spectra were run at 62.9 MHz (sweep width, 5680 Hz; 30 000–40 000 scans; 60° pulses; 0.71 Hz/pt resolution; 16K point memory blocks; acquisition time, 1.4 s with broad band of ^{1}H decoupling; repetition delay, 1 s). $DCCl_3$ was used as internal reference.

Elemental analyses were done by the Servive de Microanalyse du CNRS at Gif sur Yvette, France.

Materials. Compound **1**, PhI=X (X = $C_8H_{10}O_2$), was prepared according to ref 9. $TPPH_2$ and $TpClPPH_2$ were synthesized according to ref 16; TPP-d_{20} and TpClPP-d_8 were synthesized according to ref 17. All the porphyrins were made chlorine free[18] and were metalated by $FeCl_2{\cdot}4H_2O$ in DMF.[19] $BrCo^{III}$(TPP) was prepared according to ref 20. The preparation of complexes **3** has been previously described.[8]

Cyclic Voltammetry and Spectroelectrochemistry of Complexes 4. Experiments were carried out with a Princeton Applied Research Model 173 potentiostat, monitored with an Apple IIe microcomputer and a PAR Model 276 GPIB interface. A three-electrode system was used with a platinum-disk or a glassy-carbon-disk working electrode, a platinum-wire counter electrode and a saturated calomel electrode. The reference electrode was separated from the bulk of the solution by a fritted glass bridge and was filled with the solvent and supporting electrolyte at appropriate concentration. The spectroelectrochemical device (analogue to a previously described one[21]) consisted of a three-electrode cell, with a quartz cell as a compartment of electrolysis (optical length, 0.5 mm; inner volume, 0.08 mL). The working electrode was a platinum minigrid.

All the solutions of complexes **3** were deaerated by an argon stream before experiments and then protected by a blanket of argon. Dimethylformamide was distilled under reduced pressure; reagent grade quality $LiClO_4$ and LiCl, purchased from Fluka Co., were used without further purification.

Preparation of Complexes 4. To a deaerated solution of 84 mg (0.1 mmol) of complex **3a** in 40 mL of C_6H_6 was added 20 mL of a saturated aqueous solution of $S_2O_4Na_2{\cdot}H_2O$, previously deaerated. The brown solution turned rapidly green, indicating the formation of complex **4a**. The end of the reaction was checked by recording the electronic spectra of a sample. Similarly, complex **4b** was obtained from 100 mg (0.1 mmol) of complex **3b**. Complexes **4** were very air-sensitive and were used only in solution under these reductive conditions.

Preparation of Compound 5a, (N-$C_8H_{11}O_2$)TPPH. Complex **4a** (160 mg) was prepared as above, and the organic solution was transferred, under anaerobic conditions, directly into 100 mL of a methanolic solution of HCl. After 0.25 h of stirring, the solvents were removed, the crude product was dissolved into CH_2Cl_2, and 50 mL of a NH_4OH solution (6 N) was added. The organic layer was washed two times with distilled water and the solvent removed. Crystallization of complex **5a** was achieved by dissolving the crude product in a minimum amount of CH_2Cl_2 and adding an excess of pentane (80% yield). Anal. Calcd for (N-$C_8H_{11}O_2$)TPPH·H_2O, $C_{52}H_{42}N_4O_3$: C, 81.04; H, 5.45; N, 7.27. Found: C, 81.01; H, 5.33; N, 7.40.

Insertion of Iron into Compound 5a. To 33 mg (0.044 mmol) of compound **5a** dissolved in 50 mL of deaerated THF containing 2 drops of collidine were added 50 mg of $FeCl_2{\cdot}4H_2O$ (0.25 mmol) and 20 mg of iron powder. The solution was refluxed under argon for 3 h. The end of the reaction was checked by UV–visible spectroscopy. The solvent was evaporated, the crude product dissolved in CH_2Cl_2, washed with a HCl solution, and purified by column chromatography (SiO_2, CH_2Cl_2:acetone, 98:2), and complex **3a** (corresponding to the oxidation of complex **4a**) crystallized from CH_2Cl_2–pentane solution (70% yield). The UV–visible and ^{1}H NMR spectra are identical with those of an authentic sample.[8]

