

Adducts of Amides with Antimony and Bismuth Trichlorides: Synthesis, Characterization, and Thermochemistry

CLAUDIO AIROLDI

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The adducts $\text{SbCl}_3 \cdot \text{L}$ [$\text{L} = N,N$ -dimethylformamide (DMF), N,N -dimethylacetamide (DMA), and tetramethylurea (TMU)], $\text{MCl}_3 \cdot 2\text{L}$ ($\text{M} = \text{Bi}$ for $\text{L} = \text{DMF}$, DMA , and TMU ; $\text{M} = \text{Sb}$ for $\text{L} = \text{TMU}$), and $\text{BiCl}_3 \cdot 3\text{L}$ ($\text{L} = \text{DMA}$ and TMU) were isolated and characterized by melting points, elemental analysis, infrared spectroscopy, mass spectrometry, nuclear magnetic resonance spectroscopy, and conductometric measurements. The enthalpies of dissolution, $\Delta H^\circ_{\text{R}}$, in acetone of adducts, trichlorides, and ligands at 298.15 K, for the reactions $\text{MCl}_3(\text{s}) + n\text{L}(\text{l}) = \text{MCl}_3 \cdot n\text{L}(\text{s,l})$ resulted in the following values ($\Delta H^\circ_{\text{R}}/\text{kJ mol}^{-1}$): $\text{SbCl}_3 \cdot \text{DMF}(\text{l})$, -27.82 ± 0.15 ; $\text{SbCl}_3 \cdot \text{DMA}(\text{l})$, -37.96 ± 0.16 ; $\text{SbCl}_3 \cdot \text{TMU}(\text{s})$, -44.86 ± 0.27 ; $\text{SbCl}_3 \cdot 2\text{TMU}(\text{s})$, -76.96 ± 0.42 ; $\text{BiCl}_3 \cdot 2\text{DMF}(\text{s})$, -66.15 ± 0.61 ; $\text{BiCl}_3 \cdot 2\text{DMA}(\text{s})$, -82.36 ± 0.83 ; $\text{BiCl}_3 \cdot 2\text{TMU}(\text{s})$, -83.88 ± 0.83 ; $\text{BiCl}_3 \cdot 3\text{DMA}(\text{s})$, 93.85 ± 0.65 ; $\text{BiCl}_3 \cdot 3\text{TMU}(\text{s})$, -112.19 ± 0.98 . From $\Delta H^\circ_{\text{R}}$, the following enthalpies of formation of metal chlorides, $\Delta H^\circ_{\text{f}}(\text{MCl}_3(\text{s}))$ and $\Delta H^\circ_{\text{f}}(\text{L}(\text{l}))$, were calculated for the same sequence of adducts [$\Delta H^\circ_{\text{f}}(\text{s}, 298.15 \text{ K})/\text{kJ mol}^{-1}$]: -649.2 ± 1.3 , -698.3 ± 1.7 , -681 ± 0.3 , -967.7 ± 0.8 , -924.0 ± 3.0 , -1018.1 ± 3.8 , -971.8 ± 1.3 , -1307.9 ± 5.2 , and -1254.5 ± 3.0 . The standard enthalpies of reactions $\Delta H^\circ_{\text{M}}$ for $\text{MCl}_3(\text{g}) + n\text{L}(\text{g}) = \text{MCl}_3 \cdot n\text{L}(\text{s,l})$ and $\Delta H^\circ_{\text{D}}$ for $\text{MCl}_3 \cdot n\text{L}(\text{s,l}) = \text{MCl}_3(\text{s}) + n\text{L}(\text{g})$ have been calculated by means of thermochemical cycles, and the enthalpies of metal-oxygen bonds were estimated. The calorimetric data suggest that $\Delta H^\circ_{\text{M}}$ is the best parameter to characterize the adducts and showed the order $\text{BiCl}_3 > \text{SbCl}_3$ (acidity) and $\text{TMU} > \text{DMA} > \text{DMF}$ (basicity).

