]. Only in the case of some extremely soft acceptors is coordination through the sulfur atom preferred [3].

The change of atomic environment just discussed is admittedly a very drastic one, involving the formation of a new bond to a very electronegative atom. Even when the changes are less drastic, however, the donor properties are considerably modified. For meaningful comparisons between the stabilities of complexes formed by various donor atoms, the ligands used must therefore be analogous or nearly so.

In the present series of investigations, pertaining to the complexes formed in solution by ligands coordinating via nitrogen group donors, this uniformity has been achieved by using throughout the simple triphenyl derivatives Ph_3X, X = N, P, As, Sb, Bi, [4,5]. These ligands and their metal complexes are readily soluble in the strongly solvating aprotic solvent dimethyl sulfoxide (DMSO), a compound which also possesses several other properties favourable to the purpose in hand. It was therefore selected as the solvent for the present study. So far, the thermodynamic functions ΔG_j^0, ΔH_j^0 and ΔS_j^0 have been determined for the consecutive complexes formed between all the ligands mentioned and the soft acceptors Ag^+ and Cu^+. In the case of Hg^{2+} such measurements have been possible only for X = N, P and As, as the complexes formed by the heaviest donor atoms Sb and Bi are decomposed in redox reactions [5].

The influence exerted by the atomic environment on the coordinating properties of these donor atoms is of great interest per se, however. An obvious important question is how much the three aromatic rings present in these ligands lower the donor strength of X. To answer this, complex formation by suitable aliphatic derivatives must also be investigated.

The stronger donor properties of aliphatic relative to aromatic derivatives have been known qualitatively for a long time. For amines, a fair number of quantitative data relating to water and to mixed aqueous-organic solvents also exist, and clearly show the considerably lower stabilities of the complexes formed by, e.g., aniline relative to those formed by, e.g., ethylamine [6,7]. As to aliphatic derivatives of the heavier donor atoms, only one quantitative study seems to have been published so far [8]. In that investigation, the complexes formed between diethyl-2-hydroxyethylphosphine (Dop) and a number of metal ions were studied in aqueous solution. The alcoholic group makes the ligand sufficiently water-soluble for such a study. A comparison with the complexes formed by diphenylphosphinobenzene-*m*-sulfonate (Dpm), an aromatic phosphine made water-soluble by sulfonation, shows that the complexes formed by the aliphatic phosphine are indeed much stronger for all acceptors where the available data allow a comparison, viz. Zn^{2+}, Cd^{2+}, Hg^{2+}; Cu^+, Ag^+; and Co^{2+} [9]. In the case of Ag^+, its affinity for a mixed aromatic-aliphatic phosphine, viz. diphenylphosphinopropane γ-sulfonate (Dsp), has recently been investigated [10]. As might be expected, the stabilities of the complexes formed are intermediate between those formed by the purely aromatic-aliphatic phosphine, viz. phosphine.

One might nevertheless ask, how these differences are influenced by the various modes of substitution. Also, at least in the case of Dop ($\simeq$ 20 mM) and of salts of Dpm, the solubilities are still too low to allow very precise calorimetric work. As an elucidation of the enthalpy and entropy contributions to the stabilities must finally be aimed at, higher solubilities are desirable.

When phosphines are used as ligands in DMSO the possibility of their oxidation to phosphine oxides by the solvent must be considered. Though attacked over a long period triphenylphosphine is certainly less sensitive than any of the aliphatic derivatives in this respect [4,11].

Among the latter, however, the easily available tri-n-butylphosphine, Bu_3P, is fairly stable in DMSO. Furthermore this compound is a liquid at ordinary temperatures and it can be conveniently added in the pure form to the metal ion solutions. In this way, contact between DMSO and the ligand can be avoided until the moment of complex formation.

As before, the establishment of the complex equilibria was followed potentiometrically by measuring the free metal ion concentration after each addition of ligand [4,5]. Steady and reproducible potentials, which stayed practically constant for at least 12 h, were rapidly attained. This indicates that no perceptible oxidation of the ligand took place during the time needed for a series of measurements.