Preparation of Complex 6a, Zn((N-$C_8H_{10}O_2$)TPP). To 150 mg (0.2 mmol) of compound **5a** dissolved in 80 mL of CH_2Cl_2 was added 110 mg (0.5 mmol) of $Zn(OAc)_2{\cdot}2H_2O$ in 20 mL of CH_3OH, and the mixture was stirred at 40 °C for 1 h. After solvent evaporation, the crude product was dissolved in CH_2Cl_2, washed with a NaCl solution, and recrystallized from a CH_2Cl_2–pentane solution (95% yield). Anal. Calcd for Zn(TPP)($C_8H_{10}O_2$), $C_{52}H_{38}N_4O_2Zn$: C, 76.51; H, 4.69; N, 6.86. Found: C, 76.19; H, 5.12; N, 6.26. Chlorine has been also analyzed and found to be less than 0.2% (probably due to traces of CH_2Cl_2 used for the recrystallization).

Preparation of Complex 8a, Co((N-$C_8H_{10}O_2$)TPP)(Br). To a solution of 150 mg (0.2 mmol) of Co^{III}(TPP)(Br) in 50 mL of C_6H_6 was added 340 mg (1 mmol) of iodonium ylide **1**. The reaction mixture was stirred for 48 h at room temperature. After evaporation of the solvent, the crude product was purified by column chromatography (SiO_2, cyclohexane, and CH_2Cl_2–CH_3COCH_3 as eluents) and recrystallized from CH_2Cl_2–pentane (85% yield). Anal. Calcd for Co(TPP)($C_8H_{10}O_2$)·H_2O, $C_{52}H_{40}N_4O_3BrCo$: C, 68.80; H, 4.44; N, 6.17; Br, 8.80. Found: C, 68.85; H, 4.41; N, 6.19; Br, 8.62.

Acknowledgment. We thank Dr. A. Gouyette (Institut Gustave Roussy, Villejuif, France) for mass spectrometry measurements.

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Solvation of Triphenylamine, -phosphine, -arsine, -stibine, and -bismuthine in Polar and Nonpolar Solvents

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Received June 25, 1986

The enthalpies of solvation for the triphenyl compounds $(C_6H_5)_3X$ (X = N, P, As, Sb, Bi) have been studied in seven nonaqueous solvents of different properties, at 25 °C. The values were determined from the known heats of crystallization and the heats of solution, which were measured calorimetrically. In both polar and nonpolar solvents low values of much the same magnitude are found. This indicates that the solvation is essentially due to London forces. Even lower heats of solvation are found for the tetraphenylarsonium, $(C_6H_5)_4As^+$, and the tetraphenylborate, $B(C_6H_5)_4^-$, ions, which implies that these also interact with the solvent essentially through London forces. This affords further support to the TATB assumption, viz. that the enthalpies of solvation (as well as the free energies, and entropies, of solvation) are indeed equal for these two ions.

Introduction

The simple triphenyl derivatives $(C_6H_5)_3X$ (X = N, P, As, Sb, Bi), abbreviated Ph_3X, are suitable ligands for the investigation of the affinities of various metal acceptors for donor atoms of the nitrogen group.[1] Such investigations must be performed in polar nonaqueous solvents where the ligands, and also the complexes formed, are readily soluble, which is not the case in aqueous solutions. Thus, in dimethyl sulfoxide, successful studies of the thermodynamics of the copper(I) and silver(I) systems of all of these ligands have been carried out.[2,3] For mercury(II), only the

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Table I. Heats of Solution ($\Delta H_s°$/kJ mol^{-1}) of the Ligands Ph_3X in Various Nonaqueous Solvents, at 25 °C

X	Meth	Me_2SO	AN	py	THT	Benz	CTet
N	24.5 ± 0.6[a]	22.4 ± 0.7	27.8 ± 0.5[a]	18.2 ± 0.7	16.9 ± 0.2	21.2 ± 0.7	17.1 ± 0.6
P	23.2 ± 0.4[a]	22.6 ± 1.3	27.5 ± 0.7[a]	17.5 ± 1.2	14.4 ± 0.6	18.3 ± 0.3	19.1 ± 0.7
As	23.2 ± 0.3[a]	22.5 ± 0.6	26.4 ± 0.2[a]	16.3 ± 0.7	12.7 ± 1.1	18.0 ± 0.8	18.3 ± 0.7
Sb	26.7 ± 0.7[a]	23.8 ± 0.7	27.7 ± 0.1[a]	18.4 ± 0.7	14.8 ± 0.6	22.4 ± 0.8	21.0 ± 0.8
Bi	30.8 ± 2.8	25.9 ± 0.7	31.3 ± 3.0	21.0 ± 1.0	17.3 ± 1.0	28.1 ± 0.4	26.4 ± 0.8

[a] Values of Burgess and Peacock.[9] These were all checked in the present investigation, by one or more experiments, and confirmed within the limits of error.

