Thermochemical Study of Adducts of Tetramethylurea with Zinc, Cadmium, and Mercury Halides

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The adducts $[Zn(tmu)_2X_2]$ (X = Cl, Br, or I), $[Cd(tmu)_2I_2]$, and $[M(tmu)X_2]$ (M = Cd or Hg and X = Cl or Br) have been characterized. The shift of the CO stretching vibration to low frequency indicated that tetramethylurea (tmu) is oxygen bonded to the metals. The standard enthalpy values ($\Delta H_R^\ominus$) for the reactions $MX_2(s) + n\,tmu(l) \longrightarrow [M(tmu)_nX_2](s)$ were determined by means of solution calorimetry. The values of standard enthalpy of formation ($\Delta H_f^\ominus$) of the above adducts in kJ mol^{-1} were: −1 006 ($ZnCl_2$), −926 ($ZnBr_2$), −844 (ZnI_2), −690 ($CdCl_2$), −602 ($CdBr_2$), −775 (CdI_2), −515 ($HgCl_2$), and −454 ($HgBr_2$). The standard enthalpy of vaporization of tmu ($\Delta H_v^\ominus = 51.12 \pm 0.73$ kJ mol^{-1}) was obtained from vapour-pressure measurements. The values of the standard enthalpy of the reactions: $MX_2(s) + n\,tmu(g) \longrightarrow [M(tmu)_nX_2](s)$, $MX_2(g) + n\,tmu(g) \longrightarrow [M(tmu)_nX_2](s)$, and $MX_2(g) + n\,tmu(g) \longrightarrow [M(tmu)_nX_2](g)$ were also determined.

TETRAMETHYLUREA (tmu) is one of the few urea derivatives which are liquid at room temperature. This gives it considerable importance in non-aqueous solvent studies. Although it has a high dipole moment, strong ionic salts are only modestly soluble in this medium. In contrast, the effect of four methyl groups leads to high dissolving power for many organic compounds, including polymers.[1,2]

The characteristic chemical behaviour of tmu as a ligand is that it forms adducts with metals through oxygen.[3-11] Nitrogen is the other possible site of co-ordination but the steric effect of the methyl groups makes it uncompetitive.[1] The evidence for co-ordination *via* oxygen can be easily visualized by the decrease of the CO stretching vibration.

There is little in the literature on adducts of metal halides with tmu.[3,4,7,9,12] In relation to our studies of tmu adducts of zinc, cadmium, and mercury, only work on the adducts $[Zn(tmu)_2X_2]$ (X = Br or I) has been reported.[4]

The present work is concerned with the adducts $[Zn(tmu)_2X_2]$ (X = Cl, Br, or I), $[Cd(tmu)_2I_2]$, and $[M(tmu)X_2]$ (M = Cd or Hg and X = Cl or Br). We report their preparation, characterization, and thermochemistry.

EXPERIMENTAL

Reagents.—Anhydrous zinc and cadmium chloride were prepared as previously described.[13] The anhydrous zinc and cadmium bromides were obtained by treating zinc carbonate (Fisher) and cadmium carbonate (Carlo Erba) respectively, with a solution of 25% hydrobromic acid (Carlo Erba). After filtering off the excess of carbonate, the solution was concentrated and dried *in vacuo* at 180 °C for several days. Zinc iodide (E. Merck), cadmium iodide (Carlo Erba), mercury chloride (Fisher), and mercury bromide (Fisher) were dried *in vacuo* before use. Tetramethylurea (Carlo Erba) was purified and distilled through an efficient column, and the median fraction was collected.[1] Absolute ethanol or methanol were chosen for calorimetric determinations and all other solvents were dried according to standard procedures.