As a consequence of the choice of tri-n-butylphosphine, tri-n-butylamine, Bu_3N, was used as the aliphatic N-donor to be compared with the aromatic triphenylamine, and was also added in the pure form. In this way, the highest possible concentration of ligand could be reached, and this is necessary because of its fairly low solubility in DMSO.

The metal ions selected were Ag^+, Cd^{2+} and Zn^{2+}. As mentioned above, stability data referring to the aromatic derivatives already exist in the case of Ag^+ [4]. For Cd^{2+} and Zn^{2+} such data were determined in the present work.

The same perchlorate medium was used as before, viz. ionic strength I 0.1 M, with ammonium perchlorate as supporting electrolyte [4,5]. The temperature was 25°C.

Experimental

Chemicals

DMSO was purified and analyzed as described previously [4]. The source of Ag^+ was anhydrous $AgClO_4$; for Cd^{2+} and Zn^{2+} the hexasolvates $Cd(DMSO)_6$-$(ClO_4)_2$ and $Zn(DMSO)_6)ClO_4)_2$ were used. These were prepared and analyzed as before [2]. Tri-n-butyl-amine and -phosphine were commercial products (from BDH and Strem Chemical, respectively; the density of the latter, 0.8120, agreed well with literature data [12]). The other chemicals, as well as the cadmium and zinc amalgams, were similar to those used previously [13].

Potentiometric measurements

As before the potentiometric titrations were performed in a glove-box filled with dry carbon dioxide; in addition a stream of dry and oxygen-free nitrogen was passed through the solutions. For M = Cd and Zn, the emf of the following cells were measured:

$$\begin{array}{l|l|l|l|l}
 & 0.02\,M\ \mathrm{Cd}^{2+} & & C_{\mathrm{M}}\ \mathrm{M}^{\mathrm{II}} & \\
+\mathrm{Cd(Hg)} & I\ 0.1\,M & 0.1\,M & C_{\mathrm{L}}\ \text{ligand} & \mathrm{M(Hg)}- \\
 & (\mathrm{NH_4ClO_4}) & \mathrm{NH_4ClO_4} & I\ 0.1\,M & \\
 & & & (\mathrm{NH_4ClO_4}) &
\end{array}$$

The Cd(Hg) half-cell to the left served as a very reproducible and stable reference electrode (cf. [5,13]) *. The right half-cell initially contained only cadmium or zinc perchlorate, of a concentration $C'_{\mathrm{M}} = 5$ or 10 mM. Once a stable potential had been reached, portions of ligand were added, either as the pure compound ($\mathrm{Bu_3N}$, $\mathrm{Bu_3P}$), or as a DMSO solution ($\mathrm{Ph_3N}$, $\mathrm{Ph_3P}$, $\mathrm{Ph_3As}$). In the case of silver(I), the following cells were measured:

$$\begin{array}{l|l|l|l|l}
 & C'_{\mathrm{M}}\mathrm{Ag}^{+} & & C_{\mathrm{M}}\ \mathrm{Ag}^{\mathrm{I}} & \\
+\mathrm{Ag} & I\ 0.1\,M & 0.1\,M & C_{\mathrm{L}}\ \text{ligand} & \mathrm{Ag}- \\
 & (\mathrm{NH_4ClO_4}) & \mathrm{NH_4ClO_4} & I\ 0.1\,M & \\
 & & & (\mathrm{NH_4ClO_4}) &
\end{array}$$

Initially, both half-cells contained only silver perchlorate, of the same concentration, C'_{M}, varying between 5 and 20 mM. The emf was thus $\simeq 0$. To the right half-cell pure ligand was added from a microburette in portions of 0.010 ml. The left half-cell served as a reference electrode. The silver electrodes were platinum wires electrolytically coated with silver.

The emfs measured were usually reproducible within $\simeq 1$ mV, except for the strongly complex phosphinesilver(I) system. Not unexpectedly, larger deviations were found in this case where very large emfs, up to $\simeq 800$ mV, were measured. Here, the various series often differed by a few mV; in the neighbourhood of the equivalence points even considerably more. The emfs generally stayed virtually constant for several hours, except for very high phosphine concentrations, where a fairly rapid decrease of the emfs was observed, indicating an increase of the silver ion concentration. This increase might be due to an oxidation of either the silver electrode, or the ligand, by DMSO.