Table II. Heats of Solvation ($\Delta H_{sv}°$/kJ mol^{-1}) of the Ligands Ph_3X and of the TATB Ions[a,25,26] Ph_4As^+ and BPh_4^- in the Solvents Investigated (of Dipole Moments μ'/D[15,16] and Formula Weights M'), Heats of Crystallization ($\Delta H_{cr}°$/kJ mol^{-1}) and Dipole Moments (μ/D) of the Ligands Ph_3X,[12,13] and Covalent Radii (r_{cov}/Å) of Their Donor Atoms[14]

	Meth	Me_2SO	AN	py	THT	Benz	CTet
μ'	1.70	3.96	3.92	2.19	1.90	0	0
M'	32.04	78.13	41.05	79.10	81.17	78.11	153.82

	$-\Delta H_{sv}°$									
	Meth	Me_2SO	AN	py	THT	Benz	CTet	$-\Delta H_{cr}°$	μ	r_{cov}
Ph_3N	67.5	69.6	64.2	73.8	75.1	70.8	74.9	92.0	0.43	0.74
Ph_3P	73.0	73.6	68.7	78.7	81.8	77.9	77.1	96.2	1.44	1.10
Ph_3As	75.1	75.8	71.9	82.0	85.6	80.3	80.0	98.3	1.14	1.21
Ph_3Sb	79.6	82.5	78.6	87.9	91.5	83.9	85.3	106.3	0.86	1.41
Ph_3Bi	80.1	85.0	79.6	89.9	93.6	82.8	84.5	110.9	0.47	1.52
Ph_4As^+ BPh_4^-	47	56	55	68	61					

[a] Calculated from the heats of transfer between water and the solvents concerned, assuming the heats of hydration $\Delta H_h°(Ph_4As^+) = \Delta H_h°(BPh_4^-) = -45$ kJ mol^{-1}. The value is an average of the values quoted previously[25] for Ph_4As^+ and BPh_4^- and implies that the TATB assumption is applied also on the values of $\Delta H_h°$ for those ions.

phosphine and arsine systems can be similarly investigated.[2] Silver(I) and mercury(II) complexes of these, and related, ligands have recently been studied also in pyridine.[4,5]

The stabilities of the complexes formed depend, as always, not only on the affinity between the acceptor and the ligand but also on the solvation of the species reacting. Thus, the silver(I) and mercury(II) complexes are much more stable in dimethyl sulfoxide than in pyridine, which is very much due to the stronger solvation of these soft d^{10} acceptors in the softer solvent pyridine. The aim of the present study is to investigate the solvation of the ligands in various solvents, in order to ascertain its influence on the complex formation. It is also of interest to compare the strength of solvation of these neutral ligands with that previously found for ionic ligands, such as the halides.[6]

Quantitatively, the strength of solvation is expressed by the heat of solvation, $\Delta H_{sv}°$, i.e. the enthalpy change of the reaction $Ph_3X(g) \rightarrow Ph_3X(sv)$. In this investigation, the values of $\Delta H_{sv}°$ for all ligands Ph_3X have been compared for the polar solvents methanol (Meth), dimethyl sulfoxide (Me_2SO), acetonitrile (AN), pyridine (py), and tetrahydrothiophene (THT), as well as for the nonpolar solvents benzene (Benz) and carbon tetrachloride (CTet).

The heat of solvation is the sum of the heat of crystallization, $\Delta H_{cr}°$, and the heat of solution, $\Delta H_s°$, pertaining to the reactions $Ph_3X(g) \rightarrow Ph_3X(s)$ and $Ph_3X(s) \rightarrow Ph_3X(sv)$, respectively. From the heats of sublimation $\Delta H_{sub}°$ known for all ligands Ph_3X,[7,8] the heats of crystallization are immediately found as $\Delta H_{cr}° = -\Delta H_{sub}°$. By measurement of $\Delta H_s°$, $\Delta H_{sv}°$ can be calculated from $\Delta H_{sv}° = \Delta H_s° - \Delta H_{sub}°$.

