Thermochemical Data for Adducts of Zinc, Cadmium, and Mercury Halides with Hexamethylphosphoramide

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From the standard enthalpies of dissolution of metal halides (MX_2), hexamethylphosphoramide (hmpa), and the adducts MX_2·2hmpa (M = Zn, Cd, or Hg; X = Cl, Br, or I) in an appropriate calorimetric solvent at 298.15 K, the following $\Delta H_R^{\ominus}$ (kJ mol^{-1}) values for the reactions $MX_2(s) + 2hmpa(l) \longrightarrow MX_2{\cdot}2hmpa(s)$ were determined: $ZnCl_2$·2hmpa(s), -113.08 ± 0.79; $ZnBr_2$·2hmpa(s), -135.53 ± 1.18; ZnI_2·2hmpa(s), -131.86 ± 0.86; $CdCl_2$·2hmpa(s), -55.12 ± 0.81; $CdBr_2$·2hmpa(s), -77.73 ± 0.67; CdI_2·2hmpa(s), -94.58 ± 0.50; $HgCl_2$·2hmpa(s), -63.97 ± 1.24 (ethanol), -63.01 ± 0.94 (1,2-dichloroethane); $HgBr_2$·2hmpa(s), -65.42 ± 1.78; and HgI_2·2hmpa, -53.41 ± 0.78. From values of $\Delta H_f^{\ominus}$ (MX_2, s) and $\Delta H_f^{\ominus}$ (hmpa, l) were calculated the $\Delta H_f^{\ominus}$ (MX_2·2hmpa, s) values for the same sequence of adducts: −1 596, −1 532, −1 408, −1 514, −1 462, −1 366, −1 356, −1 304, and −1 227 kJ mol^{-1}. The standard enthalpies of the reactions $MX_2{\cdot}2hmpa(s) \longrightarrow MX_2(s) + 2hmpa(g)$, $\Delta H_D^{\ominus}$, and $MX_2{\cdot}2hmpa(s) \longrightarrow MX_2(g) + 2hmpa(g)$, $\Delta H_M^{\ominus}$, were also calculated and the mean dissociation enthalpy of the metal–oxygen bond, $\bar{D}$(M–O), was estimated and compared with that for analogous adducts. The results show a slight dependence of $\bar{D}$(M–O) on the radical attached to the phosphorus atom.

The growing application of hexamethylphosphoramide (hmpa), $P(NMe_2)_3O$, as a solvent in the last decades is related to its aprotic polar properties and high donor number.[1,2] These favourable features have led to its use as a solvent for gases, for many organic and inorganic salts, and for polymers as well as in polymerization processes as a co-catalyst.[1] The oxygen atom of the PO group of a large majority of phosphoryl compounds acts as a donor to metals in the formation of adducts.[3–5] For example, a series of complexes of hmpa have been isolated with neutral molecules such as BF_3,[1] $BCl(C_6H_5)_2$,[6] $OPCl_3$, and $OPBr_3$, first-row transition-metal halides and perchlorate,[7,8] with cations of Ag^I, Pb^{II}, and Sn^{II},[1] and also with zinc, cadmium, and mercury halides.[8] Its high basicity favours reactions with organic compounds such as hydrocarbon chlorides, carboxylic acids, phenols, *etc.*, as well as organometallic compounds involving zinc and magnesium.[1]

Despite the existence of some thermodynamic data in the literature for metal–ligand interaction in solid adducts containing PO ligands,[9,10] these data are relatively sparse in relation to the great number of compounds that have already been prepared and characterized.[3] The main objective of this publication is to present thermodynamic data for the adducts formed between hmpa and zinc family halides, and to discuss some relevant points with respect to their thermal behaviour and to the metal–oxygen bonds of these compounds. All adducts studied have been described before[8] and their spectral features interpreted. In all cases there is straightforward evidence of co-ordination of the metal *via* the oxygen atom of the PO group of the ligand.

