the expense of the N–P(III) bond in the P(V)–N–P(III) motif (see detailed discussion in part 3 of this series[4]).

But the one striking general feature revealed by this study is certainly that *all* six compounds investigated showed a surprising and unanticipated degree of disorder. This manifests itself in (1) the lack of precision in the atomic positions resulting in low accuracy of individual bond lengths and angles, (2) a wide spread in bond length for the chemically equivalent bonds of a given molecule, and (3) in some cases gross disorder of an intriguing kind, as with $S_4P_4(NCH_3)_6$, in which one of the sulfur atoms appears to occupy two or even three—depending on temperature—distinct positions in the unit cell.[2b] The polymorphism (orthorhombic or monoclinic, depending on the crystallization procedure) observed for $SP_4(CH_3)_6$[3] is probably related to this tendency to disorder. The wide dispersion in bond length observed in all cases for chemically equivalent bonds was disappointing. Indeed, the presence of 12 equivalent P–N bonds in the molecules having T_d symmetry, i.e., $P_4(NCH_3)_6$, $O_4P_4(NCH_3)_6$, and $S_4P_4(NCH_3)_6$, was expected to lead to very accurate measurements of the P–N bond lengths and was our main incentive for choosing this particular series of molecules, a priori the best suited to our purpose. But in fact the spread of the 24 or 48 crystallographically independent P–N distances (for two or four independent molecules in the unit cells) turned out to be surprisingly wide. The case of $O_4P_4(NCH_3)_6$ is exemplary in this respect: the P–N distances spread from 1.59 to 1.75 Å! with a precision of no better than ±0.02 Å on the mean value 1.667 Å.[2b]

This tendency to disorder thus appears to be a prominent feature of the whole series of closo phosphorimide derivatives and probably, as far as we can judge from the general poor accuracy of hitherto published data on phosphorus oxides and sulfides,[15] a prominent feature of the whole class of closo phosphorus compounds. It can be attributed (1) to their globularity or close-to-spherical nature, which tends to favor rotational disorder and/or a large amplitude of librational motion in crystals and in the extreme cases leads to the existence of a distinct plastic phase, characterized by virtually free rotation, as in $P_4(NCH_3)_6$ or P_4S_{10},[16] and (2) to the fact that there is no central atom tying the atoms together across the cage structure, which therefore can be compared to a soft, deflated tennis ball, subject to easy deformation under the action of crystal packing forces. The molecules reside on crystallographic sites with much less symmetry than the idealized molecules themselves would be expected to have. As a consequence the chemically identical atoms do not experience the same crystal forces, which may thus cause different displacement of individual atoms.

As a result of structural softness, it is probable that it is not the electron distributions that dictate the geometric structures. Instead, the structures easily adapt both to internal constraints, arising from their polycyclic nature, and to external constraints, when in the crystalline form, and the electron distributions then conform to the structures.

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Synthesis, Characterization, and Thermochemistry of Adducts of Zinc, Cadmium, and Mercury Halides with *N,N*-Dimethylformamide

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The adducts $ZnX_2{\cdot}nDMF$ (X = Cl, Br, I; n = 1, 2), $CdX_2{\cdot}2DMF$ (X = Cl, I), $CdX_2{\cdot}DMF$ (X = Cl, Br, I), and $HgX_2{\cdot}DMF$ (X = Cl, Br) were isolated and characterized by elemental analysis, vibrational spectroscopy, proton magnetic resonance spectroscopy, mass spectrometry, thermal analysis, conductometric measurements, and X-ray diffraction patterns. The shift of the CO stretching vibration to low frequency indicated that DMF is bonded through oxygen to the metals, and on the basis of the data obtained, structures for the adducts are proposed. The standard enthalpies of dissolution of the halides, DMF, and the adducts at 298.15 K, for the reaction $MX_2(s) + nDMF(l) = MX_2{\cdot}nDMF(s)$, $\Delta H_R^\ominus$, were as follows (kJ mol^{-1}): $ZnCl_2{\cdot}2DMF(s)$, −81.37 ± 0.77; $ZnCl_2{\cdot}DMF(s)$, −52.39 ± 0.41; $ZnBr_2{\cdot}2DMF(s)$, −90.79 ± 0.48; $ZnBr_2{\cdot}DMF(s)$, −53.78 ± 0.57; $ZnI_2{\cdot}2DMF(s)$, −86.56 ± 0.74; $ZnI_2{\cdot}DMF(s)$, −57.50 ± 0.28; $CdCl_2{\cdot}2DMF(s)$, −41.39 ± 0.53; $CdCl_2{\cdot}DMF(s)$, −26.84 ± 0.18; $CdBr_2{\cdot}DMF(s)$, −35.61 ± 0.36; $CdI_2{\cdot}2DMF(s)$, −54.39 ± 0.27; $CdI_2{\cdot}DMF(s)$, −30.72 ± 0.18; $HgCl_2{\cdot}DMF(s)$, −23.09 ± 0.42; $HgBr_2{\cdot}DMF(s)$, −19.02 ± 0.19. From $\Delta H_R^\ominus$, $\Delta H_f^\ominus(MX_2, s)$, and $\Delta H_f^\ominus(DMF, l)$ the standard enthalpies of formation were calculated for the same sequence of adducts; viz., $\Delta H_f^\ominus(s, 298.15\ K)$ = −975.2, −706.9, −898.2, −621.3, −773.3, −504.9, −911.6, −657.7, −591.2, −736.4, −473.3, −486.8, and −429.1 kJ mol^{-1}. The standard enthalpies of the reactions $MX_2{\cdot}nDMF(s) = MX_2(s) + nDMF(g)$, $\Delta H_D^\ominus$, and $MX_2(g) + nDMF(g) = MX_2{\cdot}nDMF(s)$, $\Delta H_M^\ominus$, were also calculated, and the enthalpy of the metal–oxygen bond was estimated. The calorimetric data suggest that the thermodynamic stability of the adducts decreases from zinc to mercury.