Preparation of the Complexes.—To a solution of the anhydrous metal halide (10.0 mmol) dissolved in ethanol (50 cm^3), tmu (6.0 cm^3, *ca.* 75 mmol) was added dropwise. After stirring the solution at room temperature, half of the solvent was pumped off and the remaining solution was allowed to stand at −10 °C. The adducts $[Cd(tmu)_2I_2]$, $[Hg(tmu)Cl_2]$, and $[Cd(tmu)Br_2]$ precipitated within 8 h, but the zinc adducts could be isolated only after 48 h. The solids were collected by filtration, washed twice with anhydrous diethyl ether, and dried *in vacuo* for several hours. The compounds $[Cd(tmu)Cl_2]$ and $[Hg(tmu)Br_2]$ were isolated by dissolving the respective salts (5.0 mmol) in tmu (20 cm^3) and pumping off the excess of solvent.

Analysis of the Complexes.—Spectrophotometric titrations were performed with Metrohm Herisau E 1009 apparatus, so as to determine the metals with edta (edta = ethylenediaminetetra-acetate) at pH 10. The zinc [14] was analysed at 665 nm while cadmium and mercury [15] were determined at 660 nm, after replacement with magnesium.[16] The halides were determined by means of potentiometric titration [17] using a Metrohn Herisau Potentiograph E 536. For the mercury halides, adducts were stirred with granulated zinc metal for 2 h, and the halides then titrated after filtration. A micro Kjeldahl instrument was used to determine the nitrogen.

Calorimetric Measurements.—The LKB 8700 precision calorimetric system was used and its operation and calibration followed that previously described.[13] Ampoules containing 5—100 mg of substance were broken into the glass vessel, which was charged with 90.0 cm^3 of calorimetric solvent. The measurements were made at 298.15 ± 0.02 K; ampoules of air-sensitive metal chlorides were prepared in a dry-box.

Other Measurements.—Infrared spectra and thermogravimetric curves were obtained as before.[18] Conductance measurements were carried out in nitromethane, acetone, or ethanol, using a Metrohm Conductoscope E 365 bridge, at 25.0 ± 0.1 °C. Mass spectra were recorded on a Finnigan 1015 S/L quadrupole deflection spectrometer. The enthalpy of vapourization of pure tmu was determined by a modified Ramsay–Young method.[19,20]

RESULTS

The elemental analyses, molar conductivities, and melting points of the adducts $[Zn(tmu)_2X_2]$ (X = Cl, Br, or I), $[Cd(tmu)_2I_2]$, and $[M(tmu)X_2]$ (M = Cd or Hg and X = Cl or Br) are presented in Table 1. All compounds prepared are colourless, stable to moisture, and slightly soluble in organic solvents.

TABLE 1

Elemental analyses, conductance in nitromethane and acetone, and melting point of the adducts

Adduct	Analysis (%) [a]			Conductance				M.p. (θ_c/°C)
				Nitromethane		Acetone		
	M	X	N	Amount of adduct/ mmol	Λ/ Ω^{-1} cm^2 mol^{-1}	Amount of adduct/ mmol	Λ/ Ω^{-1} cm^2 mol^{-1}	
[Zn(tmu)$_2$Cl$_2$]	17.25 (17.5)	19.25 (19.75)	15.3 (15.0)	1.00	17.6	0.97	0.79	80—82
[Zn(tmu)$_2$Br$_2$]	14.25 (14.3)	34.2 (34.95)	12.1 (12.25)	1.05	18.5	0.92	1.10	100—102
[Zn(tmu)$_2$I$_2$]	11.6 (11.85)	45.9 (46.0)	10.15 (10.15)	1.05	19.7	1.02	1.90	108—110
[Cd(tmu)Cl$_2$]	37.1 (37.55)	23.2 (23.65)	9.3 (9.35)	1.03	9.3 [b]			>300
[Cd(tmu)Br$_2$]	29.2 (28.95)	41.0 (41.15)	7.15 (7.15)	0.96	3.2 [b]	0.96	12.9	>300
[Cd(tmu)$_2$I$_2$]	18.35 (18.75)	42.6 (42.4)	9.2 (9.35)	1.02	20.6	0.97	10.9	76—78
[Hg(tmu)Cl$_2$]	52.05 (51.75)	18.55 (18.25)	7.3 (7.2)	0.96	3.8	0.99	0.16	89—91
[Hg(tmu)Br$_2$]	41.85 (42.1)	33.2 (33.55)	6.05 (5.85)	1.10	4.0	0.99	0.82	87—89

[a] Calculated values are given in parentheses. [b] Conductance in ethanol.