Experimental

Reagents.—The solvents used in preparations or in calorimetric determinations were purified and dried following methods described in the literature.[11,12] Hexamethylphosphoramide (Fluka) was purified as described previously.[13] The anhydrous metal halides were prepared by us[14] or purified[15] from commercial products (Merck or Carlo Erba). The purity of these salts was checked by analysing for the metal by spectrophotometric titration with ethylenediaminetetra-acetate (edta).[16]

Preparation of the Adducts.—All operations were carried out *in vacuo* or under an atmosphere of dried nitrogen. The general procedure has been described before.[8] Briefly, a slight excess of the ligand in relation to the desired stoicheiometry was added to a solution of the metal halide in light petroleum (b.p. 80—100 °C) or alcohol. The solution was stirred and warmed to 60 °C to dissolve the salt completely. Upon cooling, the adduct starts to precipitate, at which point light petroleum was added and the solution left with continuous stirring in an ice-bath for 2 h. The solid was filtered off, washed with solvent, and dried *in vacuo*. The adduct HgI_2·2hmpa is extremely sensitive to moist air and was stored in sealed ampoules.

Characterization of the Adducts.—Metal, halide, and nitrogen contents were determined respectively by spectrophotometric titration with edta,[16] by potentiometric titration with silver nitrate,[17] and by the Kjeldahl method modified by Ogg.[18] All results agreed, within the experimental error, with the proposed stoicheiometry of the adducts listed in Table 1. For the halide determinations in mercury adducts, the sample was first treated with zinc powder in an aqueous suspension. After filtration the mercury cation was then titrated.[19] All i.r. spectra were obtained in the 4 000—400 cm^{-1} range with a Perkin-Elmer 399 B apparatus, samples being in the form of Nujol mulls. The spectra were in complete agreement with those given in the literature.[20–23]

Calorimetric Measurements.—A LK 8700-1 precision calorimeter was used for all determinations in solution. Details of the procedure, the apparatus, and data processing have already been described.[9,10,24] An ampoule containing 6—60 mg (15—250 μmol) of the material was broken in calorimetric solvent (90 cm^3) at 298.15 ± 0.02 K. Calorimetric solvents were chosen by taking into account their ability to dissolve the halide, the ligand, and the adduct. The compounds were rigorously dried *in*

Table 1. Thermochemical (kJ mol^{-1}) and thermogravimetric (°C) data for the adducts

Adduct	Solvent	$\Delta H_1^{\ominus}$	$\Delta H_2^{\ominus}$	$\Delta H_3^{\ominus}$	$\Delta H_R^{\ominus}$	Decomposition point[a]	M.p.[b]
$ZnCl_2$·2hmpa	EtOH	-43.33 ± 0.27	-22.72 ± 0.33	47.03 ± 0.66	-113.08 ± 0.79	115.0	106.0—106.5
$ZnBr_2$·2hmpa	EtOH	-47.69 ± 0.37	-25.64 ± 0.70	62.20 ± 0.88	-135.53 ± 1.18	125.0	121.5—122.5
ZnI_2·2hmpa	EtOH	-52.88 ± 0.35	-20.32 ± 0.62	58.66 ± 0.49	-131.86 ± 0.86	145.0	122.0—122.5
$CdCl_2$·2hmpa	MeOH	-18.30 ± 0.15	-29.54 ± 0.54	7.28 ± 0.58	-55.12 ± 0.81	70.0	76.5— 77.5
$CdBr_2$·2hmpa	MeOH	-6.13 ± 0.12	-22.22 ± 0.38	49.38 ± 0.54	-77.73 ± 0.67	95.0	100.5—101.5
CdI_2·2hmpa	MeOH	-15.48 ± 0.19	-23.70 ± 0.32	55.40 ± 0.33	-94.58 ± 0.50	100.0	109.5—110.0
$HgCl_2$·2hmpa	EtOH	4.50 ± 0.04	-26.29 ± 1.11	42.18 ± 0.56	-63.97 ± 1.24	55.0	58.0— 59.0
$HgCl_2$·2hmpa	*c*	13.40 ± 0.30	-28.64 ± 0.43	47.91 ± 0.25	-63.01 ± 0.94		
$HgBr_2$·2hmpa	EtOH	3.14 ± 0.03	-24.53 ± 0.37	44.03 ± 1.74	-65.42 ± 1.78	75.0	77.5— 78.5
HgI_2·2hmpa	EtOH	10.01 ± 0.59	-22.15 ± 0.07	41.27 ± 0.51	-53.41 ± 0.78	60.0	62.5— 64.0

[a] Beginning of decomposition in thermogravimetric determinations. [b] Interval of decomposition in melting-point determinations. [c] 1,2-Dichloroethane.

vacuo before preparing the ampoules, which were filled in a dry-box.