The values of $\Delta H_s°$ have been measured by the present authors, except for those pertaining to the four lighter ligands (X = N to Sb) in methanol and acetonitrile, which have been adopted from the investigation of Burgess and Peacock.[9] Checks showed that the same values are obtained, within the experimental errors, with our experimental setup.

All values of $\Delta H_s°$ have been determined calorimetrically, at a temperature of 25 °C.

Experimental Section

Chemicals. The ligands and solvents were all of analytical grade. Before use, the ligands were dried under vacuum over silica gel. Methanol was dried over CaO. Dimethyl sulfoxide and acetonitrile were distilled over CaH_2 and kept over molecular sieves, pore size 3 Å. Pyridine and benzene were kept over molecular sieves. Tetrahydrothiophene was distilled under dry N_2 atmosphere.

Calorimetry. The calorimeter and the procedure have been described earlier.[10,11] The substances, in amounts of 2.5–60 mg, were transferred into weighed ampules, which were then sealed and weighed again. In most solvents, the sealing must be done by melting off the side tube of the ampule, by a special device. The ampules were broken in the calorimeter and the substances then dissolved in 80 mL of the solvent, in less than 4 min. After the breaking of three or four ampules, the solution was changed for fresh solvent. The values of $\Delta H_s°$ measured were independent of the concentration of Ph_3X. At least six concordant determinations were performed for each ligand–solvent pair.

Results and Discussion

The values of $\Delta H_s°$ determined are collected in Table I, where the reproducibility of the results is also indicated. All heats of solution are endothermic, implying that for all of the ligands solvation is a less exothermic process than crystallization. The values of $\Delta H_{sv}°$ and $\Delta H_{cr}°$ are listed in Table II, and also plotted in Figure 1.

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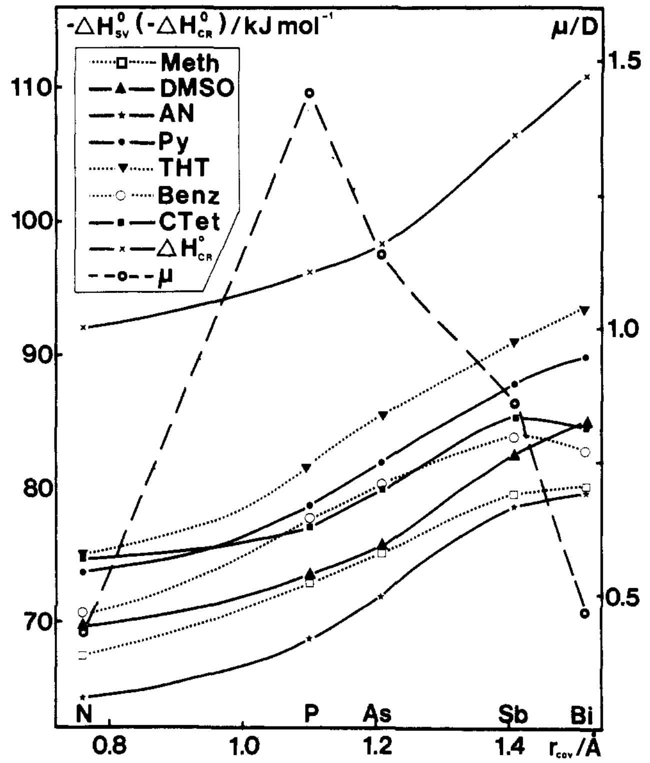

Figure 1. Heats of solvation ($\Delta H_{sv}°$/kJ mol^{-1}) and crystallization ($\Delta H_{cr}°$/kJ mol^{-1}) (left ordinate) and dipole moments (μ/D; right ordinate) of Ph_3X as functions of the covalent radii of the donor atoms X.

