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

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The adducts $SbCl_3{\cdot}L$ [L = *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), and tetramethylurea (TMU)], $MCl_3{\cdot}2L$ (M = Bi for L = DMF, DMA, and TMU; M = Sb for L = TMU), and $BiCl_3{\cdot}3L$ (L = 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, $\Delta H^\ominus_R$, in acetone of adducts, trichlorides, and ligands at 298.15 K, for the reactions $MCl_3(s) + nL(l) = MCl_3{\cdot}nL(s,l)$ resulted in the following values ($\Delta H^\ominus_R$/kJ mol$^{-1}$): $SbCl_3{\cdot}DMF(l)$, $-27.82 \pm 0.15$; $SbCl_3{\cdot}DMA(l)$, $-37.96 \pm 0.16$; $SbCl_3{\cdot}TMU(s)$, $-44.86 \pm 0.27$; $SbCl_3{\cdot}2TMU(s)$, $-76.96 \pm 0.42$; $BiCl_3{\cdot}2DMF(s)$, $-66.15 \pm 0.61$; $BiCl_3{\cdot}2DMA(s)$, $-82.36 \pm 0.83$; $BiCl_3{\cdot}2TMU(s)$, $-83.88 \pm 0.83$; $BiCl_3{\cdot}3DMA(s)$, $93.85 \pm 0.65$; $BiCl_3{\cdot}3TMU(s)$, $-112.19 \pm 0.98$. From $\Delta H^\ominus_R$, the following enthalpies of formation of metal chlorides, $\Delta H^\ominus_f(MCl_3(s))$ and $\Delta H^\ominus_f(L(l))$, were calculated for the same sequence of adducts [$\Delta H^\ominus_f$(s, 298.15 K)/kJ mol$^{-1}$]: $-649.2 \pm 1.3$, $-698.3 \pm 1.7$, $-681 \pm 0.3$, $-967.7 \pm 0.8$, $-924.0 \pm 3.0$, $-1018.1 \pm 3.8$, $-971.8 \pm 1.3$, $-1307.9 \pm 5.2$, and $-1254.5 \pm 3.0$. The standard enthalpies of reactions $\Delta H^\ominus_M$ for $MCl_3(g) + nL(g) = MCl_3{\cdot}nL(s,l)$ and $\Delta H^\ominus_D$ for $MCl_3{\cdot}nL(s,l) = MCl_3(s) + nL(g)$ have been calculated by means of thermochemical cycles, and the enthalpies of metal–oxygen bonds were estimated. The calorimetric data suggest that $\Delta H^\ominus_M$ is the best parameter to characterize the adducts and showed the order $BiCl_3 > SbCl_3$ (acidity) and TMU > DMA > 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 aducts $SbCl_3{\cdot}DMA$ and $BiCl_3{\cdot}DMF$ 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 $SbCl_3{\cdot}H_2NPh$ and $SbCl_3{\cdot}20AsPh_3$ 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 $\sigma$ 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 sulfoxide[22] showed the formation of 1:3 complexes, and the heats of formation were −35.1 and −53.1 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 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 donors atoms[25] 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 donors 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*-Dimethylformamide[26] (Carlo Erba), *N,N*-dimethylacetamide[27] (E. Merck), and tetramethylurea[28] (Carlo Erba)

