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Enthalpy of Raction of Dimethylsulphoxide with Zirconium, Hafnium and Tin Tetrahalides

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We are searching for preparative and analytical complexing reactions in which there is an enhancement of the difference between zirconium and hafnium: two elements which usually are hardly distinguishable. We have previously shown [1, 2] that hafnium especially favours complexing with Br^- rather than Cl^- and that enthalpies of adduct formation [3] show that $ZrCl_4$ and $HfCl_4$ have virtually the same affinity for an ether (THF). On the other hand, $HfCl_4$ excels over $ZrCl_4$ in bonding to the sulphur analogue, tetrahydrothiophene. We feel that the greatest enhancement of the acceptor ability of hafnium would be achieved in an adduct in which all the ligands have the highest possible polarizability. In the present work we contrast the metal bromides and chlorides in order to show that this principle indeed holds.

Because we found previously that steric hindrance occurs when a sulphur atom bonds to a tetrabromide, we felt that it was necessary to limit the choice of base to one in which the donor atom is small. Dimethylsulphoxide (DMSO) was selected for this study as it has been shown that in it the SO group has a polarizability of 3.40×10^{-24} cm^3 which compares favorably with 3.08×10^{-24} cm^3 for the S atom in $(CH_3)_2S$ [4]. By contrast the O atom in dimethyl ether has a polarizability of 0.65×10^{-24} cm^3 [5]. Tin(IV) chloride and bromide were included in the study in order to allow comparison with a main group element.

Experimental

Preparation of Compounds

Tetrahalides

Tin(IV) chloride (Fisher, certified) was freshly distilled from P_4O_{10} (b.p. 114–115 °C). The other halides were prepared from granulated tin (Fisher, 0.02% foreign metals) or crystal bar Zr or Hf (Ventron 99.95%) and purified chlorine or bromine. All products were analytically pure.

Adducts

The tetrachlorides and $SnBr_4$ were complexed as follows: the metal halide (2–3 g) was put into a Schlenk tube which contained 50–60 ml of freshly-distilled dried, sulfur-free benzene. To this was added a 1- to 2-fold excess of dimethylsulfoxide. The latter had been previously dried over molecular sieves. The mixture was stirred for 1 to 2 days after which the product was separated by filtration under dry nitrogen. The product was washed several times with dry benzene and dried *in vacuo*.

The product formed as described above with $ZrCl_4$ was a 1:3 adduct. A 1:2 adduct was prepared by causing the stoichiometric ratio of reactants to combine or, alternatively, by heating the 1:3 adduct for 20 hr at 100–105 °C *in vacuo*.

$ZrBr_4$ and $HfBr_4$ gave non-stoichiometric products in benzene with MBr_4 to DMSO ratios of less than 1:2, but in hexane, 1:2 adducts were formed. These were kept in a refrigerator as they decomposed slowly at room temperature.

TABLE I. Elemental Analyses of Complexes.

Compound	Carbon %		Hydrogen %		Halogen %		Sulphur %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$ZrCl_4 \cdot 3DMSO$	14.4	15.4	3.2	3.9	30.3	30.4	20.5	20.6
$ZrCl_4 \cdot 2DMSO$	11.7	12.3	3.9	3.1	36.0	36.4	16.4	16.5
$ZrBr_4 \cdot 2DMSO$	8.5	8.5	2.3	2.1	56.1	56.4		
$HfCl_4 \cdot 2DMSO$	10.2	10.1	2.5	2.5	29.3	29.8	13.3	13.2
$HfBr_4 \cdot 2DMSO$	7.7	7.3	2.4	1.9	47.1	48.8		
$SnCl_4 \cdot 2DMSO$	11.8	11.5	2.6	2.9	33.3	34.0	15.2	15.4
$SnBr_4 \cdot 2DMSO$	7.7	8.1	1.6	2.0	52.7	53.8	10.7	10.8

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TABLE II. Mean Molar Heats of Solution of Reactants.

Compound	Solvent	$-\Delta H$ kJ mol^{-1}
$ZrCl_4$	DMSO	259 ± 3[a]
$ZrBr_4$	HCl[b]	286 ± 1
$HfCl_4$	DMSO	255 ± 2
$HfBr_4$	HCl[b]	312 ± 2
$SnCl_4$	DMSO	180 ± 5[c]
$SnBr_4$	HCl[b]	147 ± 1[c]
DMSO	HCl[b]	18.6 ± 0.1[c]

[a]The range shown here and elsewhere represents a 95% confidence limit based on three or four determinations. [b]The solvent consisted of 200 cm^3 of 4.02 *M* HCl + 2.5 cm^3 DMSO. [c]Mean of two measurements.

All compounds were handled in dry nitrogen and stored in sealed ampoules. Analyses are given in Table I.