Introduction

N,N-Dimethylformamide, the simplest disubstituted amide, has been extensively utilized not only for many laboratory reactions but also in industrial processes as a polymer solvent.[1] Structural features for DMF have been well established by vibrational[2,3] and proton nuclear magnetic resonance[3] spectroscopies. The ^1H NMR spectrum of free DMF shows two

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different kinds of methyl protons (cis and trans to the carbonyl oxygen) due to the restricted rotation about the carbon–nitrogen bond, which has partial double-bond character.[4] However, these peaks coalesce at higher temperature. The first application of ^{1}H NMR spectroscopy to characterize the interaction of DMF with Lewis acids of the 2B family was illustrated with zinc chloride in nitropropane.[5] The retention of the two separate signals for the methyl groups, with a shift to low field, is interpreted as a preservation of the partial double-bond character of the carbon–nitrogen bond and indicates coordination through oxygen. The same characteristic of coordination for adducts, such as $Hg_3Cl_6\cdot 2DMF$[6] and $Cd_2Cl_4\cdot 3DMF$,[7] is demonstrated by the fact that the CO stretching vibration of the free ligand at 1678 cm^{-1} shifts to low frequency in the compounds formed. An expected increase of the CN stretching frequency for these kinds of adducts is not always observed because of the high degree of coupling of this band with CO and CH vibrations.[2]

It is worth mentioning that, from the study of solubilities[8] of various salts in DMF, the adducts $MCl_2\cdot n$DMF (M = Zn, Cd, Hg; n = 1, 2) were isolated and characterized by elemental analysis. Also calorimetric investigations in dioxane[9] involving $CdCl_2\cdot L$ (L = DMF, MeOH, EtOH, H_2O) led to the conclusion that the DMF adduct is thermodynamically the most stable.[9]

As part of our interest is devoted to the thermochemical study of adducts of amides[10–12] and halides of zinc family elements, 13 compounds of DMF were synthesized. Crystal structures are proposed, and thermochemical data allow us to obtain the energetics involved in the formation of the adducts.

Experimental Section

Materials and Manipulations. Zinc and cadmium chlorides and bromides were prepared as described previously.[11] Zinc (E. Merck), cadmium (Carlo Erba), and mercury iodides (E. Merck) and mercury chloride and bromide (Fisher) were dried in vacuo and stored under nitrogen before use. *N*,*N*-Dimethylformamide, dried over anhydrous sodium carbonate, was distilled in an efficient column, and the median fraction was redistilled under vacuum.[13] Solvents for preparation of the adducts, for calorimetry, and for physical measurements were carefully dried, distilled, and stored over molecular sieves. Chemicals and reactions were handled under a dry-nitrogen atmosphere, in a vacuum line, or in a drybox. After isolation, the adducts were rigorously dried in vacuo for several hours and stored under dry nitrogen.

Preparation of the Adducts. (i) $ZnX_2\cdot 2DMF$ (X = Cl, Br, I), $CdX_2\cdot 2DMF$ (X = Cl, I), $CdBr_2\cdot DMF$, and $HgX_2\cdot DMF$ (X = Cl, Br) were prepared by dissolving 10.0 mmol of the anhydrous metal halide in 25.0 mL of ligand. After the solution was stirred for 2 h at room temperature, excess ligand was pumped off to dryness.

(ii) $ZnX_2\cdot DMF$ (X = Cl, Br) was isolatd by heating at 120 °C 10.0 mmol of zinc halide with an equimolar amount of ligand in a sealed ampule for 3 h. $ZnBr_2\cdot DMF$ crystallized immediately on cooling; however, $ZnCl_2\cdot DMF$ was isolated only after allowing the mixture to stand at 4 °C for several days.