Introduction

It is known that N,N -dimethylacetamide (DMA), N,N -dimethylformamide (DMF), and tetramethylurea (TMU) have a strong tendency to coordinate metals through oxygen as the donor atom. In spite of the diversity of adducts formed by antimony and bismuth trichlorides with oxygen donors,¹⁻¹⁰ only the adducts $\text{SbCl}_3 \cdot \text{DMA}$ and $\text{BiCl}_3 \cdot \text{DMF}$ have been isolated with amides.¹¹⁻¹³ Structurally the interest in these compounds is linked with the inert electron pair, the strain of which is thought to cause a distortion of the regular geometry of the formed compound.¹⁴ For example, the X-ray structures of $\text{SbCl}_3 \cdot \text{H}_2\text{NPh}$ and $\text{SbCl}_3 \cdot 20\text{AsPh}_3$ illustrate four-¹⁵ and five-coordination,¹⁶ respectively, but a highly distorted geometry was found instead of the regular geometry expected for these coordination numbers. In fact, a stereochemically active lone pair of electrons can be visualized in each structure. On the other hand, X-ray structures of bismuth trichloride with ligands containing sulfur donor atoms have been determined, and the metal is octahedrally coordinated as an anion or is in polymer chains as a cation.¹⁷⁻¹⁹

Antimony and bismuth atoms in their trichlorides have Lewis acid properties, so that an increase in coordination number of the metal is observed through the formation of a

σ ligand-metal bond. This acid-base behavior has been studied by infrared techniques with nitrogen ligands,²⁰ and the acidity of SbCl_3 was inferred to be greater than that of BiCl_3 .²¹ Calorimetric titrations of BiCl_3 dissolved in acetonitrile with formamide and dimethyl sulfoxide²² showed the formation of 1:3 complexes, and the heats of formation were -35.1 and $-53.1 \text{ kJ mol}^{-1}$, respectively. The interactions of SbCl_3 in benzene and chloroform solution with aliphatic and aromatic amides, in which DMA is included, were followed by vibrational studies.^{23,24} What was observed was a great perturbation of CO and Sb-Cl stretching vibrations with formation of 1:1 and 1:2 complexes. The stability constants were found to be $K_1 > K_2$, and the enthalpies of formation of these complexes varied between -9.5 and $-13.5 \text{ kJ mol}^{-1}$, lower values than those reported for BiCl_3 . Recently, antimony(III) halides were titrated calorimetrically in 1,2-dichloroethane solution with a series of ligands, which contain oxygen donor atoms²⁵ such as dimethyl sulfoxide, triphenylphosphine oxide (Ph_3PO), and pyridine N -oxide (pyNO). These ligands form 1:1 and 1:2 complexes, where $K_1 > K_2$, and no abrupt difference was observed with the enthalpies in distinct steps of formation. Although Ph_3PO and pyNO gave high stability constants at the former step of complexation, in comparison with the analogous phosphorus and nitrogen donor atoms, small enthalpies of formation were observed for the same complexes.

In this paper attempts have been made to synthesize and characterize adducts of DMF, DMA, and TMU with antimony and bismuth trichlorides. For this purpose, a thermochemical study has allowed us to obtain the energetics involved in the formation of the adducts.

Experimental Section

Chemicals. N,N -Dimethylformamide²⁶ (Carlo Erba), N,N -dimethylacetamide²⁷ (E. Merck), and tetramethylurea²⁸ (Carlo Erba)

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Table I. Analytical Data, Melting Points, and Conductance Measurements

compd	% M		% Cl		% N		mp, °C	amt of sample, mmol	Λ_M^a	amt of sample, mmol	Λ_M^b
	calcd	found	calcd	found	calcd	found					
SbCl ₃							73	1.10	1.58	1.00	7.23
SbCl ₃ ·DMF	40.48	41.0	35.31	34.6	4.65	4.4		1.41	1.83	1.38	3.49
SbCl ₃ ·DMA	38.62	38.0	33.74	32.8	4.44	4.6		1.20	3.26	1.21	10.3
SbCl ₃ ·TMU	35.36	35.0	30.89	30.0	8.14	7.9	52-55	1.17	0.17	1.50	11.9
SbCl ₃ ·2TMU	26.44	26.6	23.09	22.9	12.17	11.9	75-77	0.90	3.23	1.07	15.0
BiCl ₃							232	1.11	0.92	0.97	7.89
BiCl ₃ ·2DMF	45.18	44.9	22.98	22.8	6.06	5.9	65-67	1.12	2.22	1.04	8.13
BiCl ₃ ·2DMA	42.6	43.0	21.68	21.5	5.71	5.6	101-103	1.10	31.5	1.02	59.4
BiCl ₃ ·2TMU	38.08	37.9	19.38	18.8	10.21	10.2	65-67	1.19	2.59	1.14	45.3
BiCl ₃ ·3DMA	36.17	36.3	18.41	18.3	7.27	7.0	91	1.04	4.58	1.17	29.2
BiCl ₃ ·3TMU	31.43	31.5	15.99	16.0	12.64	12.6	80-81	0.94	2.08	0.96	20.5