Results

The overall stability constants β_j calculated for the $\mathrm{Bu_3N}$ and $\mathrm{Bu_3P}$ systems are listed in Table 1. In the case of $\mathrm{Bu_3N}$, the silver complex formation was followed to the limit set by the solubility of the ligand, $\simeq 50$ mM, while for the cadmium and zinc the highest concentrations of free ligand obtained were $[\mathrm{L}] \simeq 25$ mM. In the case of $\mathrm{Bu_3P}$, the silver solutions started to deteriorate even at $[\mathrm{L}] \simeq 6$ mM. In the cadmium and zinc solutions the upper limit of $[\mathrm{L}]$

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* For the reference half-cell of Scheme 1 in ref. [5], I was also 0.1 M, not 1.0 M as erroneously stated.

TABLE 1

OVERALL STABILITY CONSTANTS (β_j/M^{-j}) CALCULATED FOR THE COMPLEXES FORMED BY SILVER (I), CADMIUM (II) AND ZINC (II) WITH TRI-n-BUTYLAMINE AND TRI-n-BUTYLPHOSPHINE IN DMSO, AT 25°C AND IONIC STRENGTH I 0.1 $M(NH_4ClO_4)$(The errors stated are three times the standard deviations given by the computer)

	Ag^+	Cd^{2+}	Zn^{2+}
Bu_3N			
β_1	127 ± 11	28.2 ± 2.7	20 ± 9
β_2	2200 ± 600		3200 ± 600
Bu_3P			
β_1	$(1.90 \pm 0.08) \times 10^9$	5.8 ± 0.9	$\lesssim 0.5$
β_2	$(8.1 \pm 0.5) \times 10^{15}$		
β_3	$(6.6 \pm 0.7) \times 10^{19}$		

was again set by the solubility of the ligand, ≃130 mM. For zinc, no perceptible change of the metal ion concentration was recorded in this range, which means that β_1 is certainly $\lesssim 0.5\ M^{-1}$.

The aromatic ligands Ph_3N and Ph_3P do not form complexes in appreciable amounts with Cd^{2+} or Zn^{2+} up to concentrations of $[L] \simeq 80$ mM, implying values of $\beta_1 \lesssim 1\ M^{-1}$. Certainly, no complexes are formed with the ligands Ph_3X, X = As, Sb or Bi. For Cd^{2+} there is also no complexing with Ph_3As.

Discussion

From the constants β_j primarily determined, the stepwise constants K_j and the ratios between consecutive constants have been computed. For the silver complexes these data are listed in Table 2, where the analogous data pertaining

TABLE 2

COMPARISON BETWEEN THE CONSECUTIVE STABILITY CONSTANTS (K_j/M^{-1}) OF THE COMPLEXES FORMED BY SILVER (I) WITH ALIPHATIC AND AROMATIC AMINES AND PHOSPHINES IN DMSO AND WATER, AT 25°C (Dop 22°C).

	DMSO		Water			
	Bu_3N [a]	Ph_3N [b]	Et_3N [c]	Trea [d]	Pabs [e]	Pdbs [e]
log K_1	2.10	0.19	2.6	2.34	1.14	0.76
log K_2	1.23		2.1	1.75	0.95	0.6
K_1/K_2	7		3	3.9	1.5	1.4
	Bu_3P [a]	Ph_3P [b]	Dop [f]	Dsp [g]	Dpm [e]	
log K_1	9.28	6.58	11.83	9.2	8.15	
log K_2	6.63	4.15	9.02	6.4	5.95	
log K_3	3.91	2.44	4.86	5.5	5.40	
K_1/K_2	450	269	650	600	160	160
K_2/K_3	520	52	14 500	8	8	3.5