(iii) $ZnI_2\cdot DMF$ and $CdX_2\cdot DMF$ (X = Cl, I) were prepared by reacting an ethanolic solution of 10.0 mmol of the metal halide with the ligand in a suitable molar ratio. The solution was stirred for 10 h, and the adducts were isolated after removing the solvent.

Analytical Methods. The metals were titrated spectrophotometrically with standard EDTA solution at pH 10 by means of a Metrohm-Herisau E 1009 spectrocolorimeter. The end point of the titration for zinc[14] was detected at 665 nm while cadmium and mercury were analyzed at 660 nm after displacement with magnesium.[15]

The halides were determined by argentometric titration through a potentiometric end-point detection[16] using a Metrohm-Herisau E 536 Potentiograph. Adducts of mercury halides were stirred with granulated zinc metal for 2 h. After filtration the percentage weight of mercury was determined.[17] Nitrogen was determined with use of a micro Kjeldahl apparatus.

Calorimetric Measurements. All the solution calorimetric determinations were carried out in a LKB 8700-1 precision calorimeter system by following the described procedure.[18] For these determinations glass ampules containing ca. 10^{-4} mol of reactant were broken into the reaction vessel charged with 100 mL of calorimetric solvent. Each measurement was performed at 298.15 ± 0.02 K, and a drybox was used to prepare ampules of air-sensitive substances.

Other Determinations. Thermogravimetric curves were obtained in the range 30–700 °C by using a Perkin-Elmer Model TGS-1 thermobalance with a programmed speed of heating of 5 °C min^{-1}. A Finnigan 1015 S/L spectrometer was used to obtain the mass spectra of the ligand and adducts. Conductance measurements were carried out in nitromethane, acetone, and ethanol with use of a Metrohm Conductoscope E 365 bridge at 25.0 ± 0.1 °C. Infrared spectra were obtained with sample mulls in Nujol and Fluorolube by using a Perkin-Elmer 180 spectrophotometer. Raman spectra were obtained with a Cary Model 82 of a Jarrel-Ash Model 25-300 spectrophotometer. ^{1}H NMR spectra were obtained in methylene chloride solvent with tetramethylsilane as the internal standard by means of a Varian T-60 apparatus. Melting points were determined in sealed capillary tubes on a Thomas-Hoover or a Reichert instrument. For all adducts that are nonsensitive to moisture X-ray diffraction patterns were obtained on a Norelco Philips instrument by using a Cu Kj radiation source. The relative peak heights were used to estimate the relative intensities.

Results

The analytical data for the 13 adducts of general formulas $MX_2\cdot 2DMF$ (M = Zn, X = Cl, Br, I; M = Cd, X = Cl, I) and $MX_2\cdot DMF$ (M = Zn, Cd, X = Cl, Br, I; M = Hg, X = Cl, Br) are given in Table SI (supplementary material). The white adducts are soluble in methanol and ethanol and insoluble in chloroform and carbon tetrachloride. With the exception of $ZnI_2\cdot 2DMF$, all zinc adducts are very sensitive to moisture. The millimolar conductivities of the adducts in nitromethane (specific conductivity 1.0×10^{-6} Ω^{-1} cm^{-1}), acetone (specific conductivity 1.0×10^{-7} Ω^{-1} cm^{-1}), and ethanol (specific conductivity 4.0×10^{-7} Ω^{-1} cm^{-1}) are listed in Table I. Due to the insolubility of the cadmium adducts in nitromethane, the conductivity measurements were made in ethanol. The conductivities of the adducts are lower than the values reported for 1:1 electrolytes,[19] which are in the ranges 75–95, 160–200, and 70–90 Ω^{-1} cm^2 mol^{-1} for nitromethane, acetone, and ethanol, respectively.

The adducts show narrow ranges of fusion, which are summarized in Table I. However, the melting point was not reproducible after cooling and reheating. Actually, these temperatures correspond to those for decomposition of the adducts. $CdCl_2\cdot 2DMF$ and $CdX_2\cdot DMF$ (X = Cl, Br) did not decompose at temperatures lower than 340 °C.

The thermogravimetric results demonstrate that the adducts started to decompose at lower temperatures than the melting points. An exception is observed for the adducts $ZnX_2\cdot DMF$