Other Measurements.—Thermogravimetric curves were obtained in a dynamic atmosphere of nitrogen in the range 30—700 °C by using a Perkin-Elmer model TGS-1 thermobalance with programmed speeds of 2.5 and 5.0 °C min^{-1}. A Finnigan 1015 S/L spectrometer was used to obtain the mass spectra of the ligand and adducts. Melting points were determined in sealed capillary tubes with a Thomas-Hoover instrument.

Table 2. Auxiliary data (kJ mol^{-1})

	$\Delta H_f^{\ominus}$	Ref.	$\Delta H_{(s,l-g)}^{\ominus}$	Ref.
$ZnCl_2$	-415.05	*a*	149.0	*a*
$ZnBr_2$	-328.7	*a*	131.0	*b*
ZnI_2	-208.0	*a*	120.0	*b*
$CdCl_2$	-391.5	*a*	181.2	*c*
$CdBr_2$	-316.2	*a*	151.2	*b*
CdI_2	-203.3	*a*	137.7	*b*
$HgCl_2$	-224.3	*a*	83.3	*b*
$HgBr_2$	-170.7	*a*	84.1	*d*
HgI_2	-105.4	*d*	88.2	*d*
hmpa	-533.88	*e*	56.56	*f*

[a] D. D. W. H. Evans, V. B. Parker, Z. Halow, S. M. Bailey, and R. H. Schumm, 'Selected Values of Thermodynamic Properties,' Technical Note 270—3, National Bureau of Standards, Washington, D.C., 1968 and 1969. [b] O. Kubaschewiski, E. Ll. Evans, and C. B. Alcock, 'Metallurgical Thermochemistry,' 4th edn., Pergamon, London, 1967. [c] F. J. Keneshea and D. D. Cubicciotti, *J. Chem. Phys.*, 1964, **40**, 1778. [d] L. G. Hepler and G. Olofsson, *Chem. Rev.*, 1975, **75**, 585. [e] S. B. Hartley, W. S. Holmes, J. K. Jaques, M. F. Mole, and J. C. McCoubrey, *Q. Rev. Chem. Soc.*, 1963, **17**, 204. [f] M. F. Mole, W. S. Holmes, and J. C. McCoubrey, *J. Chem. Soc.*, 1964, 4144.

Results and Discussion

These adducts are clearly unstable on heating, however, a narrow melting-point range (Table 1) was observed. After cooling the melted sample and heating again, the previous narrow interval was not reproduced. From the thermograms it was found that the zinc adducts start to decompose after melting, in contrast to the behaviour of the other compounds. The zinc and mercury adducts decompose in a single step, showing that the mass is totally lost at 470 and 250 °C, respectively. The cadmium adducts lose mass in two poorly defined stages: in the first step the ligands are lost, followed by sublimation of the metal halides, which are completely volatilized at 630, 600, and 430 °C for chloride, bromide, and iodide, respectively. The lack of a well defined inflection in the thermograms shows that during the process of decomposition several reactions occur simultaneously, such as the loss of ligand, ligand decomposition, and volatilization of the metal halide.

The mass spectrum obtained for hmpa is very similar to that described in the literature.[25] The adducts show peaks due to the ligand and its fragmentation and some peaks related to the metal halides. All adduct spectra were obtained at temperatures 10 °C below the beginning of the decomposition and also 5—10 °C below the interval of melting. Neither type of spectra shows the adduct parent ion. The fragmentations for hmpa are: *m/e* 179 (hmpa), 136 ($[N(CH_3)_2]_2HPO$), 135 ($[N(CH_3)_2]_2PO$), 93 ($[N(CH_3)_2]H_2PO$), 92 ($[N(CH_3)_2]HPO$), 91 ($[N(CH_3)_2]PO$), 90 ($[N(CH_3)]_2HP$), 76 ($[N(CH_3)_2]HP$), 75 ($[N(CH_3)_2]P$), 73 ($[H_3CNN(CH_3)_2]$), 60 ($[N(CH_3)]P$), 58 ($[N(CH_3)]_2$), 49 (H_2PO), 47 (PO), 46 $[H_2N(CH_3)_2]$, 45 $[HN(CH_3)_2]$, 44 $[N(CH_3)_2]$, 43 (HN_3), 32 (O_2), 30 (C_2H_6), 28 (N_2), 18 (H_2O), and 15 (CH_3). The adducts $ZnCl_2$·2hmpa and $ZnBr_2$·2hmpa yielded similar hmpa spectra: *m/e* 179, 136, 135, 92, 91, 88 ($[N(CH_3)_2]_2$), 75, 58, 46, 45, 44, 32, and 28. ZnI_2·2hmpa yielded the ligand peaks as well as those at *m/e* [Zn(hmpa)], 319 (ZnI_2), 192 (ZnI), 127 (I), and 68, 66, and 65 (Zn). $CdCl_2$·2hmpa, $CdBr_2$·2hmpa, and CdI_2·2hmpa gave the spectra of the ligand in the range *m/e* 28—179, and also peaks at *m/e* 120 $[N_2(CH_3)_3PO]$ and 118 ($[N(CH_3)]_3P$).