[a] I 0.1 $M(NH_4ClO_4)$; this work. [b] I 0.1 $M(NH_4ClO_4)$; ref. 4. [c] I 0.4 $M(HNO_3)$; ref. 14. [d] Trea = $N(CH_2CH_2OH)_3$; I 0.5 $M(KNO_3)$; ref. 15. [e] Pabs = $p\text{-}H_2NC_6H_4SO_3^-$; Pdbs = $p\text{-}Me_2NC_6H_4SO_3^-$; Dpm = $m\text{-}Ph_2PC_6H_4SO_3^-$; I 0.1 $M(NaClO_4)$; ref. 16. [f] Dop = $Et_2P(CH_2)_2OH$; I 1 $M(KNO_3)$; ref. 8. [g] Dsp = $Ph_2P(CH_2)_3SO_3^-$; I 1 $M(KNO_3)$; ref. 10.

to aromatic ligands in DMSO, and aliphatic and aromatic ligands in aqueous solution are also listed for comparison.

For aqueous solutions, the data collected clearly bear out the point made above that complexes formed by aliphatic ligands are all more stable than those formed by aromatic ligands.This applied to both amines and phosphines. Moreover, in both cases, the differences in K_1 seem roughly to be just over one power of ten per aromatic ring. For the amines especially when the aromatic derivatives contain only one ring, the differences are clearly much influenced by other substituents. The intermediate position of Dsp also stands out very clearly. Remarkably enough, the values of K_3 are much the same for the three phosphines. As a consequence, the ratio K_2/K_3 is very much higher for Dop than for Dsp or Dpm. In this respect, Dop behaves similarly to NH_3, and amines generally, while the ratios found for Dsp and Dpm are remarkably low as far as silver complexes are concerned [6,7].

This increase of stability between aromatic and aliphatic complexes also occurs in DMSO, as shown by the results in Table 2. As to K_1 and K_2, the difference per aromatic ring seems somewhat smaller than in aqueous solution, viz. just below one power of ten for P and even less for N. On the other hand, also K_3 is considerably larger for the aliphatic phosphine, which was not the case in aqueous solution. For Bu_3P in DMSO, the value of K_2/K_3 is therefore much lower than for Dop in water, but the ratio is still considerably higher than for the aromatic Ph_3P. The values of K_1/K_2, on the other hand, are of rather similar magnitude in all the phosphine systems investigated. These ratios are fairly high compared to most other silver systems, indicating a rather special mode of coordination for P and related donor atoms.

The difference in log K_1 between analogous N and P donors seems to be $\simeq 7$ in DMSO, and somewhat larger, viz. $\simeq 9$, in aqueous solution. In any case, the difference in stability of complexes formed by N and by P donors with a typically soft acceptor as Ag^+ is very large.

Complexes of ligands of the same type are all less stable in DMSO than in water. Thus the difference in log K_1 between Dop and Bu_3P is 2.6, between Dpm and Ph_3P 1.6. Larger or smaller differences in the same direction are also found between the higher phosphine complexes, and between the complexes formed by the amines Et_3N, or Trea, in water and Bu_3N in DMSO, as shown in Table 2. The main cause of these differences is certainly the much stronger solvation of Ag^+ in DMSO (transfer enthalpy between water and DMSO ΔH^0_{tr} ($H_2O \rightarrow$ DMSO) $= -54$ kJ mol^{-1} [17]). The solvent thus exerts a much stronger competition for the coordination sites of Ag^+ in DMSO than in water.

The characteristic features of the various silver phosphine systems discussed are illustrated by the complex formation curves shown in Fig. 1.

The data for the cadmium and zinc complexes are given in Table 3. For cadmium, the results for aqueous solutions show that aliphatic amines and phosphines form considerably stronger complexes than aromatic ones. Between the amines Trea and Pabs, the difference is even larger than in the case of silver, while between the phosphines Dop and Dpm it is somewhat smaller. In DMSO, the same trend persists, though the actual differences remain unknown in this solvent as no perceptible complex formation takes place with the aromatic ligands Ph_3N and Ph_3P.