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Table I. Conductance, Melting Point,[a] and Infrared Results

	nitromethane		acetone			infrared/cm^{-1}	
substance	amt of adduct/mmol	$\Lambda/\Omega^{-1}\ cm^2\ mol^{-1}$	amt of adduct/mmol	$\Lambda/\Omega^{-1}\ cm^2\ mol^{-1}$	mp (θ_c)/°C	ν(CO)	ν(CN)
DMF						1678 vs[c]	1490 m
$ZnCl_2\cdot 2DMF$	1.00	3.95	1.08	9.86	114-115	1646 vs	1488 m
$ZnCl_2\cdot DMF$	0.86	4.08	0.96	10.45	95-96	1643 vs	1486 m
$ZnBr_2\cdot 2DMF$	0.66	5.29	0.90	1.67	118-119	1644 vs	1484 w
$ZnBr_2\cdot DMF$	1.02	4.12	0.81	2.07	77-78	1652 vs	1484 m
$ZnI_2\cdot 2DMF$	1.00	4.52	0.71	2.00	103-104	1648 vs	1485 m
$ZnI_2\cdot DMF$	0.85	5.17	0.61	2.53	95-96	1647 vs	1482 m
$CdCl_2\cdot 2DMF$	0.86[b]	5.88			>340	1649 vs	1487 w
$CdCl_2\cdot DMF$	1.22[b]	4.39			>340	1658 vs	1493 w
$CdBr_2\cdot DMF$	0.95[b]	3.82	0.63	11.55	>340	1646 vs	1487 m
$CdI_2\cdot 2DMF$	1.18[b]	2.05	0.52	10.65	67-68	1648 s	1487 w
$CdI_2\cdot DMF$	0.88[b]	1.90	0.73	10.43	76-77	1640 vs	1480 w
$HgCl_2\cdot DMF$	0.67	3.00	0.71	2.31	121-123	1665 vs	1497 m
$HgBr_2\cdot DMF$	0.66	1.32	0.81	1.86	93-94	1652 vs	1480 w

[a] Melting or decomposition point (θ_c). [b] Conductance in ethanol. [c] Abbreviations: m, medium; s, strong; w, weak; v, very.

(X = Cl, Br, I). The stoichiometries of the adducts established by elemental analysis are confirmed by the total weight loss observed by using this technique. With the exception of $CdCl_2\cdot 2DMF$, which loses ligands in discrete distinguishable stages, all the other adducts lose the ligand or ligands in one step. The last stage always corresponds to the sublimation of the halides at higher temperature. The stages of loss of ligand and metal halides occur almost simultaneously for adducts of mercury.

Mass spectra of ligand and adducts were also determined, and fragmentation of the ligand was observed as before.[10] The adducts did not show the parent ion peak, while fragments of metal halides and pure metal could be observed for adducts of mercury.[11] The ^1H NMR spectra of the zinc adducts in methylene chloride are reported in Table SII (supplementary material). The cis and trans methyl groups of DMF shifted to low field after coordination.[10] These results agree with the spectra previously obtained with the adducts of zinc chloride.[5]

The vibrational spectra show that the CO stretching peak of DMF shifts to low frequency upon complexation. However, an opposite shift was observed for the CN stretching frequency. Metal–oxygen and metal–halide (Table II) peaks were attributed to the adducts after correlating the number of active bands with the symmetry established for each adduct.[20-22]

The diffractograms show the existence of isomorphism with the adducts of mercury. $CdI_2\cdot DMF$ is not isomorphous with the other monoadducts of this metal, which form another isomorphic series. It is not possible, with the evidence available, to say whether or not the $CdX_2\cdot DMF$ (X = Cl, Br) adducts are isomorphous with the mercury adducts. $ZnCl_2\cdot 2DMF$ differs structurally from those bisadducts of cadmium $CdX_2\cdot 2DMF$. The thermograms of the two bisadducts of cadmium suggest that they differ from each other.

The standard enthalpy of the reaction $MX_2(s) + nDMF(l) = MX_2\cdot nDMF(s)$, $\Delta H_R^\ominus$, can be obtained through the following standard enthalpies of the reactions in solution:

$$MX_2(s) + \text{calorimetric solvent} = MX_2(sol),\ \Delta H_1^\ominus$$
$$DMF(l) + \text{calorimetric solvent} = DMF(sol),\ \Delta H_2^\ominus$$
$$nDMF(l) + MX_2(sol) = MX_2\cdot nDMF(sol),\ \Delta H_3^\ominus$$
$$MX_2(s) + nDMF(sol) = MX_2\cdot nDMF(sol),\ \Delta H_4^\ominus$$
$$MX_2\cdot nDMF(s) + \text{calorimetric solvent} = MX_2\cdot nDMF(sol),\ \Delta H_5^\ominus$$

Table II. Infrared and Raman Spectral Results for Adducts at Low Frequency[a]