^a Molar conductance in nitromethane ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). ^b Molar conductance in acetone ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

were dried, purified by distillation through an efficient column, and stored over molecular sieves. Nitromethane (Fisher) and acetone (Carlo Erba) were purified for conductance measurements. The first solvent was dried over P₂O₅, and acetone was treated with KMnO₄ and dried with K₂CO₃. Both solvents were distilled in a efficient column and stored over molecular sieves. All other solvents were dried prior to use. Antimony chloride (E. Merck) and bismuth chloride (Carlo Erba) were sublimed in vacuo before use. Acetone was chosen as the calorimetric solvent because of its ability to dissolve salts, ligands, and adducts. Trichlorides and adducts were rigorously dried in vacuo before preparing the ampules, and a drybox was used for air-sensitive compounds.

Preparation of the Adducts. All operations involved in the preparations and purifications were carried out either in vacuo or in a drybox under an atmosphere of dried nitrogen. The following procedures were used to obtain the adducts.

(a) SbCl₃·L (L = DMF, DMA), SbCl₃·2TMU, BiCl₃·2DMF, and BiCl₃·3L (L = DMA, TMU) were obtained by reacting a solution of metal chloride in either acetone or methyl acetate (Bi) or benzene (Sb), with a large excess of ligand, at 0 °C and under continuous stirring. The solution was allowed to stand overnight at 4 °C, and then the solvent was pumped off to obtain the dried compound. Attempts to precipitate the adduct by addition of another solvent to the reaction mixture were unsuccessful. To illustrate the procedure, we describe a typical preparation below.

To a solution of 1.18 g of BiCl₃ (3.80 mmol) in 10 mL of methyl acetate at 0 °C was added slowly and dropwise with stirring 2.0 mL of TMU (25 mmol); stirring was continued at room temperature for 2 h and the mixture allowed to stand overnight at 4 °C. After removal of the solvent, the residual oil crystallized as BiCl₃·3TMU, which was then dried for several hours in vacuo. SbCl₃·TMU was prepared following the same procedure, but with a donor:acceptor ratio of 1:1.

(b) BiCl₃·2DMA was obtained by adding dropwise 1.60 mL of DMA (17.4 mmol) to a solution of 2.76 g of BiCl₃ (8.70 mmol) dissolved in 50 mL of acetone while being stirred. An oil formed immediately, which crystallizes after vigorous agitation. The solid was filtered, washed with acetone, and dried for several hours in vacuo.

(c) When BiCl₃·3TMU was heated in vacuo at 30 °C, an amorphous mass was obtained which started to crystallize after 10 h; the process was completed in 24 h. The resulting solid was dried in vacuo at room temperature for several hours, and the analysis showed it to be BiCl₃·2TMU.

Analytical Section. Samples of bismuth adducts in a small amount of 6 N nitric acid were immediately titrated with standard EDTA solution. After dissolution of the adducts of antimony in tartar emetic and sodium bicarbonate solutions, the titration was carried out with standard iodine solution just to the appearance of the starch blue color.²⁹ Chloride was determined by potentiometric titration with standard silver nitrate solution, after the compounds have been dissolved in 6 N nitric acid. A typical micro-Kjeldahl apparatus was used to determine the nitrogen. Thus, the adducts were digested in a mixture of potassium sulfate and mercury oxide. Free ammonia

Table II. Chemical Shifts (Hz) for Ligands and Adducts

substance	cis	trans	aldehydic	acetic
	methyl	methyl	H	methyl
DMF	168	178	483	
SbCl ₃ ·DMF	174	184	486	
BiCl ₃ ·2DMF	171	181	484	
DMA	171	181		118
SbCl ₃ ·DMA	176	184		126
BiCl ₃ ·2DMA	175	186		124
BiCl ₃ ·3DMA	174	184		126
TMU		167		
SbCl ₃ ·TMU		170		
SbCl ₃ ·2TMU		169		
BiCl ₃ ·2TMU		171		
BiCl ₃ ·3TMU		168		

was distilled over boric acid solution and titrated with standard sulfuric acid solution.

