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# THERMOCHEMISTRY OF AMIDE AND THIOAMIDE COMPLEXES OF ARSENIC TRIHALIDES

P.O. DUNSTAN * and L.C.R. DOS SANTOS

*Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, CEP 13081, Campinas, São Paulo (Brazil)*

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## ABSTRACT

The complexes $AsX_3 \cdot nL$ (L ≡ 1,1,3,3-tetramethyl-2-thiourea (TMTU), thiourea (TU), *N,N*-dimethylthioacetamide (DMTA), thioacetamide (TA), *N,N*-dimethylthioformamide (DMTF), *N,N*-dimethylacetamide (DMA) or acetamide (A); $n = 1$, 3/2 or 2 for X ≡ Cl; $n = 1$ or 2 for X ≡ Br, and $n = 1$ for X ≡ I) were prepared and characterized by melting point, elemental analysis, TG analysis, mass spectra and IR spectroscopy. From the enthalpies of dissolution in acetone, 10, 15, 20 or 25% aqueous ethanolamine, 10, 20 or 25% ethanolic ethanolamine, 10% diethanolamine in acetone, 10 or 20% ethanolic diethanolamine and 10 or 20% aqueous diethanolamine of the complexes, arsenic trihalides and ligands at 298.15 K, the standard enthalpies ($\Delta_r H^\ominus$) for the Lewis acid/base reactions were determined. From $\Delta_r H^\ominus$, the standard enthalpies of formation of arsenic trihalides and the standard enthalpies of formation of ligands, the standard enthalpies of formation of the complexes ($\Delta_f H^\ominus$) were calculated. The standard enthalpies of decomposition of the complexes ($\Delta_D H^\ominus$), as well as the lattice standard enthalpies ($\Delta_M H^\ominus$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\ominus_{(g)}$) were calculated by means of thermochemical cycles, and the standard enthalpies of arsenic–sulphur ($\bar{D}$(As–S)) and arsenic–oxygen ($\bar{D}$(As–O)) bonds were estimated. The mean energies of these bonds range from 89 to 150 kJ mol$^{-1}$ in the amide complexes, and from 89 to 225 kJ mol$^{-1}$ in the thioamide complexes.

The thermochemical data suggested the order $AsCl_3 > AsBr_3 > AsI_3$ for acidity and, in general, DMTF > TA = TMTU > DMA > A > DMTA > TU for basicity. Correlations between several thermochemical parameters and between thermochemical parameters and the type of donation atom, the degree of substitution of hydrogen atoms by methyl groups in the ligands, etc., were established.

## INTRODUCTION

In a recent article [1], we have described the synthesis, characterization and thermochemistry of arsenic trihalide complexes with heterocycle amines, in which the mean arsenic–nitrogen coordinate bond energies were de-

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* Author to whom correspondence should be addressed.

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termined. In this paper we describe the interaction of arsenic trihalides with amides and thioamides. The sulphur atom in the thioamides and the oxygen atom in the amides are the coordinating atoms of the ligands. The mean metal–sulphur coordinate bond energies in thiourea complexes of the first transition series range from 125 to 148 kJ mol$^{-1}$ [2]. They are noticeably weaker than the metal–oxygen coordinate bonds in comparable complexes [3]. However, there is no information in the literature concerning the strength of As–S and As–O coordinate bonds. It is also true that very few arsenic trihalide complexes have been synthesized until now [1]. In this paper, we report the calorimetric measurements made on a series of arsenic trihalide complexes in order to increase the thermochemical data for these complexes.

## EXPERIMENTAL

Owing to the moisture sensitivity and toxic nature of the compounds involved, all preparations were carried out in polyethylene glove bags under a dry nitrogen atmosphere.

### *Chemicals*

Arsenic trihalides were prepared as described in a previous paper [1]. DMA (Merck) and DMTA (Eastman) were purified by methods outlined in the literature. Solvents were purified by distillation. TMTU, TU, DMTF and A were all used without further purification.

### *Analysis*

Carbon and hydrogen were determined by microanalytical procedures. Halogen analysis was obtained by gravimetry using N/10 $AgNO_3$ solution [4], after dissolution of the complexes in water. Nitrogen was determined by Kjeldahl's method [5].

### *Synthesis of the complexes*

The complexes were prepared as described in a previous paper [1]. A typical procedure is given below.