	ν(M-X)/cm^{-1}		ν(M-O)/cm^{-1}	
adduct	IR	R	IR	R
$ZnCl_2\cdot 2DMF$	332 vs, 297 vs	338 w, 300 s	415 s	418 m
$ZnCl_2\cdot DMF$	328 vs, 244 vs	340 w, 250 w	420 s	420 w
$ZnBr_2\cdot 2DMF$	254 s, 222 s	256 w, 216 m	412 s	415 m
$ZnBr_2\cdot DMF$	250 vs, 172 s	255 w, 164 m	415 s	
$ZnI_2\cdot 2DMF$	215 s, 157 m	216 m, 153 s	414 s	415 w
$ZnI_2\cdot DMF$	211 s, 153 m	213 m, 160 sh	415 s	415 w
$CdCl_2\cdot 2DMF$	198 s, 176 s	195 w	371 vs	374 vw
$CdCl_2\cdot DMF$	205 sh, 180 s	204 sh, 182 vw		362 vw
$CdBr_2\cdot DMF$	178 sh	182 vw		367 vw
$CdI_2\cdot 2DMF$	170 s	168 w, 153 w	368 s, b	364 vw
$CdI_2\cdot DMF$	170	173 w, 127 sh		360 vw
$HgCl_2\cdot DMF$	285 w	285 s, 162 sh	335 vs	
$HgBr_2\cdot DMF$	245 s	245 w, 142 w		

[a] Abbreviations: m, medium; s, strong; w, weak; sh, shoulder; b, broad; v, very.

The enthalpies of dissolution, $\Delta H_1^\ominus$–$\Delta H_5^\ominus$, are listed in Table SIII (supplementary material). From these values $\Delta H_R^\ominus$ can be obtained by applying Hess' law: $\Delta H_R^\ominus = \Delta H_1^\ominus + \Delta H_3^\ominus - \Delta H_5^\ominus$; $\Delta H_R^\ominus = n\Delta H_2^\ominus + \Delta H_4^\ominus - \Delta H_5^\ominus$. The choice of the thermodynamic cycle to calculate $\Delta H_R^\ominus$ is determined by technical considerations such as the solubility of reagents and the thermal effect values produced, to result in a minimum standard deviation.[10,11]

Discussion

The melting point and thermogravimetric and mass spectrometric data indicate that the adducts are thermolabile and that probably these compounds do not exist in appreciable amounts in the liquid or gas phase.[10,11] The low conductivities presented by these adducts in nitromethane, acetone, and ethanol correlate with the typical behavior of nonelectrolyte compounds.[19]

The ^1H NMR spectra show a single peak for each methyl group, which has been shifted to low field, indicating coordination of the metal to the oxygen of the ligand. If the nitrogen was involved in coordination, the methyl groups would become equivalent and consequently only one peak would be observed because of the loss of carbon–nitrogen double-bond character.[5,10] The infrared data also support this mode of coordination. All adducts show a decrease of CO stretching vibration in comparison with the free ligand.[10] However, the expected increase in the CN stretching vibration[3] was only observed for $MCl_2\cdot DMF$ (M = Cd, Hg). This fact can be explained by the complexity of the CN stretching vibration, which might couple with the CO stretching and CH deformation vibrations.[2,3]

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The free DMF presents a medium-strength band at 404 cm^{-1}, which was attributed to a deformation of the CH_3–N–CH_3 group. This band remains in some Raman spectra of the adducts in the range 400–407 cm^{-1}. However, the infrared and Raman spectra of the adducts show a strong band in the range 412–420 cm^{-1}, which can be assigned to the zinc–oxygen stretching frequency.[20,22] In the infrared spectra of the adducts of cadmium only $CdCl_2$·2DMF and CdI_2·2DMF show a strong band at 371 and 368 cm^{-1}, which could be attributed to the cadmium–oxygen band, but through Raman spectra, it was possible to assign the cadmium–oxygen frequency for all adducts as lying in the range 360–374 cm^{-1}. For the adducts of mercury, only $HgCl_2$·DMF presented a mercury–oxygen band at 335 cm^{-1} in the infrared spectrum.

The observed infrared and Raman spectral frequencies for the adducts in the solid state at low frequency, together with the proposed assignments, are given in Table II. Beyond the metal–oxygen region of absorption the infrared and Raman spectra for the ZnX_2·2DMF adducts show two intense peaks for infrared and weak to medium peaks for the Raman in the range 340–150 cm^{-1}. Both of these bands shift progressively to lower frequencies as X is changed from chloride to iodide, and the frequency ratios are obeyed.[20] Thus, there can be little doubt that these bands are associated with the vibrations of the metal–halogen bonds. The higher frequency bands are assigned to the symmetric modes and the lower ones to the antisymmetric modes of metal–halide vibrations.[20] The existence of these two infrared- and Raman-active bands, which can be attributed to metal–halogen vibrations, is in good agreement with C_{2v} symmetry for the adducts in a tetrahedral arrangement of atoms.[20,21] The adducts ZnX_2·DMF presented a band at a much lower frequency than the adducts ZnX_2·2DMF. This behavior suggests that the monoadducts exist as dimeric structures with a halogen bridging the metals. The higher frequency bands correspond to zinc–halogen terminal modes (ν_t) and the lower ones to zinc–halogen bridging[20,22] modes (ν_b). Table SIV (supplementary material) reports the ratios of metal–halogen stretching frequencies, taking into account the infrared as well as the Raman data. The results show that the ratios $\nu_b(M–X)/\nu_t(M–X)$ are in the ranges 0.69–0.73 and 0.64–0.75 for the infrared and Raman data, respectively. When our results are compared with the $\nu_b(M–X)/\nu_t(M–X)$ ratios of binuclear compounds, which were deduced to vary from 0.63 to 0.83, there is a clear indication that ZnX_2·DMF adducts are binuclear.[22] Therefore, the presence of only one infrared-active terminal metal–zinc stretching mode, as well as only one Raman-active terminal metal–zinc stretching mode, suggests that these adducts have a dimeric trans symmetric tetrahedral structure (C_{2h}).