Calorimetric Measurements. All the solution calorimetric determinations were carried out in a LKB 8700-1 precision calorimeter system. Each measurement was performed at 25.04 ± 0.02 °C, with a thin-walled ampule containing reactant being broken in a 100-mL glass reaction vessel containing 90.0 mL of solvent. Details of the procedure and calibration of the calorimeter have already been described.³⁰

Other Determinations. Melting points and proton nuclear magnetic resonance and mass spectra were obtained as previously reported.³¹ Conductance measurements were carried out in nitromethane and acetone, using a Metrohm Conductoscope E 365 bridge at 25.0 ± 0.1 °C. Infrared spectra were obtained with samples mulls in Fluorolube and Nujol with use of a Perkin-Elmer 180 spectrophotometer.

Results

Despite the apparent facility of preparing adducts by direct addition of ligand to the metal chloride, using the exact donor-acceptor stoichiometry, all attempts to obtain 1:1 bismuth adducts were unsuccessful.

SbCl₃·DMF and SbCl₃·DMA are viscous liquids: the former is colorless, and the second is slightly yellow. All other compounds are white solids. SbCl₃ adducts are extremely hygroscopic; however, the trisadduct of BiCl₃ is less sensitive to moisture than the bisadduct. The analytical data, melting points, and conductance results are summarized in Table I. The millimolar conductivities of the adducts in nitromethane (specific conductivity 6.0 × 10⁻⁶ Ω⁻¹ cm⁻¹) and acetone (specific conductivity 5.0 × 10⁻⁷ Ω⁻¹ cm⁻¹) are lower than the values reported for 1:1 electrolytes,³² which are in the range of 75-95 and 100-160 Ω⁻¹ cm² mol⁻¹, respectively. Except for BiCl₃·2DMA, which has the highest value of conductivity in

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Table III. Infrared Results (cm⁻¹) for Ligands and Adducts^a

DMF	SbCl ₃ ·DMF	BiCl ₃ ·2DMF	DMA	SbCl ₃ ·DMA	BiCl ₃ ·2DMA	BiCl ₃ ·3DMA	TMU	SbCl ₃ ·TMU	SbCl ₃ ·2TMU	BiCl ₃ ·2TMU	BiCl ₃ ·3TMU	assignt
1668 vs	1635 vs	1660 vs, 1635 sh	1645 vs	1590 vs	1570 vs	1585 vs, 1660 w	1640 vs	1510 vs	1535 vs	1578 vs	1555 vs, 1595 sh	ν(CO)
1495 m			1495 m	1510 m	1510 m	1515 m	1495 s	1550 vs	1553 vs	1505 vs	1525 vs	ν(CN)
650 vs	665 s	670 s	585 s	592 m	590 w	590 m	775 m	780 m	772 m	770 m	775 m	δ(OCN)
	410 m	410 s		445 w (?)	440 w (?)	426 m, 342 m		425 m	412 s	412 s	412 m, 358 m	ν(M-O)
	321 vs, 318 vs	280 w, 248 s, b		300 vs, 285 vs	274 s, 258 vs	270 sh, 228 vs		315 w, 280 vs, b	300 s, 250 w, b	267 s, 250 vs	276 s, 248 vs	ν(M-Cl)

^a Abbreviations: m, medium; s, strong; b, broad; w, weak; sh, shoulder; vs, very strong.

both solvents, the conductivity results in nitromethane are near those obtained for the respective trichlorides.

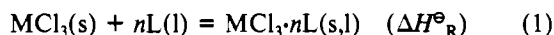
The ¹H NMR spectra in acetone-*d*₆ show that *cis* and *trans* methyl groups of DMA and DMF are shifted to low field after coordination. The single TMU signal is also shifted, and these results are presented in Table II. Several mass spectra of the adducts were obtained below and above the melting point, and no parent ion was detected. Otherwise, the free ligands presented the parent ion and the main cleavage is characterized by the rupture of nitrogen-carbon bond.^{33,34} The ligand mass spectral results are listed, indicating temperature, mass, and fragmentation.

DMF (35 °C): 73, DMF; 72, (CH₃)₂NCO; 58, CH₃NC-OH; 57, CH₃HCO; 45, HN(CH₃)₂; 44, CH₃COH; 44, N(CH₃)₂. DMA (35 °C): 87, DMA; 72, (CH₃)₂NCO; 58, CH₃COCH₃; 57, CH₃NCO; 45, HN(CH₃)₂; 44, CH₃OH; 44, N(CH₃)₂. TMU (35 °C): 116, TMU; 87, (CH₃)₂NCOCH₃; 73, (CH₃)₂NCOH; 72, (CH₃)₂NCO; 58, CH₃NCOH; 57, CH₃NCO; 45, HN(CH₃)₂; 44, N(CH₃)₂; 44, CH₃COH.