Calorimetric Measurements

The calorimeter and its method of operation have been described previously [1]. In the present study it contained dry DMSO (200 cm^3) when used with $SnCl_4$, $SnBr_4$, $ZrCl_4$ and $HfCl_4$ and their adducts. $ZrBr_4$ and $HfBr_4$ did not dissolve easily in DMSO so 4.02 *M* hydrochloric acid was used as the calorimeter liquid with these compounds and their adducts. The sample to be dissolved was contained in a thin-walled glass bulb which was crushed under the calorimeter liquid. $SnCl_4$ and $SnBr_4$ were vacuum-distilled into the bulbs with aid of an all-glass apparatus free of joints.

When DMSO was used as the calorimeter liquid, residual moisture in the calorimeter was scavenged prior to the run by breaking a bulb containing the corresponding tetrahalide. The calorimeter in such cases contained an atmosphere of dry nitrogen.

Results and Discussion

The Zr and Hf complexes are reported for the first time. The compounds were all sensitive to moist air. They were insoluble in common organic solvents but dissolved in DMSO and DMF. They decomposed without melting at temperatures in excess of 200 °C.

An attempt was made to determine molecular weights by osmometry. N,N'-dimethylformaide was the only solvent which could be used and even this one is either too strongly coordinating or ionizing. Thus for $ZrCl_4\cdot3DMSO$ a value of 110 was obtained which is close to one-quarter of 467, the molecular weight. The molar conductivity of a 5 X 10^{-4} *M* solution in DMF was 79 ohm^{-1} mol^{-1} which indicates 1:1 electrolyte behaviour. The formulation $[ZrCl_3\cdot DMSO\cdot xDMF]^+\ Cl^-$ is therefore indicated. In DMSO, $ZrCl_4\cdot3DMSO$ had a molar conductivity of 150 ohm^{-1} mol^{-1}. Such a high value shows that the compound may be $[Zr(DMSO)_xCl]^{3+}\ 3Cl^-$ or $[Zr(DMSO)_xCl_2]^{2+}[ZrCl_6]^{2-}$ in this solvent.

TABLE III. Mean Molar Heats of Solution of the Adducts.

Compound	Solvent	$-\Delta H$ kJ mol^{-1}
$ZrCl_4\cdot3DMSO$	DMSO	56 ± 2
$ZrCl_4\cdot2DMSO$	DMSO	89 ± 1
$ZrBr_4\cdot2DMSO$	HCl	168 ± 1
$HfCl_4\cdot2DMSO$	DMSO	70 ± 1
$HfBr_4\cdot2DMSO$	HCl	157 ± 1
$SnCl_4\cdot2DMSO$	DMSO	6.61 ± 0.17
$SnBr_4\cdot2DMSO$	DMSO	4.62 ± 0.06

The infrared spectra show a shift in SO- stretching and C–S–O deformation bands to lower frequencies. This indicates that the DMSO is coordinated through its oxygen to the metal atoms [6, 7]. The spectrum of the 1:3 adduct reveals no uncoordinated DMSO, therefore the complex is possibly 7-coordinate.

Six-coordinate complexes of the type $ZrX_4\cdot2L$, where L may contain a Group V or VI donor atom, usually assume a *cis* arrangement of ligands [8–11]. The assignments have been based on the appearance of complex i.r. spectra in the 400–200 cm^{-1} range caused by Zr–Cl stretching. Assignments in this region were made difficult by the fact that two C–S–O deformation modes occur between 400 and 300 cm^{-1}. Ray and Westland found that Zr–Cl and Hf–Cl stretching frequencies in several amine complexes lie in the range 340–270 cm^{-1} [12].

Thermochemical Data

Tin(IV) chloride and bromide and zirconium and hafnium chlorides were dissolved in pure dimethylsulphoxide and the heats of solution measured. The bromides of zirconium and hafnium formed a gum when added to pure DMSO so these compounds were dissolved in 4*M* hydrochloric acid in the calorimeter. The heats of solution are given in Table II. The heats of solution of the adducts in the respective solvents are recorded in Table III. The heats of solution did not appear to depend upon the sample size so that extrapolation of data to infinite dilution was not required. The heats of complexing, ΔH_{comp}, are given in Table IV.

The heat of solution of $SnCl_4\cdot2DMSO$ is very low compared to that of the transition metal analogues. If we assume that lattice and solvation energies of all complexes containing a given halogen are equal*, we may attribute the greater part of the heat of

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*Please see opposite page for footnote.

TABLE IV. Mean Molar Heats of Complexing for the Formation of Dimethylsulphoxide Complexes.

Compound Formed	$-\Delta H_{comp}$ [a] kJ mol^{-1}	$-\Delta Hg$ [b] kJ mol^{-1}
$ZrCl_4$·3DMSO	203 ± 4	432
$ZrCl_4$·2DMSO	170 ± 3	379
$ZrBr_4$·2DMSO	155 ± 2	367
$HfCl_4$·2DMSO	185 ± 2	392
$HfBr_4$·2DMSO	192 ± 2	399
$SnCl_4$·2DMSO	173 ± 5	319
$SnBr_4$·2DMSO	142 ± 1	311

[a] ΔH_{comp} refers to the heat of complexing when all reactants are in their standard states. [b] ΔHg refers to the heat of complexing from gaseous MX_4 and DMSO at 298 K.

solution of $ZrCl_4$·2DMSO to additional complexing by DMSO. As this heat (89 kJ mol^{-1}) is considerably greater than the heat for the process

$$ZrCl_4\cdot 2DMSO(c) + DMSO(l) \rightarrow ZrCl_4\cdot 3DMSO(c)$$

we conclude that more than three molecules of DMSO coordinate in solution.