The vibrational data (Table II) for CdX_2·2DMF (X = Cl, I) show two infrared bands and one Raman-active band for the chloro adduct whereas the inverse was observed for the iodo adduct. When the structures of adducts involving monodentate ligands (L) CdX_2·2L, which can be tetrahedral,[23] are considered and as the great majority of adducts with halogen bridging are polymeric octahedral,[24–26] the cadmium–chlorine frequency at 200 cm^{-1} for $CdCl_2$·2DMF is consistent with the nonexistence of a terminal cadmium–halogen bond;[27] a polymeric octahedral structure is proposed for the iodo adduct.

Two cadmium–chlorine bands were observed in the infrared and Raman spectra for $CdCl_2$·DMF. For $CdBr_2$·DMF only one cadmium–bromide band could be assigned, however; the infrared instrument cut off the bands below 150 cm^{-1}, and in the Raman spectra the corresponding band is overlapped by a strong band at 141 cm^{-1}. The iodo adduct presented one active infrared band at 170 cm^{-1} and two bands in the Raman spectrum at 168 and 153 cm^{-1}. The structure of these monoadducts could be supposed to be polymeric octahedral,[28,29] considering the following arguments: (i) the assigned metal–halogen bands are near or below[27] 200 cm^{-1}, (ii) these adducts are isomorphous, despite the major distortion of the structure of the iodo adduct due to the size of the halogen, (iii) the X-ray diffraction pattern of $CdCl_2$·MU (MU = methylurea) shows a polymeric octahedral structure,[28] and (iv) there is a great similarity in the structures of the monodentate ligands MU and DMF.

The infrared spectra of the isostructural adducts of mercury show a weak-bridge mercury–chlorine stretching frequency at 175 cm^{-1}, which was not observed in the bromo adduct. Accordingly, the existence of one infrared terminal active frequency for the adduct of mercury chloride is itself an indication that the compound is dimeric with a C_{2h} skeletal symmetry.[22] In Table SIV the 0.86 ratio for the terminal mercury–halogen frequencies is very close to the 0.84 ratio for zinc–iodine terminal/zinc–bromine terminal frequencies.[22] In spite of the lower ratio for mercury–chlorine frequencies a dimeric trans symmetric tetrahedral structure is proposed for these adducts of mercury.

The standard enthalpy of formation of the adducts in the condensed phase ($\Delta H_R^\ominus$) can be obtained from the standard enthalpies of dissolution of the halides, DMF, and adducts listed in Table SIII. With the exception of mercury chloride (13.40 ± 0.05 kJ mol^{-1}) and mercury bromide (3.14 ± 0.013 kJ mol^{-1}) all $\Delta H_1^\ominus$ values are exothermic, the highest being those of the zinc halides. In contrast all standard enthalpies of dissolution of adducts are exothermic. The standard enthalpy of dissolution of the metal halide in DMF solution ($\Delta H_4^\ominus$) is practically identical with the $\Delta H_1^\ominus$ value. As examples, dissolutions of zinc iodide in ethanol ($\Delta H_1^\ominus = -52.88 \pm 0.35$ kJ mol^{-1}) and zinc iodide in DMF solution ($\Delta H_4^\ominus = -52.07 \pm 0.72$ kJ mol^{-1}) illustrate this fact. This slight difference in enthalpy indicates that there is no appreciable interaction of metal halide with DMF in solution. The pertinent result for elucidation of this observation is then obtained by calculations involving a thermodynamic cycle: the variation of enthalpy of the process $MX_2(sol) + nDMF(sol) = MX_2 \cdot nDMF(sol)$, $\Delta H_6^\ominus$, where the term sol means solution of MX_2, DMF, and adducts in an appropriate solvent. Thus, with the expression $\Delta H_6^\ominus = \Delta H_R^\ominus - \Delta H_1^\ominus - n\Delta H_2^\ominus + \Delta H_5^\ominus$, the calculated values for interactions varied over a small range from 4.22 ± 1.09 to −3.56 ± 0.69 kJ mol^{-1}. These results suggest a weak metal–ligand interaction in solutions of these calorimetric solvents. However, the thermochemical parameter that defines the occurrence of a reaction is the free energy. Consequently, despite the low $\Delta H_6^\ominus$ values, it is possible that there exist interactions between DMF and metal halides in solution, as was shown by the proton chemical shifts in methylene chloride (Table SII). If these interactions exist in the calorimetric solvents, they should be due to the entropic factors.