In addition to the peaks above, BiCl₃ compounds presented the following peaks: 209, Bi; 244 and 246, BiCl; 279, 281, and 283, BiCl₂; 314, 316, and 318, BiCl₃. Observed for the SbCl₃ compounds were the following peaks: 121 and 123, Sb; 156, 158, and 160, SbCl; 191, 193, and 195, SbCl₂; 226, 228, 230, and 232, SbCl₃.

The main infrared bands of ligands and adducts are listed in Table III. The CO stretching frequency shifts, upon complexation of DMF, DMA, and TMU, to lower frequency values. The metal-oxygen and metal-chloride bands were assigned after correlating the number of active bands with the probably stabilized symmetry for each adduct.^{3,4,6,7,9}

The standard enthalpies (ΔH^o_R) of the adducts MCl₃·*n*L, where *n* = 1 for M = Sb and L = DMF, DMA, TMU, *n* = 2 for M = Sb and L = TMU and for M = Bi and L = DMF, DMA, TMU, and *n* = 3 for M = Bi and L = DMA TMU, can be determined from reaction 1. These standard enthalpy



results were obtained through the standard enthalpy of reactions 2-7 in solution.

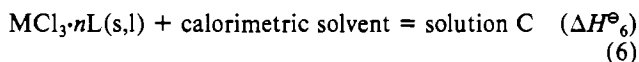
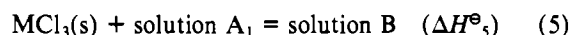
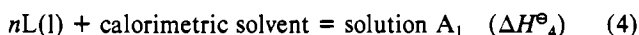
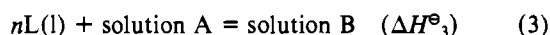
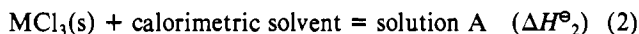
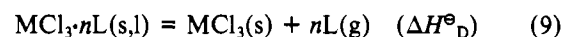
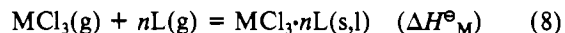


Table IV. Enthalpies of Dissolution at 298 K

substance	calorimetric solvent	ΔH ^o /kJ mol ⁻¹
DMF(l)	acetone	1.46 ± 0.03
DMA(l)	acetone	1.18 ± 0.01
TMU(l)	acetone	0.95 ± 0.02
BiCl ₃ (s)	acetone	-33.28 ± 0.43
SbCl ₃ (s)	acetone	-23.88 ± 0.10
DMA(l)	2:1 BiCl ₃ -acetone	1.18 ± 0.02
BiCl ₃ (s)	2:1 DMF-acetone	-29.55 ± 0.15
BiCl ₃ (s)	3:1 TMU-acetone	-32.52 ± 0.22
BiCl ₃ (s)	3:1 DMA-acetone	-32.40 ± 0.12
BiCl ₃ (s)	3:1 TMU-acetone	-33.05 ± 0.32
SbCl ₃ (s)	1:1 DMF-acetone	-23.57 ± 0.09
SbCl ₃ (s)	1:1 DMA-acetone	-24.10 ± 0.07
SbCl ₃ (s)	1:1 TMU-acetone	-24.52 ± 0.11
SbCl ₃ (s)	2:1 TMU-acetone	-24.17 ± 0.07
SbCl ₃ ·DMF(l)	acetone	5.71 ± 0.03
SbCl ₃ ·DMA(l)	acetone	15.04 ± 0.08
SbCl ₃ ·TMU(s)	acetone	21.29 ± 0.14
SbCl ₃ ·2TMU(s)	acetone	54.69 ± 0.31
BiCl ₃ ·2DMF(s)	acetone	39.52 ± 0.40
BiCl ₃ ·2DMA(s)	acetone	50.26 ± 0.38
BiCl ₃ ·2TMU(s)	acetone	53.26 ± 0.39
BiCl ₃ ·3DMA(s)	acetone	64.99 ± 0.50
BiCl ₃ ·3TMU(s)	acetone	81.99 ± 0.61

The application of Hess' law to the series of reactions (2)-(7) permits one to obtain ΔH^o_R. Thus, ΔH^o_R = ΔH^o₂ + ΔH^o₃ - ΔH^o₆ or ΔH^o_R = ΔH^o₄ + ΔH^o₅ - ΔH^o₆ since the final B and C solutions originating from the dissolution of reactant and products are equivalent, and as a result ΔH^o₇ = 0. ΔH^o_R values can be derived by both procedures; however the choice of the thermodynamic cycle depends on the technique facilities, for example, the solubility, thermic effect values, etc., to give the least standard deviation. The enthalpies of dissolution of metal trichlorides, ligands, and adducts in acetone are listed in Table IV.