#### *$AsCl_3$–DMTF*

To a solution of 2.0 ml of $AsCl_3$ (23.8 mmol) in 20 ml of benzene, 1.8 ml (23.9 mmol) of DMTF was slowly added, dropwise with stirring. The stirring was maintained for at least 3 h. After removal of the solvent, the white solid formed was washed with three 20-ml portions of petroleum ether and dried for several hours in a vacuum. The compound obtained was stored in a desiccator over calcium chloride

### *IR spectra*

IR spectra were obtained from sample mulls in Nujol sandwiched between NaCl plates for adducts. A liquid cell with NaCl windows was used for DMF. The far-IR spectra were recorded with sample mulls in Nujol sandwiched between polystyrene plates for the complexes and the free ligands.

### *TG studies*

These were made in a nitrogen atmosphere in a Du Pont 1090 TG analyser, with samples varying in weight from 5 to 10 mg and a heating rate of 10 K $\text{min}^{-1}$.

### *Calorimetric measurements*

All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described before [1].

### *Mass spectra*

The mass spectra of the compounds were recorded on a Finnigan 1015 S/L spectrometer.

## RESULTS AND DISCUSSION

All the arsenic trihalide complexes were prepared using a molar ratio of 1 : 1 for $AsX_3$ and ligand. The yields of the compounds obtained range from 60 to 80%. The melting points, colours and analytical data are summarized in Table 1.

### *IR data*

The major feature in the IR spectra of the compounds is the shifting by 5–50 $\text{cm}^{-1}$ of the CO or CS stretching frequencies of the free ligands towards lower frequencies following coordination [6–19]. The CN stretching frequencies also suffered a 2–95 $\text{cm}^{-1}$ shift towards higher frequencies upon coordination. This confirmed the coordination of the ligand to the arsenic atom through the oxygen atom in the case of the amides and through the sulphur atom in the case of the thioamides. The main IR bonds of the free ligands and complexes are presented in Table 2.

TABLE 1

Melting points, appearance and analytical data of the complexes

| Compound | MP [a,b] | Appearance [b] | C (%) |  | H (%) |  | N (%) |  | Halogen (%) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| $AsCl_3$·TMTU | 116–118 | Wh.Cr. | 19.16 | 18.92 | 3.86 | 3.65 | 8.94 | 8.75 | 33.93 | 33.72 |
| 2$AsCl_3$·3DMTA | 67– 68 | Wh.Cr. | 21.44 | 21.50 | 4.05 | 4.00 | 6.25 | 6.20 | 31.65 | 31.60 |
| $AsCl_3$·DMTF | 37– 38 | Wh.Cr. | 13.32 | 13.20 | 2.61 | 2.55 | 5.18 | 5.00 | 39.33 | 39.10 |
| $AsCl_3$·2TU | 127–128 | Wh.Cr. | 7.20 | 7.12 | 2.42 | 2.35 | 16.80 | 16.00 | 31.89 | 31.73 |
| $AsCl_3$·TA | 96– 98 | Wh.Cr | 9.37 | 9.35 | 1.97 | 1.90 | 5.46 | 5.40 | 41.48 | 41.20 |
| $AsCl_3$·DMA | n.o. | Wh.Cr. | 17.90 | 17.75 | 3.38 | 3.25 | 5.22 | 5.10 | 39.63 | 39.42 |
| $AsCl_3$·A | 126–128 | Wh.Cr | 10.00 | 9.80 | 2.10 | 1.96 | 5.83 | 5.75 | 44.25 | 44.09 |
| $AsBr_3$·TMTU | 51– 52 | Ye. | 13.44 | 13.40 | 2.71 | 2.70 | 6.27 | 6.00 | 53.64 | 53.20 |
| $AsBr_3$·DMTA | 102–103 | Ye. | 11.50 | 11.35 | 2.17 | 2.10 | 3.35 | 3.30 | 57.37 | 57.50 |
| $AsBr_3$·DMTF | 63– 64 | Ye. | 8.92 | 9.00 | 1.75 | 1.70 | 3.47 | 3.48 | 59.37 | 59.07 |
| $AsBr_3$·2TU | 142–145 | Ye. | 5.15 | 5.10 | 1.73 | 1.70 | 12.00 | 11.50 | 51.15 | 50.99 |
| $AsBr_3$·2TA | 85– 89 | Ye. | 10.33 | 10.10 | 2.17 | 2.00 | 6.03 | 5.94 | 51.56 | 51.30 |
| $AsBr_3$·DMA | 68– 70 | Ye. | 11.96 | 11.80 | 2.26 | 2.12 | 3.49 | 3.30 | 59.67 | 59.43 |
| $AsBr_3$·A | 115–117 | Ye. | 6.43 | 6.33 | 1.35 | 1.22 | 3.75 | 3.70 | 64.15 | 63.89 |
| $AsI_3$·TMTU | 66– 67 | Br. | 10.22 | 10.12 | 2.06 | 2.00 | 4.77 | 4.63 | 64.76 | 64.41 |
| $AsI_3$·DMTA | 62– 63 | Br. | 8.60 | 8.50 | 1.62 | 1.50 | 2.51 | 2.49 | 68.13 | 68.05 |
| $AsI_3$·DMTF | 59– 61 | Br. | 6.61 | 6.60 | 1.30 | 1.20 | 2.57 | 2.57 | 69.88 | 69.76 |
| $AsI_3$·TU | n.o. | Br. | 2.26 | 2.24 | 0.76 | 0.74 | 5.27 | 5.20 | 71.60 | 71.20 |
| $AsI_3$·TA | 71– 73 | Br. | 4.53 | 4.42 | 0.95 | 0.90 | 2.63 | 2.58 | 71.73 | 71.60 |
| $AsI_3$·DMA | 65– 70 | Br. | 8.85 | 8.78 | 1.67 | 1.60 | 2.58 | 2.45 | 70.14 | 70.20 |
| $AsI_3$·A | 68– 72 | Br. | 4.67 | 4.65 | 0.98 | 0.90 | 2.72 | 2.66 | 73.97 | 73.85 |