The mercury adducts showed the same kind of fragmentation as the cadmium adducts in the range *m/e* 28—179. Other peaks are: $HgCl_2$·2hmpa, *m/e* 455 $[HgCl_2\{OPHN(CH_3)_2\}_2]$, 271 ($HgCl_2$), 236 (HgCl), and 200 (Hg); $HgBr_2$·2hmpa, *m/e* 407 ($HgBr_2OP$), 360 ($HgBr_2$), 280 (HgBr), 200 (Hg), and 79 (Br); and HgI_2·2hmpa, *m/e* 454 (HgI_2), 254 (I_2), 200 (Hg), and 127 (I).

The enthalpy of the reaction, $\Delta H_R^{\ominus}$, of metal halides MX_2 (M = Zn, Cd, or Hg; X = Cl, Br, or I) with hmpa to give the adducts, *e.g.* $MX_2(s) + 2hmpa \longrightarrow MX_2 \cdot 2hmpa(s)$, can be obtained by applying Hess' law to reactions (1)—(4) with an

$$MX_2(s) + \text{calorimetric solvent} \longrightarrow \text{solution A}; \Delta H_1^{\ominus} \quad (1)$$

$$2\text{hmpa(l)} + \text{solution A} \longrightarrow \text{solution B}; \Delta H_2^{\ominus} \quad (2)$$

$$MX_2 \cdot 2\text{hmpa(s)} + \text{calorimetric solvent} \longrightarrow \text{solution C}; \Delta H_3^{\ominus} \quad (3)$$

$$\text{solution B} \longrightarrow \text{solution C}; \Delta H_4^{\ominus} \quad (4)$$

appropriate solvent. Here $\Delta H_R^{\ominus} = \Delta H_1^{\ominus} + \Delta H_2^{\ominus} - \Delta H_3^{\ominus}$ and $\Delta H_4^{\ominus} = 0$, due to the thermodynamic equivalence of solutions B and C. The enthalpies were obtained from at least four individual determinations and the results are listed in Table 1. By using the existing literature data in Table 2, $\Delta H_f^{\ominus}$

Table 3. Summary of the thermochemical (kJ mol^{-1}) data for adducts

Adduct	$\Delta H_f^\ominus$	$\Delta H_M^\ominus$	$\Delta H_D^\ominus$	$\bar{D}$(M–O)
$ZnCl_2$·2hmpa	−1 596	375	226	159
$ZnBr_2$·2hmpa	−1 532	380	249	162
ZnI_2·2hmpa	−1 408	365	245	154
$CdCl_2$·2hmpa	−1 514	349	168	146
$CdBr_2$·2hmpa	−1 462	342	191	143
CdI_2·2hmpa	−1 366	345	208	144
$HgCl_2$·2hmpa	−1 356	260	177	102
$HgBr_2$·2hmpa	−1 304	263	179	103
HgI_2·2hmpa	−1 227	255	167	99

was calculated and also $\Delta H_D^\ominus$ and $\Delta H_M^\ominus$ [equations (5) and (6)]. From these equations one derives $\Delta H_D^\ominus = -\Delta H_R^\ominus + 2\Delta H_{vap}^\ominus$(hmpa) and $\Delta H_M^\ominus = \Delta H_D^\ominus + \Delta H_{sub}^\ominus(MX_2)$, where

$$MX_2\cdot 2\text{hmpa(s)} \longrightarrow MX_2\text{(s)} + 2\text{hmpa(g)};\ \Delta H_D^\ominus \quad (5)$$

$$MX_2\cdot 2\text{hmpa(s)} \longrightarrow MX_2\text{(g)} + 2\text{hmpa(g)};\ \Delta H_M^\ominus \quad (6)$$

$\Delta H_{vap}^\ominus$ and $\Delta H_{sub}^\ominus$ are the enthalpies of vaporization and sublimation, respectively. These values are given in Table 3.