The standard enthalpy of formation (ΔH^o_f) of the adducts can be determined from the standard enthalpy of formation of the metal chlorides, the standard enthalpy of formation of ligands, and the ΔH^o_R obtained for reaction 1. The standard enthalpies of reactions 8 and 9 were also determined. Table



V summarizes these standard thermochemical values for chlorides, ligands, and adducts.

Discussion

The major feature of interest in the coordinating ability of amide derivatives with metals is concerned with the carbonyl stretching frequency. All prepared compounds show a decrease in frequency of this band and an increase of CN stretching and OCN deformation frequencies when compared with the free DMF,^{26,35} DMA,^{36,37} and TMU,³⁸ as shown in Table III.

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Table V. Summary of Thermochemical Results (kJ mol⁻¹)

compd	ΔH°_R	ΔH°_f	ΔH°_{sub} or ΔH°_v	ΔH°_M	ΔH°_D	ΔH°_g	ΔH°_{M-O}
SbCl ₃ (s)		-382.0 ^a	68.2 ^a				
BiCl ₃ (s)		-379.1 ^b	114.2 ^b				
DMF(l)		-239.37 ± 1.21 ^c	45.19 ± 0.63 ^e				
DMA(l)		-278.32 ± 1.51 ^c	50.10 ± 0.20 ^f				
TMU(l)		-254.39 ^d	51.12 ± 0.73 ^g				
SbCl ₃ ·DMF(l)	-27.82 ± 0.15	-649.2 ± 1.3		-141.2	73.0	96	96
SbCl ₃ ·DMA(l)	-37.96 ± 0.16	-698.3 ± 1.7		-156.3	88.1	106	106
SbCl ₃ ·TMU(s)	-44.86 ± 0.27	-681.3 ± 0.3		-164.2	96.0	113	113
SbCl ₃ ·2TMU(s)	-76.96 ± 0.42	-967.7 ± 0.8		-247.4	179.2	196	98
BiCl ₃ ·2DMF(s)	-66.15 ± 0.61	-924.0 ± 3.0		-270.7	156.5	226	113
BiCl ₃ ·2DMA(s)	-82.36 ± 0.83	-1018.1 ± 3.8		-296.8	182.6	247	123
BiCl ₃ ·2TMU(s)	-83.88 ± 0.83	-971.8 ± 1.3		-300.3	186.1	249	125
BiCl ₃ ·3DMA(s)	-93.85 ± 0.65	-1307.9 ± 5.2		-358.4	244.2	308	103
BiCl ₃ ·3TMU(s)	-112.19 ± 0.98	-1254.5 ± 3.0		-380.7	266.5	330	110

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This behavior is characteristic of metal-ligand coordination through oxygen.³⁹ The ¹H NMR spectra of DMF and DMA adducts in Table II corroborate this mode of coordination, because two single peaks for each methyl group are observed. If the coordination occurred through the nitrogen atom of the ligands, the methyl groups would be equivalent, producing only one peak as a consequence of breaking the carbon-nitrogen double-bond character.^{13,40} Although the TMU NMR results show only a single peak for all methyl protons, the large increases in the CN stretching frequency indicates the presence of an oxygen-metal bond. This coordination effects the magnetic shielding of methyl protons neighboring the carbonyl group; consequently, a shift to low field is observed, as shown in Table II.

The infrared spectra of BiCl₃·3L (L = DMA, TMU) at low frequency show great similarity. The medium bands at 426 and 342 cm⁻¹ for BiCl₃·3DMA and at 412 and 358 cm⁻¹ for BiCl₃·3TMU were attributed to metal-oxygen bonds, the higher frequency bands are assigned to the symmetric and the lower ones to the antisymmetric stretching modes. The existence of two bands, which can be assigned to symmetric and antisymmetric Bi-Cl bonds vibrations, is in good agreement with a C_{3v} symmetry for adducts, where the ligands are in cis positions.^{3,41}

The adducts SbCl₃·2TMU and BiCl₃·2L (L = DMF, DMA, TMU) showed only one metal-oxygen band at 410 cm⁻¹. BiCl₃·2DMA presented only one band in the 400-500-cm⁻¹ range. Despite its weak intensity and higher frequency, in comparison with other adducts of the same stoichiometry,³ the band at 440 cm⁻¹ was assigned to a metal-oxygen vibration.