TABLE 2

Standard enthalpies (kJ mol^{-1}) calculated in accordance with equations (1)—(5)

Adduct	$\Delta H_1^\ominus$	$\Delta H_2^\ominus$	$\Delta H_3^\ominus$	$\Delta H_R^\ominus$
[Zn(tmu)$_2$Cl$_2$]	30.32 ± 0.51	−46.25 ± 0.53	−6.56 ± 0.12	−83.13 ± 0.96
[Zn(tmu)$_2$Br$_2$]	25.85 ± 0.89	−56.98 ± 0.93	−6.12 ± 0.30	−88.68 ± 2.12
[Zn(tmu)$_2$I$_2$]	53.06 ± 1.55	−68.42 ± 1.11	−6.35 ± 0.21	−127.83 ± 2.87
[Cd(tmu)Cl$_2$]	24.90 ± 0.39	−11.96 ± 0.16	−2.82 ± 0.07	−44.68 ± 0.62
[Cd(tmu)Br$_2$]	23.49 ± 0.11	−6.13 ± 0.12	−2.47 ± 0.06	−32.09 ± 0.29
[Cd(tmu)$_2$I$_2$]	44.99 ± 0.43	−11.89 ± 0.14	−6.08 ± 0.09	−62.96 ± 0.66
[Hg(tmu)Cl$_2$]	37.82 ± 0.41	+4.50 ± 0.04	−3.20 ± 0.02	−36.52 ± 0.47
[Hg(tmu)Br$_2$]	29.90 ± 0.16	+3.14 ± 0.03	−2.62 ± 0.04	−29.38 ± 0.23

The molar conductivities measured in acetone and nitromethane are very low. Due to the insolubility of [Cd(tmu)X$_2$] (X = Cl or Br) adducts in these solvents, measurements were carried out in ethanol. For [Zn(tmu)$_2$X$_2$] adducts the conductivity increases from chloride to iodide. Melting points increase similarly. Only [Zn(tmu)$_2$Cl$_2$] retains its melting point, unaltered, after heating. This confirms that these compounds decompose during heating.

The total weight loss observed in the thermogravimetric studies is consistent with the established stoicheiometry of the adducts. The zinc and cadmium compounds lose the ligands in the first stage and this is followed by the sublimation of the halides at a higher temperature. The zinc chloride adduct is an exception in that the final product is the oxide. The mercury adducts showed only an overall mass loss.

The mass spectrum of tmu showed peaks due to the parent ion at *m/e* 116 and the following fragments:[21] *m/e* 87 (CH$_3$)$_2$NCONH$_2$, 73 (CH$_3$)$_2$NCOH, 72 (CH$_3$)$_2$NCO, 58 CH$_3$NCOH, 57 CH$_3$NCO, 45 HN(CH$_3$)$_2$, 44 N(CH$_3$)$_2$, 44 CH$_3$COH, and 43 CH$_3$CO. These peaks were found with the adducts of zinc and cadmium. In addition to the corresponding peaks the mercury adducts also produced fragments which correspond to the metal halides. The mass spectra of all these adducts were recorded above and below the melting point. However, no parent ions were observed.

The standard enthalpies of reaction of the complexes in the calorimetric solvent [reaction (1)] were combined with the enthalpies of solution of the metal chloride in the same solvent [reaction (2)] and the enthalpy of reaction of ligand with the solution of metal chloride [reaction (3)], to give the enthalpy of reaction in the condensed phase [reaction (5)]. The resulting $\Delta H_R^\ominus$ is derived by applying the Hess law to the sequence of reactions (1)—(5), taking into account the correct stoicheiometry in each step. This leads to $\Delta H_4^\ominus = 0$ and $\Delta H_R^\ominus = \Delta H_2^\ominus + \Delta H_3^\ominus - \Delta H_1^\ominus$.