The degree of participation of $\Delta H_1^\ominus$ to $\Delta H_R^\ominus$ is notable. Values for the enthalpy of dissolution of zinc iodide and mercury bromide in ethanol are −52.88 ± 0.35 and 3.14 ± 0.03 kJ mol^{-1}, respectively, and consequently $\Delta H_R^\ominus$ values for ZnI_2·DMF and $HgBr_2$·DMF are −57.50 ± 0.28 and −19.02 ± 0.19 kJ mol^{-1}, respectively, which are the extreme values of the monoadducts. $\Delta H_R^\ominus$ values for all the adducts studied are shown in Table III.

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Table III. Thermochemical Data (kJ mol^{-1}) for Adducts

adduct	$\Delta H_R^\ominus$	$\Delta H_f^\ominus$	$\Delta H_D^\ominus$	$\Delta H_M^\ominus$	$\Delta H_{M-O}^\ominus$
$ZnCl_2·2DMF$	−81.37 ± 0.77	−975.2	176.5	−325.5	139
$ZnCl_2·DMF$	−52.39 ± 0.41	−706.9	100.0	−249.0	201
$ZnBr_2·2DMF$	−90.79 ± 0.48	−898.2	185.9	−316.9	135
$ZnBr_2·DMF$	−53.78 ± 0.57	−621.3	100.8	−231.8	184
$ZnI_2·2DMF$	−86.56 ± 0.74	−773.3	181.7	−301.7	127
$ZnI_2·DMF$	−57.50 ± 0.28	−504.9	105.1	−225.1	178
$CdCl_2·2DMF$	−41.39 ± 0.53	−911.6	136.5	−317.7	135
$CdCl_2·DMF$	−26.84 ± 0.18	−657.7	74.4	−255.6	208
$CdBr_2·DMF$	−35.61 ± 0.36	−591.2	83.2	−234.7	187
$CdI_2·2DMF$	−54.39 ± 0.27	−736.4	149.5	−287.2	120
$CdI_2·DMF$	−30.72 ± 0.18	−473.3	78.3	−216.0	168
$HgCl_2·DMF$	−23.09 ± 0.42	−486.8	70.7	−153.5	106
$HgBr_2·DMF$	−19.02 ± 0.19	−429.1	66.6	−148.7	103

The donor strength of the ligand toward specific acceptors can be illustrated by means of $\Delta H_R^\ominus$ values, which in this case reflect the Lewis acidities of the zinc-family halides.[30] In consideration of the acid–base strength, comparisons should be made for adducts of the same stoichiometry, in which crystal enthalpies, reorganization enthalpies, etc. are assumed to be the same. The ranges in variation of $\Delta H_R^\ominus$ for monoadducts of zinc, cadmium, and mercury are −57.50 to −52.39, −35.61 to −26.84, and −23.09 to −19.02 kJ mol^{-1}, respectively, indicating that the relative acceptor acidity varies in the order Zn > Cd > Hg and Zn > Cd for bisadducts. Within the zinc halides, for monoadducts the order $ZnI_2 > ZnBr_2 > ZnCl_2$ contrasts with the inverse order of halides in the cadmium series, while the acidity order $HgCl_2 > HgBr_2$ is observed. For bisadducts the acidity order is $ZnBr_2 > ZnI_2 > ZnCl_2 > CdI_2 > CdCl_2$.

The basicity of DMF can be compared with those of other similar monodentate ligands such as *N*,*N*-dimethylacetamide (DMA) and tetramethylurea (TMU). For an illustration of this fact, consider the monoadducts of cadmium chloride for which $\Delta H_R^\ominus$/kJ mol^{-1} values of $CdCl_2·TMU$ (−44.68 ± 0.62),[11] $CdCl_2·DMA$ (29.20 ± 0.23),[12] and $CdCl_2·DMF$ (−26.84 ± 0.18) correlate with the basicity order TMU > DMA > DMF, which is the same as that given for the donor number of the ligands.[31]

The standard enthalpies of formation of the adducts, $\Delta H_f^\ominus$(ad, s), were determined from $\Delta H_R^\ominus$, standard enthalpies of metal halides,[32] and the standard enthalpy of formation of DMF (−239.37 ± 1.27 kJ mol^{-1}).[33] $\Delta H_R^\ominus$ decreases from zinc to mercury for monoadducts as well as from zinc to cadmium for monoadducts. $\Delta H_f^\ominus$(ad, s) decreases from bis- to monoadducts of the same metal, $ZnCl_2·2DMF$ (−975.2 kJ mol^{-1}) and $ZnCl_2·DMF$ (−706.9 kJ mol^{-1}), and from zinc to mercury, $ZnBr_2·DMF$ (−621.3 kJ mol^{-1}) and $HgBr_2·DMF$ (−429.1 kJ mol^{-1}), resembling the trend in variation of $\Delta H_R^\ominus$ (Table III).