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

| compd | % M calcd | % M found | % Cl calcd | % Cl found | % N calcd | % N found | mp, °C | amt of sample, mmol | $\Lambda_M$[a] | amt of sample, mmol | $\Lambda_M$[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $SbCl_3$ | | | | | | | 73 | 1.10 | 1.58 | 1.00 | 7.23 |
| $SbCl_3 \cdot DMF$ | 40.48 | 41.0 | 35.31 | 34.6 | 4.65 | 4.4 | | 1.41 | 1.83 | 1.38 | 3.49 |
| $SbCl_3 \cdot DMA$ | 38.62 | 38.0 | 33.74 | 32.8 | 4.44 | 4.6 | | 1.20 | 3.26 | 1.21 | 10.3 |
| $SbCl_3 \cdot TMU$ | 35.36 | 35.0 | 30.89 | 30.0 | 8.14 | 7.9 | 52–55 | 1.17 | 0.17 | 1.50 | 11.9 |
| $SbCl_3 \cdot 2TMU$ | 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 |
| $BiCl_3 \cdot 2DMF$ | 45.18 | 44.9 | 22.98 | 22.8 | 6.06 | 5.9 | 65–67 | 1.12 | 2.22 | 1.04 | 8.13 |
| $BiCl_3 \cdot 2DMA$ | 42.6 | 43.0 | 21.68 | 21.5 | 5.71 | 5.6 | 101–103 | 1.10 | 31.5 | 1.02 | 59.4 |
| $BiCl_3 \cdot 2TMU$ | 38.08 | 37.9 | 19.38 | 18.8 | 10.21 | 10.2 | 65–67 | 1.19 | 2.59 | 1.14 | 45.3 |
| $BiCl_3 \cdot 3DMA$ | 36.17 | 36.3 | 18.41 | 18.3 | 7.27 | 7.0 | 91 | 1.04 | 4.58 | 1.17 | 29.2 |
| $BiCl_3 \cdot 3TMU$ | 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 ($\Omega^{-1}$ cm$^2$ mol$^{-1}$). [b] Molar conductance in acetone ($\Omega^{-1}$ cm$^2$ 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 $P_2O_5$, and acetone was treated with $KMnO_4$ and dried with $K_2CO_3$. 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) $SbCl_3 \cdot L$ (L = DMF, DMA), $SbCl_3 \cdot 2TMU$, $BiCl_3 \cdot 2DMF$, and $BiCl_3 \cdot 3L$ (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 $BiCl_3$ (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 $BiCl_3 \cdot 3TMU$, which was then dried for several hours in vacuo. $SbCl_3 \cdot TMU$ was prepared following the same procedure, but with a donor:acceptor ratio of 1:1.

(b) $BiCl_3 \cdot 2DMA$ was obtained by adding dropwise 1.60 mL of DMA (17.4 mmol) to a solution of 2.76 g of $BiCl_3$ (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 $BiCl_3 \cdot 3TMU$ 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 $BiCl_3 \cdot 2TMU$.

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

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

| substance | cis methyl | trans methyl | aldehydic H | acetonic methyl |
|---|---|---|---|---|
| DMF | 168 | 178 | 483 | |
| $SbCl_3 \cdot DMF$ | 174 | 184 | 486 | |
| $BiCl_3 \cdot 2DMF$ | 171 | 181 | 484 | |
| DMA | 171 | 181 | | 118 |
| $SbCl_3 \cdot DMA$ | 176 | 184 | | 126 |
| $BiCl_3 \cdot 2DMA$ | 175 | 186 | | 124 |
| $BiCl_3 \cdot 3DMA$ | 174 | 184 | | 126 |
| TMU | 167 | | | |
| $SbCl_3 \cdot TMU$ | 170 | | | |
| $SbCl_3 \cdot 2TMU$ | 169 | | | |
| $BiCl_3 \cdot 2TMU$ | 171 | | | |
| $BiCl_3 \cdot 3TMU$ | 168 | | | |

**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.

$SbCl_3 \cdot DMF$ and $SbCl_3 \cdot DMA$ are viscous liquids: the former is colorless, and the second is slightly yellow. All other compounds are white solids. $SbCl_3$ adducts are extremely hygroscopic; however, the trisadduct of $BiCl_3$ 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 $6.0 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$) and acetone (specific conductivity $5.0 \times 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$) are lower than the values reported for 1:1 electrolytes,[32] which are in the range of 75–95 and 100–160 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, respectively. Except for $BiCl_3 \cdot 2DMA$, which has the highest value of conductivity in

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Table III. Infrared Results ($\mathrm{cm}^{-1}$) 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,<br>1635 sh | 1645 vs | 1590 vs | 1570 vs | 1585 vs,<br>1660 w | 1640 vs | 1510 vs | 1535 vs | 1578 vs | 1555 vs,<br>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,<br>342 m | | 425 m | 412 s | 412 s | 412 m,<br>358 m | ν(M–O) |
| | 321 vs,<br>318 vs | 280 w,<br>248 s, b | | 300 vs,<br>285 vs | 274 s,<br>258 vs | 270 sh,<br>228 vs | | 315 w,<br>280 vs, b | 300 s,<br>250 w, b | 267 s,<br>250 vs | 276 s,<br>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, $(CH_3)_2NCO$; 58, $CH_3NCOH$; 57, $CH_3HCO$; 45, $HN(CH_3)_2$; 44, $CH_3COH$; 44, $N(CH_3)_2$. DMA (35 °C): 87, DMA; 72, $(CH_3)_2NCO$; 58, $CH_3COCH_3$; 57, $CH_3NCO$; 45, $HN(CH_3)_2$; 44, $CH_3OH$; 44, $N(CH_3)_2$. TMU (35 °C): 116, TMU; 87, $(CH_3)_2NCOCH_3$; 73, $(CH_3)_2NCOH$; 72, $(CH_3)_2NCO$; 58, $CH_3NCOH$; 57, $CH_3NCO$; 45, $HN(CH_3)_2$; 44, $N(CH_3)_2$; 44, $CH_3COH$.