[a] °C uncorrected.

[b] Wh., White; Ye., yellow; Br., brown; Cr., crystals; n.o., not observed.

TABLE 2

Main IR absorption bands ($cm^{-1}$) of complexes and free ligands

| Compound | Assignment [a] | |
|---|---|---|
| | $\nu_{CN}$ [b] | $\nu_{CS}$ [b] or $\nu_{CO}$ [b] |
| TMTU | 1500 s | 1115 s |
| $AsCl_3 \cdot TMTU$ | 1595 s | 1105 m |
| $AsBr_3 \cdot TMTU$ | 1590 vs | 1100 s |
| $AsI_3 \cdot TMTU$ | 1582 s | 1101 m |
| DMTA | 1542 vs,b | 864 s |
| | | 655 s |
| $2AsCl_3 \cdot 3DMTA$ | 1585 s,b | 861 s |
| | | 651 s |
| $AsBr_3 \cdot DMTA$ | 1598 s,b | 840 m |
| | | 635 m |
| $AsI_3 \cdot DMTA$ | 1567 s | 842 sh |
| | | 643 s |
| DMTF | 1545 s,b | 968 s |
| $AsCl_3 \cdot DMTF$ | 1570 s | 918 s |
| $AsBr_3 \cdot DMTF$ | 1590 s | 900 s |
| $AsI_3 \cdot DMTF$ | 1590 vs | 910 s |
| TA | 1398 sh | 720 s |
| $AsCl_3 \cdot TA$ | 1398 sh | 708 s |
| $AsBr_3 \cdot 2TA$ | 1398 s | 708 s |
| $AsI_3 \cdot TA$ | 1390 w | 718 s |
| TU | 1465 s | 733 s |
| $AsCl_3 \cdot 2TU$ | 1465 vs | 726 s |
| $AsBr_3 \cdot 2TU$ | 1465 s | 728 s |
| $AsI_3 \cdot TU$ | 1463 vs | 723 m |
| DMA | 1495 m | 1650 vs |
| $AsCl_3 \cdot DMA$ | 1535 w | 1620 s,b |
| $AsBr_3 \cdot DMA$ | 1546 w | 1610 s,b |
| $AsI_3 \cdot DMA$ | 1538 w | 1590 s,b |
| A | 1598 s | 1680 vs |
| $AsCl_3A$ | n.o. | 1675 s |
| $AsBr_3 \cdot A$ | 1600 w | 1670 s |
| $AsI_3 \cdot A$ | 1650 sh | 1655 s,b |

[a] m, Medium; s, strong; b, broad; w, weak; sh, shoulder; vs, very strong; n.o, not observed.

[b] $\nu$ stretching.