The mean dissociation enthalpy of the metal–oxygen bond, $\bar{D}$(M–O), can be calculated by using the reaction (7). In this case

$$MX_2\cdot 2\text{hmpa(g)} \longrightarrow MX_2\text{(g)} + 2\text{hmpa(g)};\ \Delta H_G^\ominus \quad (7)$$

$\bar{D}$(M–O) $= \frac{1}{2}\Delta H_G^\ominus$. The value of $\Delta H_G^\ominus$ can be obtained by applying Hess' law to reactions (6) and (8) whence $\Delta H_G^\ominus = \Delta H_M^\ominus - \Delta H_C^\ominus$, where $\Delta H_C^\ominus$ is the enthalpy of sublimation of

$$MX_2\cdot 2\text{hmpa(s)} \longrightarrow MX_2\cdot 2\text{hmpa(g)};\ \Delta H_C^\ominus \quad (8)$$

the adduct. The latter value is experimentally inaccessible, due to the fact that the adducts do not exist outside of the solid state, therefore it was assumed that $\Delta H_C^\ominus = \Delta H_{vap}^\ominus$(hmpa).[9,24,26] The calculated $\bar{D}$(M–O) values, from the expression $\bar{D}$(M–O) $= \frac{1}{2}(\Delta H_M^\ominus - \Delta H_C^\ominus)$, are listed in Table 3.

On examining the $\bar{D}$(M–O), $\Delta H_f^\ominus$, $\Delta H_M^\ominus$, and $\Delta H_D^\ominus$ values, it can be seen that they follow the sequence Zn > Cd > Hg for each of the halides. In general, $\bar{D}$(M–O) exhibits the sequence Cl ≈ Br > I. For $\Delta H_f^\ominus$ the variation is Cl > Br > I, for $\Delta H_D^\ominus$, it is Br > Cl > I, and for $\Delta H_M^\ominus$, it is Br > Cl > I for the zinc and mercury compounds and Cl > Br > I for the cadmium adducts. As deduced before, $\Delta H_M^\ominus = 2\bar{D}$(M–O) $+ \Delta H_C^\ominus$. Thus $\Delta H_M^\ominus$ comprises all contributions involving not only the specific acid–base interaction, but also the other non-specific interactions. The first term, due to the metal–oxygen bond, gives the main contribution, and varies from 78 to 86% of the total for the adducts reported in Table 3.

The $\bar{D}$(M–O) values in Table 3 may be compared with values previously published for analogous adducts. Thus, bis adducts of triethylphosphine oxide[10] (PEt_3O) and triphenylphosphine oxide[9] (PPh_3O) have also been isolated with zinc, cadmium, and mercury chlorides, giving the following $\bar{D}$(M–O) values: 159, 154, 102 and 133, 132, 81 kJ mol^{-1}, respectively. In addition, tribenzylphosphine oxide forms the adduct $ZnCl_2\cdot P(CH_2Ph)_3O$,[10] with $\bar{D}$(M–O) = 144 kJ mol^{-1}. The following decreasing order of $\bar{D}$(M–O) values is thus observed: hmpa > PEt_3O > $P(CH_2Ph)_3O$ > PPh_3O; PEt_3O > hmpa > PPh_3O and PEt_3O > hmpa > PPh_3O for zinc, cadmium, and mercury, respectively. These sequences seem to be associated with the basicity of the ligands, hence the similarity in donor numbers of hmpa and PEt_3O result in them appearing at the beginning of the series.[2,27] However, the $\bar{D}$(M–O) values are very similar in some cases and the differences observed in the sequences may not be very representative, but could be interpreted as due to experimental error. This leads us to conclude that the metal–oxygen bond is, in reality, not very dependent on the radical attached to the phosphorus atom.

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