$$[\mathrm{M(tmu)}_n\mathrm{X}_2](\mathrm{s}) + \text{solvent} \xrightarrow{\Delta H_1^\ominus} \text{solution A} \quad (1)$$

$$\mathrm{MX_2(s)} + \text{solvent} \xrightarrow{\Delta H_2^\ominus} \text{solution B} \quad (2)$$

$$\text{solution B} + n\ \mathrm{tmu(l)} \xrightarrow{\Delta H_3^\ominus} \text{solution C} \quad (3)$$

$$\text{solution A} \xrightarrow{\Delta H_4^\ominus} \text{solution C} \quad (4)$$

$$\mathrm{MX_2(s)} + n\ \mathrm{tmu(l)} \xrightarrow{\Delta H_R^\ominus} [\mathrm{M(tmu)}_n\mathrm{X}_2](\mathrm{s}) \quad (5)$$

The calorimetric solvents employed were methanol for zinc and ethanol for cadmium and mercury, which dissolve the anhydrous halides, the ligand, and adducts. For each calorimetric determination five runs were made, with a total volume of 90.0 cm^3 in the calorimeter vessel. Ampoules of air-sensitive compounds were prepared in a dry-box. In Table 2 the standard enthalpies of reaction (1)—(5) are tabulated.

From $\Delta H_R^\ominus$ values [reaction (5)] and values of the standard enthalpy of formation of metal halide[22] and tetramethylurea,[1] the standard enthalpy of the adduct can be calculated by expression (6).

$$\Delta H_f^\ominus(\text{adduct}) = \Delta H_R^\ominus + n\Delta H_f^\ominus(\mathrm{tmu, l}) + \Delta H_f^\ominus(\mathrm{MX_2, s}) \quad (6)$$

The standard enthalpy of vaporisation ($\Delta H_v^\ominus$) for tmu was calculated from vapour-pressure data collected in the range 343—393 K. The data were treated according to the usual literature procedure.[19] The compressibility factor (z), 0.994, was obtained as indicated by Janz.[23] In this interval of temperature 12 experimental values of pressure (mmHg) * (temperature, K) were obtained: 13.9 (344.15), 19.5 (349.95), 31.2, (359.35), 36.9 (361.65), 37.2 (362.85), 55.4 (372.25), 67.2 (375.95), 78.5 (379.15), 82.7 (381.15), 94.3 (384.75), 132.5 (392.15), and 134.8 (393.65).

The plot of log P against $1/T$ gave a straight line and applying the least-squares method expression (7) was obtained. From this $\Delta H_v^\ominus = 51.12 \pm 0.73$ kJ mol^{-1}.

$$\log P = 8.973 - 2\,687.40/T \quad (7)$$

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

Using the literature values for the standard enthalpy of sublimation of the metal halides,[22-26] $\Delta H_R^\ominus$ and $\Delta H_V^\ominus$, thermodynamic cycles can be employed to obtain $\Delta H_M^\ominus$ and $\Delta H_L^\ominus$ as in expressions (8) and (9). These values are listed with $\Delta H_f^\ominus$ in Table 3.

$$MX_2(g) + n\ \text{tmu}(g) \xrightarrow{\Delta H_M^\ominus} [M(\text{tmu})_nX_2](s) \qquad (8)$$

$$MX_2(s) + n\ \text{tmu}(g) \xrightarrow{\Delta H_L^\ominus} [M(\text{tmu})_nX_2](s) \qquad (9)$$

The i.r. spectra showed a decrease in the CO stretching frequencies. Table 3 shows the CO and CN peaks for each adduct, corresponding to the maximum observed.