The adduct SbCl₃·2TMU showed the symmetric and antisymmetric metal-chloride bands at 300 and 250 cm⁻¹, respectively, very similar to those observed with the adduct³ SbCl₃·2Me₂SO. SbCl₅²⁻ and SbCl₅·2OAsPh₃ showed two metal-chloride bands, and the X-ray structures showed a distorted square pyramid with a stereochemically active electron pair occupying the sixth position.^{16,42} BiCl₅²⁻ presented these two bands^{43,44} at 276 and 245 cm⁻¹, which are very

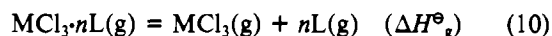
close to those in BiCl₃·2L. Again a distorted square pyramid is likely for these compounds.

The metal-oxygen bands in SbCl₃·DMF and SbCl₃·TMU were assigned to the medium bands at 410 and 425 cm⁻¹. For SbCl₃·DMA the appropriate band appeared weak, at a higher frequency, 445 cm⁻¹. The Sb-Cl stretching vibrations were assigned, one being symmetric (a₁) and the other degenerate asymmetric ⁴ (e), consistent with a C_{3v} symmetry. A trigonal-bipyramidal arrangement with the lone electron pair in the axial position is proposed.

The melting points and mass spectra showed the decomposition of the adducts, which makes it difficult to obtain gas-phase enthalpies of formation, and consequently no information about metal-ligand strength could be derived. However, the standard enthalpy of formation of the adducts in the solid state was calculated. ΔH°_M and ΔH°_D were obtained by means of thermodynamic cycles to provide information about energetics of formation of solid adducts from gaseous reagents or to demonstrate the facility of releasing ligands during heating.

The thermodynamic stability of an adduct is given by the free energy (ΔG) of its formation, but, generally, it is difficult to obtain the entropy (ΔS). However for a series of adducts with the same stoichiometry, ΔS values can be considered constant, leading to a direct correlation between ΔG and ΔH values. Thus the stability of the adduct can be discussed in terms of ΔH . Considering ΔH°_R , ΔH°_f , ΔH°_M , and ΔH°_D , the sequence of stability is shown to be tris- > bis- > mono-adduct.

The standard enthalpy of interaction of metal chloride with ligands in the gas phase



can be used to calculate the standard enthalpy of the metal-oxygen bond, ΔH°_{M-O} , if the values of enthalpy of sublimation of the adducts are known.^{30,31,45-47} As shown above, these adducts decompose on heating, and to evaluate the relative strengths of metal-oxygen bonds, it was necessary to assume that the molar enthalpy of sublimation of each adduct was equal to the enthalpy of vaporization of 1 mol of ligand.^{31,45} For adducts of the same stoichiometry, ΔH°_{M-O} values follow the sequence of donor number of the ligands,⁴⁸ i.e., TMU >

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DMA > DMF. ΔH_g^\ominus and ΔH_{M-O}^\ominus values are listed in Table V.

The values of standard enthalpy of formation of adducts in the condensed phase (ΔH_R^\ominus) have been used to relate the donor strength of the ligand.^{49,50} For adducts of a given stoichiometry formed between a fixed acceptor and the studied ligands, the energy involved can be considered constant and the observed ΔH_R^\ominus values reflect the basicity order TMU > DMA > DMF, which is the same as that given by ΔH_{M-O}^\ominus . On the other hand, the comparison of the same base with different acids gives the acidity order $\text{BiCl}_3 > \text{SbCl}_3$.

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All enthalpy values display the same trend of variation, consequently all are equally satisfactory for characterizing the enthalpy involved in the formation of the adduct. However, ΔH_M^\ominus can be understood as a better parameter because it reflects the acid-base interaction in the gas phase.⁵¹

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Registry No. SbCl_3 , 10025-91-9; $\text{SbCl}_3 \cdot \text{DMF}$, 41322-22-9; $\text{SbCl}_3 \cdot \text{DMA}$, 22995-10-4; $\text{SbCl}_3 \cdot \text{TMU}$, 75949-51-8; $\text{SbCl}_3 \cdot 2\text{TMU}$, 75949-52-9; BiCl_3 , 7787-60-2; $\text{BiCl}_3 \cdot 2\text{DMF}$, 75949-53-0; $\text{BiCl}_3 \cdot 2\text{DMA}$, 75949-54-1; $\text{BiCl}_3 \cdot 2\text{TMU}$, 75949-55-2; $\text{BiCl}_3 \cdot 3\text{DMA}$, 75949-56-3; $\text{BiCl}_3 \cdot 3\text{TMU}$, 75949-57-4; DMF, 68-12-2; DMA, 127-19-5; TMU, 632-22-4.