Far-IR spectra of the $AsX_3 \cdot L$ compounds and the free ligands were recorded to obtain the structural information necessary to choose between two isomeric trigonal bipyramidal structures (TBP): one with the ligand in an axial position (I) and the second with the ligand in an equatorial position (II) in a TBP array around the arsenic atom, with the arsenic lone electron pair also in an equatorial position in both structures [20]. In the light of the

TABLE 3

Far-IR data for arsenic trihalide complexes ($cm^{-1}$)

| Modes [a] | $AsCl_3\cdot$ DMTF | $AsCl_3\cdot$ TA | $AsCl_3\cdot$ TMTU | $AsCl_3\cdot$ A | $AsCl_3\cdot$ DMA | $AsBr_3\cdot$ DMTF | $AsBr_3\cdot$ DMTA | $AsBr_3\cdot$ TMTU | $AsBr_3\cdot$ A | $AsBr_3\cdot$ DMA |
|---|---|---|---|---|---|---|---|---|---|---|
| $\nu_{(L)}$ |  | 468 s |  | 465 s | 470 s | 475 m | 470 s | 473 m | 480 m | 470 s |
| $\nu_{(L)}$ |  | 450 sh | 450 m |  |  |  |  | 450 m |  |  |
| $\nu_{(L)}$ | 398 m | 427 w | 388 s |  | 393 m | 405 m | 393 m | 383 m | 392 m |  |
|  |  | 415 w |  |  |  |  |  |  |  |  |
|  | 380 s | 375 m,b |  |  | 369 m |  |  |  |  |  |
| $\nu_{(L)}$ | 358 s | 350 s |  |  | 345 m | 340 m | 358 m |  |  | 368 m |
| $\nu_{(L)}$ |  |  |  | 355 w |  |  | 300 w | 320 m |  |  |
|  |  |  |  | 345 w |  |  |  | 298 w |  |  |
| $\nu_{(L)}$ |  |  |  |  |  |  | 280 m | 277 s |  |  |
| $\nu_{(As-X_{eq})}$ | 335 s | 335 m | 342 s |  |  | 248 s | 230 s | 240 s |  |  |
|  |  |  |  | 330 w |  |  |  |  |  |  |
| $\nu_{(L)}$ |  |  | 327 s |  | 325 m |  |  |  | 328 m | 328 m |
|  |  |  |  | 320 w | 318 m |  |  |  |  | 303 m |
| $\nu_{asym(X_{eq}-As-X_{eq})}$ |  |  |  | 310 w | 310 w |  |  |  | n.o. | n.o. |
| $\nu_{sym(X_{eq}-As-X_{eq})}$ |  |  |  | 292 w | 290 m |  |  |  | n.o. | n.o. |
|  |  |  |  |  |  |  |  |  |  | 289 w |
| $\nu_{(L)}$ | 292 s |  |  |  |  |  |  |  |  |  |
| $\nu_{(L)}$ | 285 s |  |  |  | 280 m |  |  |  |  |  |
|  | 270 m |  |  |  |  |  |  |  |  | 280 s |
|  | 260 w |  |  |  |  |  |  |  |  |  |
| $\nu_{(L)}$ |  |  |  | 260 m |  |  |  |  | 260 m | 270 w |
| $\nu_{asym(X_{ax}-As-X_{ax})}$ | 248 m | 250 m | 245 s |  |  | n.o. | n.o. | n.o. |  |  |
| $\nu_{sym(X_{ax}-As-X_{ax})}$ | 228 m | 230 s | 233 w |  |  | n.o. | n.o. | n.o. |  |  |
| $\nu_{(As-X_{ax})}$ |  |  |  | 220 s | 222 m |  |  |  | n.o. | n.o. |
| $\nu_{(L)}$ | 210 m |  |  |  |  | 228 s |  | 230 s |  | 230 s |
| $\nu_{(L)}$ |  |  |  |  |  | 210 s | 212 s | 210 m |  |  |

[a] $\nu$ stretching; L, ligand; X, halide; eq, equatorial, ax, axial.

[b] vs, Very strong; s, strong; m, medium; w, weak; b, broad; n.o., not observed; sh, shoulder.

observed As–X frequency modes obtained comparing the far-IR spectra of complexes and free ligands, and the expected As–X frequency modes [21], we propose the structure I for the amide complexes and structure II for the thioamide complexes. Thus, two high frequency modes (primarily equatorial) are expected for structure I together with an additional mode (primarily axial) whose frequency depends on the donor strength of the *trans*-base, according to our observations. For structure II, one high and two low frequency modes are expected, as we have observed. For the $AsBr_3$ complexes, these frequency modes are expected to be lower than for the $AsCl_3$ complexes. The far-IR spectral data of the complexes is presented in Table 3.