TABLE 3

Thermochemical (kJ mol⁻¹) and i.r. (cm⁻¹) data for ligand and adducts

Compound	$\Delta H_f^\ominus$	$\Delta H_M^\ominus$	$\Delta H_L^\ominus$	$\Delta H^\ominus$ (M–O)	i.r. ν(CO)	i.r. ν(CN)
tmu	−254.4				1 640	1 495
$[Zn(tmu)_2Cl_2]$	−1 006	−334	−185	−142	1 550	
$[Zn(tmu)_2Br_2]$	−926	−322	−191	−135	1 545	
$[Zn(tmu)_2I_2]$	−844	−350	−230	−149	1 542	
$[Cd(tmu)Cl_2]$	−690	−277	−96	−226	1 620	1 530
$[Cd(tmu)Br_2]$	−602	−235	−83	−184	1 608	1 515
$[Cd(tmu)_2I_2]$	−775	−303	−165	−126	1 535	
$[Hg(tmu)Cl_2]$	−515	−170	−88	−119	1 577	1 515
$[Hg(tmu)Br_2]$	−454	−165	−81	−113	1 525	1 515

DISCUSSION

Most of the bands in the i.r. absorption spectra of tetramethylurea arise from mixed vibrations, which causes great difficulty in making the band assignments.[27] This difficulty is aggravated when the ligand co-ordinates to metals, causing shifts of the bands due to CO and CN vibrations. All adducts studied here showed a shift of CO stretching vibration to low frequency, indicating that the tetramethylurea is co-ordinated to the metal through its oxygen atom.[3-12] Furthermore, in the $[M(tmu)_2X_2]$ adducts the decrease in the CO stretching vibration is accompanied by an increase in the CN stretching vibration, resulting in only one large band with shoulders. On the other hand, smaller shifts observed in $[M(tmu)X_2]$ adducts produce two distinguishable bands. The other bands in which CO and CN are coupled are found at 1 244, 1 140, 913, 577, and 553 cm⁻¹ in the free ligand, remaining in the same position upon complexation. The CO out-of-plane vibration at 783 cm⁻¹ and the CN stretching vibration at 740 cm⁻¹ in the ligand increase in intensity and do not show any shift due to complex formation. For the former an increase in frequency was expected as shown in other amides.[28,29]

The molar conductivities indicated that the adducts are non-electrolytes.[30] The physical measurements obtained on the solids, melting point, thermogravimetry, and mass spectral studies, showed that there is decomposition on heating. These results suggest that the adducts probably do not exist in significant amounts in the gas phase.[13,18]

The standard enthalpy of the adducts in the condensed phase ($\Delta H_R^\ominus$) has been considered as a measure of donor strength of the ligands towards a specific acceptor.[31,32] Tetramethylurea with its high donor number can be considered as a standard base for this kind of comparison. In the case of adducts of the same stoicheiometry like zinc halides, although the structures are unknown, the relative acidity increases from chloride to iodide. The acidity of the chlorides is higher than that of the bromides for cadmium and mercury in the mono-adducts.

In an attempt to compare and systematize the adducts, the parameters $\Delta H_M^\ominus$ and $\Delta H_L^\ominus$ were also calculated.[33] Their values followed the same trend observed with $\Delta H_R^\ominus$.

The standard enthalpy of reaction (10) in the gas phase may be calculated for each complex by means of a thermodynamic cycle.[13,18] From these values the standard enthalpy of the metal–oxygen bond can be calculated.

$$MX_2(g) + n\ \text{tmu}(g) \longrightarrow [M(\text{tmu})_nX_2](g) \qquad (10)$$

Unfortunately, the standard enthalpy of sublimation of the adducts is not experimentally accessible due to decomposition on heating. However, the standard enthalpy of the metal–oxygen bond can be evaluated by relating the enthalpy of sublimation of the adduct with the enthalpy of vaporization of the ligand.[18] The values of $\Delta H^\ominus$(M–O) are higher for $[M(tmu)X_2]$ adducts than for $[M(tmu)_2X_2]$ adducts, see Table 3. The same trend was observed for *NN*-dimethylacetamide adducts.[18]

As the CO stretching frequency is extensively coupled with other modes of vibrations, no correlation with any thermodynamic parameters could be found.

We thank CAPES for the award of a fellowship (to F. P. A.) and FINEP for support.

[9/1736 *Received, 29th October*, 1979]

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