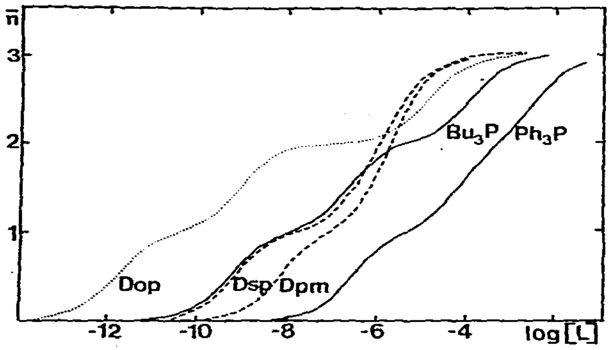

Fig. 1. Complex formation functions for the silver phosphine systems discussed. The curves give the ligand number $\bar{n}$, i.e. the average number of L coordinated per Ag^+, as a function of log [L]. Solid lines refer to systems measured in DMSO, dashed and dotted lines to systems measured in aqueous solution (for abbreviations, see Table 2).

In contrast to Ag^+, the difference in stability between analogous amine and phosphine complexes of Cd^{2+} are not large. While the affinity for Bu_3N is somewhat stronger than for Bu_3P, the opposite is true for Trea relative to Dop.

TABLE 3

COMPARISON BETWEEN THE CONSECUTIVE STABILITY CONSTANTS (K_j/M^{-1}) OF THE COMPLEXES FORMED BY CADMIUM (II) AND ZINC (II) WITH ALIPHATIC AND AROMATIC AMINES AND PHOSPHINES IN DMSO AND WATER, AT 25°C (abbreviations see Table 2)

	DMSO		Water	
	Bu_3N [a]	Ph_3N [a]	Trea [b]	Pabs [c]
Cadmium (II)				
log K_1	1.45	<0	2.70	0.25
log K_2			1.90	0.3
K_1/K_2			6.3	$\simeq$1
	Bu_3P [a]	Ph_3P [a]	Dop [d]	Dpm [c]
log K_1	0.76	<0	3.94	0.9
log K_2			3.75	2.5
log K_3			3.05	
K_1/K_2			1.2	0.03
K_2/K_3			5.0	
	Bu_3N [a]	Ph_3N [a]	Trea [e]	
Zinc (II)				
log K_1	1.3	<0	2.00	
log K_2	2.2			
K_1/K_2	0.1			
	Bu_3P [a]	Ph_3P [a]	Dop [d]	
log K_1	<−0.3	<0	log β_2 4.4	

[a] I 0.1 $M(NH_4ClO_4)$; this work. [b] I 0.1 $M(KNO_3)$; ref. 18. [c] I 1 M for Pabs, 0.1 M for Dpm($NaClO_4$); ref. 19. [d] I 1 $M(KNO_3)$; ref. 8. [e] I 0.5 $M(KNO_3)$; ref. 20.

In this case it has to be remembered, however, that Trea carries three oxy groups and Dop only one, which must considerably weaken the donor properties of the former ligand relative to the latter. This behaviour of Cd^{2+} is to be expected in view of its character as a soft-hard borderline acceptor [21].

As for Ag^+, rather much stronger complexes are formed in water than in DMSO by ligands of the same type, and the cause is also certainly the same, i.e. the stronger solvation of the metal ion in DMSO. The differences are even larger than for Ag^+, e.g. 3.2 between the values of log K_1 of Dop and Bu_3P, against 2.6 in the case of Ag^+. This is also to be expected in the light of the even larger difference between the solvation enthalpies found for Cd^{2+} (ΔH^0_{tr} ($H_2O \rightarrow$ DMSO) -67 kJ [22]).

The zinc complexes formed by the present ligands are generally very weak, but stronger complexes are formed by Bu_3N than by Bu_3P. These features are characteristic of a hard acceptor such as Zn^{2+}. It is also evident, however, that the affinity for Bu_3N is considerably stronger than for Ph_3N, again confirming the stronger donor properties of aliphatic relative to aromatic ligands.

Acknowledgements

This work was supported by the Swedish Natural Science Research Council. Our cooperation has been greatly facilitated by grants from Oehlenschläger-Tegnérs Stipendiefond and Hovrättsnotarie Gunnar Svenssons Legat to one of us (T.B.). The stay at the University of Lund for one of us (E.A.) was made possible by a Guest Scholarship from the Swedish Institute.

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