In addition to the peaks above, $BiCl_3$ compounds presented the following peaks: 209, Bi; 244 and 246, BiCl; 279, 281, and 283, $BiCl_2$; 314, 316, and 318, $BiCl_3$. Observed for the $SbCl_3$ compounds were the following peaks: 121 and 123, Sb; 156, 158, and 160, SbCl; 191, 193, and 195, $SbCl_2$; 226, 228, 230, and 232, $SbCl_3$.

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 ($\Delta H^{\ominus}_{\mathrm{R}}$ of the adducts $MCl_3 \cdot nL$, 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

$$MCl_3(s) + nL(l) = MCl_3 \cdot nL(s,l) \quad (\Delta H^{\ominus}_{\mathrm{R}}) \qquad (1)$$

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

$$MCl_3(s) + \text{calorimetric solvent} = \text{solution A} \quad (\Delta H^{\ominus}_2) \qquad (2)$$

$$nL(l) + \text{solution A} = \text{solution B} \quad (\Delta H^{\ominus}_3) \qquad (3)$$

$$nL(l) + \text{calorimetric solvent} = \text{solution } A_1 \quad (\Delta H^{\ominus}_4) \qquad (4)$$

$$MCl_3(s) + \text{solution } A_1 = \text{solution B} \quad (\Delta H^{\ominus}_5) \qquad (5)$$

$$MCl_3 \cdot nL(s,l) + \text{calorimetric solvent} = \text{solution C} \quad (\Delta H^{\ominus}_6) \qquad (6)$$

$$\text{solution B} = \text{solution C} \quad (\Delta H^{\ominus}_7) \qquad (7)$$

Table IV. Enthalpies of Dissolution at 298 K

| substance | calorimetric solvent | $\Delta H^{\ominus}/\mathrm{kJ\ mol^{-1}}$ |
|---|---|---|
| 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 $\Delta H^{\ominus}_{\mathrm{R}}$. Thus, $\Delta H^{\ominus}_{\mathrm{R}} = \Delta H^{\ominus}_2 + \Delta H^{\ominus}_3 - \Delta H^{\ominus}_6$ or $\Delta H^{\ominus}_{\mathrm{R}} = \Delta H^{\ominus}_4 + \Delta H^{\ominus}_5 - \Delta H^{\ominus}_6$ since the final B and C solutions originating from the dissolution of reactant and products are equivalent, and as a result $\Delta H^{\ominus}_7 = 0$. $\Delta H^{\ominus}_{\mathrm{R}}$ 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 ($\Delta H^{\ominus}_{\mathrm{f}}$) 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 $\Delta H^{\ominus}_{\mathrm{R}}$ obtained for reaction 1. The standard enthalpies of reactions 8 and 9 were also determined. Table

$$MCl_3(g) + nL(g) = MCl_3 \cdot nL(s,l) \quad (\Delta H^{\ominus}_{\mathrm{M}}) \qquad (8)$$

$$MCl_3 \cdot nL(s,l) = MCl_3(s) + nL(g) \quad (\Delta H^{\ominus}_{\mathrm{D}}) \qquad (9)$$

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 | $\Delta H^\ominus_R$ | $\Delta H^\ominus_f$ | $\Delta H^\ominus_{sub}$ or $\Delta H^\ominus_v$ | $\Delta H^\ominus_M$ | $\Delta H^\ominus_D$ | $\Delta H^\ominus_g$ | $\Delta H^\ominus_{M-O}$ |
|---|---|---|---|---|---|---|---|
| $SbCl_3$(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 $BiCl_3$·3L (L = DMA, TMU) at low frequency show great similarity. The medium bands at 426 and 342 $cm^{-1}$ for $BiCl_3$·3DMA and at 412 and 358 $cm^{-1}$ for $BiCl_3$·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 $SbCl_3$·2TMU and $BiCl_3$·2L (L = DMF, DMA, TMU) showed only one metal–oxygen band at 410 $cm^{-1}$. $BiCl_3$·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 $SbCl_3$·2TMU showed the symmetric and antisymmetric metal–chloride bands at 300 and 250 $cm^{-1}$, respectively, very similar to those observed with the adduct[3] $SbCl_3$·2$Me_2SO$. $SbCl_5^{2-}$ and $SbCl_3$·2$OAsPh_3$ 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] $BiCl_5^{2-}$ presented these two bands[43,44] at 276 and 245 $cm^{-1}$, which are very close to those in $BiCl_3$·2L. Again a distorted square pyramid is likely for these compounds.