In all of the solvents, the solvation of Ph_3X generally becomes stronger, the larger the donor atom X, as shown by the monotonous increases of $\Delta H_{sv}°$. The same trend is found for the interactions in solid phase, as shown by the increase of $\Delta H_{cr}°$. The forces acting are not primarily due to the permanent dipoles of the ligands, as clearly indicated by the very different trend of their dipole moments μ. This quantity has its highest value at X = P, while the values are very low for both X = N and Bi (Table II and Figure 1). Nor is the polarity of the solvent molecules, as expressed by their dipole moments μ', of any consequence for the strength of the solvation. The values $\Delta H_{sv}°$ are in fact generally lower for the strongly polar Me_2SO and AN than for the nonpolar Benz and CTet, while the highest values are found for THT, of intermediate polarity.

Also the donor strength of the solvent is unimportant. Neither the Drago base parameters[17] C_b and E_b, nor the Gutmann donor numbers,[18] which purport to measure this quantity, are in any way correlated with the $\Delta H_{sv}°$ sequences reported in Table II. This is indeed natural as the species Ph_3X to be solvated have no acceptor properties (with a possible exception for Ph_3Bi; see below); they are themselves donors. On the other hand, the experimental facts are throughout compatible with the presumption that the interactions are essentially governed by London forces. This conclusion is further strengthened by the circumstance that the values of $-\Delta H_{sv}°$ are smallest for the solvents of the lowest M, viz. Meth and AN (Table II). The relatively high values found for Benz and py indicate, however, that also π-bonding between the aromatic systems might contribute significantly to the solvation.[19]

Compared to most species carrying a net ionic charge, the neutral molecules Ph_3X have very small values of $-\Delta H_{sv}°$. Thus, for the halide ions, the values are in the range 300–360 kJ/mol for the polar solvents used presently.[6] Contrary to what is found for Ph_3X, these values decrease as the donor atom becomes larger. For the halides, the strength of solvation is evidently very much governed by the charge density. The lighter halide ions are moreover electronegative enough to be specially favored by protic solvents, e.g. methanol, through the formation of hydrogen bonds. No such tendency can be discerned for the lighter donor atoms of the N group; the methanol curve of Figure 1 runs practically parallel to those found for the aprotic solvents. The courses of the various curves in Figure 1 might even be considered as unexpectedly parallel, considering the large differences in chemical character between the solvents investigated. In one point, however, benzene and carbon tetrachloride deviate in an interesting way. In these solvents, the monotonous increase of $-\Delta H_{sv}°$ with the size of X generally found is broken at the last step; the values found for Ph_3Bi are lower than for Ph_3Sb (Table II). It might be that in the case of Bi, an element of distinctly metallic character, the donor properties of the solvent are of some importance. If so, the lack of donor atoms in benzene and carbon tetrachloride would to some extent disfavor the solvation of Ph_3Bi in these solvents.

The approximately parallel courses also imply that, for the complexes formed by a certain acceptor, no change in the stability sequence is to be expected between various solvents. For the typically soft d^{10} acceptor silver(I),[3] the sequence N $\ll$ P > As > Sb > Bi is found for the Ph_3X complexes in Me_2SO. The same sequence should persist for these complexes in pyridine, as has in fact been found.[4]

The present results further reveal that, also for certain very large monovalent ions, the London forces are in fact the predominating forces of interaction. Thus the sum of the values of $\Delta H_{sv}°$ for the ions Ph_4As^+ and BPh_4^- is considerably less than twice the value of $\Delta H_{sv}°$ for the neutral molecule Ph_3As in the same solvent (Table II). For the latter, the solvation has just been proved to be due essentially to London forces. For the interactions of the solvents with Ph_4As^+ and BPh_4^-, on the average even weaker than those with Ph_3As, the same must be true. Moreover, both ions are strictly tetrahedral, with the bulky phenyl groups effectively shielding the central atoms from the environment. The solvents thus interact only with the phenyls, and there is no reason that the strength of the interactions should be more than marginally different between Ph_4As^+ and BPh_4^-. Consequently, the TATB assumption,[20–24] postulating that, in a given solvent, the value of $\Delta H_{sv}°$ is the same for the two ions, should be close to the truth. The values of $\Delta H_{sv}°(Ph_4As^+) = \Delta H_{sv}°(BPh_4^-)$ calculated on this assumption for those solvents where ionic compounds dissolve, i.e. for the polar ones, have also been entered in Table II.

Registry No. Ph_3N, 603-34-9; Ph_3P, 603-35-0; Ph_3As, 603-32-7; Ph_3Sb, 603-36-1; Ph_3Bi, 603-33-8; $Ph_4As^+BPh_4^-$, 15627-12-0.

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