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Contribution from the Department of Chemistry and Chemical Physics Program, Washington State University, Pullman, Washington 99164

Water Exchange with Ferric Ion and Oligomerized Iron in Acidic Aqueous Solutions

HAROLD W. DODGEN,* GORDON LIU, and JOHN P. HUNT

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The water-exchange rate with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ in 1.5 M HClO_4 has been measured with use of ^{17}O NMR and gives $\Delta H^\ddagger = 18.5$ kcal/mol, $\Delta S^\ddagger = 13.8$ cal/(mol K), and $k_1 = 167$ s⁻¹ at 25 °C for a particular water leaving the first coordination sphere. Solutions heated above 110 °C developed a species which exchanged water $(2-15) \times 10^4$ times faster than $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and which persists at room temperature for months. This species is likely an oligomer of iron(III) formed in the first stage of the process leading to precipitation of the iron(III) at high temperatures.

Introduction

Water exchange in and out of the first coordination sphere of ferric ion is known to be relatively slow although there is some uncertainty about the exact rate.¹ It is desirable to know the rate in order to interpret substitution rates on ferric² ion, and knowledge of the contact interaction with $^{17}\text{OH}_2$ is needed in order to determine the number of bound waters in ferric complexes such as porphyrin complexes which we are currently studying. The method involves measuring the $^{17}\text{OH}_2$ line broadening over a wide temperature range so that one can go from the slow-exchange to the fast-exchange region.³ Ferric ion is known to hydrolyze⁴ and oligomerize as the pH is raised, so this study was carried out on strongly acidic solutions and at relatively low Fe(III) concentrations with the hope that only $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ would be present. The measurements involved determination of the broadening and shift of the ^{17}O resonance for the bulk water in the solutions.

Experimental Section

Most solutions were prepared by adding 12 M reagent grade HClO_4 to ^{17}O -enriched water and then dissolving reagent grade $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. One solution was prepared by dissolving iron wire, 99.95% pure, in HClO_4 , fuming, and then diluting. Other solutions were prepared from $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ recrystallized from concentrated HClO_4 . Solutions containing Al^{3+} or Ga^{3+} in place of Fe^{3+} were used as blanks. The composition of solutions used is listed in Table I.

Table I. Composition of Solutions Used

solution	$m_{\text{Fe(III)}}$	m_{HClO_4}	m_{NaClO_4}
A	0.367 ^a	1.74	0.75
B	0.398 ^a	1.89	0.81
C	0.388 ^a	1.84	0.79
D	0.0106 ^b	1.49	0
E	0.0106 ^b	1.49	0
F	0.0053 ^b	1.49	0

^a Perchlorate. ^b Nitrate.

NMR spectra were obtained with a field-locked, frequency-swept CW spectrometer using 5-Hz side-band modulation. The Lorentzian dispersion lines were fit with an on-line microprocessor based computer to give the line widths and frequencies. Measurements at each temperature were made at several rf levels for the sample and blank, and the widths were extrapolated to zero rf level by a computer program in order to eliminate saturation effects. A value of T_1 was obtained in the extrapolation process. Temperature was controlled to ± 0.1 °C by pumping silicone oil from a thermostat around the sample and was measured by a copper-constantin thermocouple placed immediately below the sample and rf coil.

The measured line broadenings and shifts were converted to T_{2p} and Q defined by eq 1 and 2, where W_s and W_0 are the half-widths

$$1/T_{2p} = 2\pi(W_s - W_0) \frac{m_{\text{H}_2\text{O}}}{m_{\text{Fe}}} \quad (1)$$

$$Q = TS \frac{m_{\text{H}_2\text{O}}}{m_{\text{Fe}}} \quad (2)$$

at half-maximum absorption of the sample and blank, respectively (in Hz), $m_{\text{H}_2\text{O}}$ and m_{Fe} are molalities of H_2O and Fe(III) in the sample, T is the temperature in K, and S is the absorption frequency of the sample minus the frequency of the blank divided by the frequency

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