The metal–oxygen bands in $SbCl_3$·DMF and $SbCl_3$·TMU were assigned to the medium bands at 410 and 425 $cm^{-1}$. For $SbCl_3$·DMA the appropriate band appeared weak, at a higher frequency, 445 $cm^{-1}$. The Sb–Cl stretching vibraions were assigned, one being symmetric ($a_1$) 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. $\Delta H^\ominus_M$ and $\Delta H^\ominus_D$ 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 ($\Delta G$) of its formation, but, generally, it is difficult to obtain the entropy ($\Delta S$). However for a series of adducts with the same stoichiometry, $\Delta S$ values can be considered constant, leading to a direct correlation between $\Delta G$ and $\Delta H$ values. Thus the stability of the adduct can be discussed in terms of $\Delta H$. Considering $\Delta H^\ominus_R$, $\Delta H^\ominus_f$, $\Delta H^\ominus_M$, and $\Delta H^\ominus_D$, 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

$$MCl_3\cdot nL(g) = MCl_3(g) + nL(g) \quad (\Delta H^\ominus_g) \qquad (10)$$

can be used to calculate the standard enthalpy of the metal–oxygen bond, $\Delta H^\ominus_{M-O}$, 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, $\Delta H^\ominus_{M-O}$ values follow the sequence of donor number of the ligands,[48] i.e., TMU >

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DMA > DMF. $\Delta H^{\ominus}_{g}$ and $\Delta H^{\ominus}_{M-O}$ values are listed in Table V.

The values of standard enthalpy of formation of adducts in the condensed phase ($\Delta H^{\ominus}_{R}$) 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 $\Delta H^{\ominus}_{R}$ values reflect the basicity order TMU > DMA > DMF, which is the same as that given by $\Delta H^{\ominus}_{M-O}$. On the other hand, the comparison of the same base with different acids gives the acidity order $BiCl_3$ > $SbCl_3$.

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, $\Delta H^{\ominus}_{M}$ 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; $SbCl_3$·DMF, 41322-22-9; $SbCl_3$·DMA, 22995-10-4; $SbCl_3$·TMU, 75949-51-8; $SbCl_3$·2TMU, 75949-52-9; $BiCl_3$, 7787-60-2; $BiCl_3$·2DMF, 75949-53-0; $BiCl_3$·2DMA, 75949-54-1; $BiCl_3$·2TMU, 75949-55-2; $BiCl_3$·3DMA, 75949-56-3; $BiCl_3$·3TMU, 75949-57-4; DMF, 68-12-2; DMA, 127-19-5; TMU, 632-22-4.

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

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The water-exchange rate with $Fe(H_2O)_6^{3+}$ in 1.5 *m* $HClO_4$ has been measured with use of $^{17}O$ NMR and gives $\Delta H^{*}$ = 18.5 kcal/mol, $\Delta S^{*}$ = 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) × $10^4$ times faster than $Fe(H_2O)_6^{3+}$ 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 ferric[2] ion, and knowledge of the contact interaction with $^{17}OH_2$ 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 $^{17}OH_2$ 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 hydrolyze[4] 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 $Fe(H_2O)_6^{3+}$ 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 $Fe(NO_3)_3·6H_2O$. One solution was prepared by dissolving iron wire, 99.95% pure, in $HClO_4$, fuming, and then diluting. Other solutions were prepared from $Fe(ClO_4)_3·6H_2O$ 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 | $m_{Fe(III)}$ | $m_{HClO_4}$ | $m_{NaClO_4}$ |
|---|---|---|---|
| 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

$$1/T_{2p^*} = 2\pi(W_s - W_0)\frac{m_{H_2O}}{m_{Fe}} \qquad (1)$$

$$Q = TS\frac{m_{H_2O}}{m_{Fe}} \qquad (2)$$

at half-maximum absorption of the sample and blank, respectively (in Hz), $m_{H_2O}$ 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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