The heat of solution of $ZrCl_4$·2DMSO in excess ligand is significantly greater than that of $HfCl_4$·2DMSO. The greater part of such heat of solution seems to be due to additional ligand addition. The fact that we prepared $ZrCl_4$·3DMSO but not the hafnium analogue conforms with this interpretation.

The values of ΔH_{comp} refer to the formation of crystalline adducts from the reactants in their standard states at 25 °C. A better comparison of Lewis acid strength is afforded by the reactions in which the participants are gaseous. It is not possible to estimate the lattice energies of the adducts so we consider the processes:

$$MX_4(g) + 2DMSO(g) \rightarrow MX_4\cdot 2DMSO(c)$$

The various heats of complex formation from gaseous reactants, ΔHg, may be obtained from a thermochemical cycle by making use of the following heats of sublimation: $ZrCl_4$, 103 ± 1; $HfCl_4$, 101 ± 2; $ZrBr_4$, 106 ± 3.5, $HfBr_4$, 101.0; $SnBr_4$, 62. 9 kJ mol^{-1} [14–18]. The heats of evaporation of $SnCl_4$ and DMSO have been reported as 40 ± 1 [18] and 52.9 ± 0.4 [19] kJ mol^{-1} respectively. The values of ΔHg are given in Table IV.

The gaseous tin halides are much poorer acceptors than the transition metal halides. The affinity of gaseous $HfCl_4$ for two DMSO is 13 kJ mol^{-1} greater than that of $ZrCl_4$. In the case of the bromides the difference is 32 kJ mol^{-1}. Thus our original premise that hafnium(IV) bromide is the best acceptor toward more polarizable ligands is borne out. The Lewis acidity of the hafnium halides does not conform to the electronegativity difference between Cl and Br. We believe that this is due, as in boron trihalides, to a cancellation of the electronegativity effect by halogen–metal π-bonding.

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*It may be assumed that the lattice energy for MX_4·2DMSO is nearly independent of the metal as the covalent radii of the three metals differ but little from one another. These have been reported as 1.45, 1.44 and 1.40 Å for Zr, Hf and Sn respectively [13]. Admittedly, the charge distribution may vary, particularly in the halogen atoms, but we have previously seen [3] that the heats of solution of $ZrCl_4$·2THF and $HfCl_4$·2THF in excess ligand are virtually identical. This was true also for the alkali salts K_2MCl_6 [1]. It thus seems unlikely that the lattice energies of corresponding compounds differ greatly.

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References

1 P. Gelbman and A. D. Westland, *J. Chem. Soc. Dalton*, 1598 (1975).
2 R. Makhija and A. D. Westland, *J. Chem. Soc. Dalton*, 1707 (1977).
3 H. F. Chung and A. D. Westland, *Can. J. Chem., 47*, 195 (1969).
4 W. Strecker and R. Spitaler, *Ber., 59*, 1764 (1926).
5 R. Mallemann, F. Suhner and A. Malevergne, *Compt. rend., 232*, 1385 (1951).
6 F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem., 64*, 1534 (1960).
7 H. G. Langer and A. H. Blut, *J. Organometal. Chem., 5*, 288 (1966).
8 I. R. Beattie and L. Rule, *J. Chem. Soc.*, 3267 (1964).
9 G. W. A. Fowles and K. F. Gadd, *J. Chem. Soc. A*, 2232 (1970).
10 G. W. A. Fowles, K. C. Moss, D. A. Rice and N. Rolfe, *J. Chem. Soc. Dalton*, 915 (1972).
11 W. M. Graven and R. V. Peterson, *J. Inorg. Nucl. Chem., 31*, 1743 (1969).
12 T. C. Ray and A. D. Westland, *Inorg. Chem., 4*, 1501 (1965).
13 R. T. Sanderson, "Inorganic Chemistry", Reinhold, New York (1967) p. 74.
14 A. A. Polko, A. D. Ryon and D. W. Kuhn, *J. Phys. Chem., 62*, 319 (1958).
15 S. In'-Chzhu and I. S. Morozov, *Russ. J. Inorg. Chem., 4*, 222 (1959).
16 A. S. Normanton and R. A. J. Shelton, *Trans. Faraday Soc., 66*, 33 (1970).
17 S. S. Berdonosov, V. I. Tsirel'nikov and A. V. Lapitskii, *Vestn. Mosk. Univ., Ser. II, Khim., 20*, 26 (1965).
18 "Selected Values of Chemical Thermodynamic Properties", Natl. Bur. Standards Technical Note 270-3, Washington (1968).
19 T. B. Douglas, *J. Am. Chem. Soc., 70*, 2001 (1948).