The standard enthalpies of decomposition of the adducts ($\Delta H_D^\ominus$) and the standard enthalpy of formation of adducts from reagents in the gas phase ($\Delta H_M^\ominus$) were calculated for the following reactions: $MX_2·nDMF(s) = MX_2(s) + nDMF(g)$, $\Delta H_D^\ominus$; $MX_2(g) + nDMF(g) = MX_2·nDMF(s)$, $\Delta H_M^\ominus$. The first parameter reflects the variation in enthalpy involved in the breakage of the metal–ligand bond[34] and the rearrangement of the structure of MX_2 to its original form. Besides, the metal–ligand interaction $\Delta H_M^\ominus$ considers other factors linked with formation of the lattice of the adducts. Both parameters were used to compare and systematize adduct thermochemical data.[10,11,35] Table III shows the trends in variation, which are very close to those of $\Delta H_f^\ominus$. The thermodynamic stability of these adducts can therefore be discussed in terms of ΔH.[10] When $\Delta H_f^\ominus$, $\Delta H_D^\ominus$, and $\Delta H_M^\ominus$ values are considered, the sequence in stability is shown to decrease from zinc to mercury[11,12,17,36] and the bisadducts are more stable than the monoadducts. For example, the adducts $ZnCl_2·2DMF$, $CdCl_2·2DMF$, and $HgCl_2·DMF$ present the values −325.5, −317.7, −153.5 and 176.5, 136.5, 70.7 kJ mol^{-1} for $\Delta H_M^\ominus$ and $\Delta H_D^\ominus$, respectively.

The physical measurements are consistent with the proposition that all adducts have the ligand bonded via oxygen to the metal, and attempts were made to obtain the enthalpy of the metal–oxygen bond. For this a thermochemical cycle was established to calculate the enthalpy of the reaction $MX_2(g) + nDMF(g) = MX_2·nDMF(g)$, $\Delta H_g^\ominus$, where $\Delta H_g^\ominus/n = \Delta H_{M-O}^\ominus$. Although the adducts decompose on heating, the enthalpy of the metal–oxygen bond can be estimated[12] by assuming that the enthalpy of sublimation of the adduct is approximately equal to the enthalpy of vaporization[37] of 1 mol of DMF, which is 47.57 ± 1.26 kJ mol^{-1}. The calculated values of $\Delta H_{M-O}^\ominus$ are given in Table III. These results suggest the same tendency as that observed for other amides.[11,12] Broadly speaking, they follow the other thermochemical parameters. $\Delta H_{M-O}^\ominus$ values for monoadducts $ZnCl_2·DMF$ (201 kJ mol^{-1}) and $CdCl_2·DMF$ (208 kJ mol^{-1}) are higher than for the bisadducts $ZnCl_2·2DMF$ (139 kJ mol^{-1}) and $CdCl_2·2DMF$ (135 kJ mol^{-1}). Within the adducts of the same metal the sequence observed is Cl > Br > I, for example, $ZnCl_2·DMF$ (201 kJ mol^{-1}), $ZnBr_2·DMF$ (184 kJ mol^{-1}), and $ZnI_2·DMF$ (178 kJ mol^{-1}). For adducts of the same stoichiometry the $\Delta H_{M-O}^\ominus$ values for $ZnBr_2·DMF$, $CdBr_2·DMF$, and $HgBr_2·DMF$, viz., 184, 187, and 103 kJ mol^{-1}, show that the zinc and cadmium values are very close and much higher than the mercury values. This behavior demonstrates that mercury has the least preference to coordinate to oxygen.[18]

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Registry No. $ZnCl_2·2DMF$, 920-18-3; $ZnBr_2·2DMF$, 31248-15-4; $ZnI_2·2DMF$, 83379-89-9; $CdCl_2·2DMF$, 83434-89-3; $CdI_2·2DMF$, 83379-91-3; $CdBr_2·DMF$, 83379-93-5; $HgCl_2·DMF$, 83379-94-6; $HgBr_2·DMF$, 83379-95-7; $ZnCl_2·DMF$, 83379-96-8; $ZnBr_2·DMF$, 83379-97-9; $ZnI_2·DMF$, 83379-98-0; $CdCl_2·DMF$, 83379-99-1; $CdI_2·DMF$, 83380-01-2.

Supplementary Material Available: Listings of analytical data (Table SI), NMR data for zinc halide adducts (Table SII), enthalpies of dissolution at 298 K (Table SIII), and metal–halogen stretching frequency ratios (Table SIV) (4 pages). Ordering information is given on any current masthead page.

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