## *TG data*

The TG data of the complexes are similar. Nearly all of them involve the ligand together with arsenic trihalide in a single step. The exceptions are as follows: $AsCl_3 \cdot 1.5DMTA$ showed a two-step mass loss, the first with elimination of the arsenic trichloride and the second with elimination of the ligand; $AsCl_3 \cdot DMTF$ showed a three-step mass loss; $AsCl_3 \cdot TA$ also lost mass in three steps, the first with elimination of 1/7 mol of $AsCl_3$, the second with elimination of 4/7 mol of $AsCl_3$ and the third with elimination of the rest of the $AsCl_3$ and the TA; $AsBr_3 \cdot 2TU$ lost mass in three steps, the first with elimination of $AsBr_3$, the second with elimination of 1 mol of TU and the third with elimination of 1 mol of TU; $AsBr_3 \cdot 2TA$ lost mass in three steps, the first with elimination of 1/5 mol of $AsBr_3$, the second with elimination of 2/5 mol of TA and 2/5 mol of $AsBr_3$, and the third with elimination of 2/5 mol of $AsBr_3$ and 8/5 mol TA; $AsBr_3 \cdot A$ lost mass in two steps, the first with elimination of 1 mol of $AsBr_3$ and the second with elimination of 1 mol of A; $AsI_3 \cdot TU$ lost mass in two steps, the first with elimination of $AsI_3$ and the second with elimination of TU. Table 4 lists the thermoanalytical data of the complexes.

## *Mass spectra*

The mass spectra of the complexes did not show the parent ion and resembled the spectra of free ligands [22–34] plus the pure trihalide. The mass fragmentation of ligands as well as the sample temperature are listed below.

A, 110 °C: *m/e* 42, $CH_2CO$ or $NC_2H_4$; 43, $CH_3CO$ or $NC_2H_5$; 44, $CH_3COH$ or $N(CH_3)_2$ or $NH_2CO$; 45, $HN(CH_3)_2$; 58, $CH_3CONH$ or $CH_2CONH_2$; 59, $CH_3CONH_2$.

DMA, 110C: *m/e* 42, $CH_2CO$ or $NC_2H_4$; 43, $CH_3CO$ or $NC_2H_5$; 44, $CH_3COH$ or $N(CH_3)_2$ or $NH_2CO$; 45, $HN(CH_3)_2$; 57, $CH_3NCO$ or $CH_3COCH_2$ or $CH_2COH$; 58, $CH_3COCH_3$ or $CH_3CONH$ or $CH_2COH_2$; 72, $(CH_3)_2NCO$ or $(C_2H_5)_2N$; 87, $(CH_3)_2NCOCH_3$.

TABLE 4

Thermoanalytical data of the compounds $AsX_3\cdot nL$

| Compound | Weight loss (%) | | Temperature range (K) | Attribution |
|---|---|---|---|---|
| | Calc. | Obs. | | |
| $AsCl_3\cdot TMTU$ | 100.0 | 99.0 | 338– 748 | $-AsCl_3$, $-TMTU$ |
| $2AsCl_3\cdot 3DMTA$ | 53.9 | 54.0 | 313– 398 | $-2AsCl_3$ |
| | 46.1 | 44.0 | 398– 948 | $-3DMTA$ |
| $AsCl_3\cdot DMTF$ | | 10.0 | 311– 378 | ? |
| | | 40.0 | 378– 513 | ? |
| | | 45.0 | 513–1048 | ? |
| $AsCl_3\cdot 2TU$ | 100.0 | 97.5 | 348– 748 | $-AsCl_3$, $-2TU$ |
| $AsCl_3\cdot TA$ | 9.9 | 10.0 | 343– 403 | $-1/7AsCl_3$ |
| | 40.4 | 40.0 | 403– 528 | $-4/7AsCl_3$ |
| | 49.7 | 50.0 | 528– 993 | $-2/7AsCl_3$, $-TA$ |
| $AsCl_3\cdot DMA$ | 100.0 | 100.0 | 303– 793 | $-AsCl_3$, $-DMA$ |
| $AsCl_3\cdot A$ | 100.0 | 100.0 | 333– 528 | $-AsCl_3$, $-A$ |
| $AsBr_3\cdot TMTU$ | 100.0 | 99.0 | 333– 548 | $-AsBr_3$, $-TMTU$ |
| $AsBr_3\cdot DMTA$ | 100.0 | 98.0 | 328– 898 | $-AsBr_3$, $-DMTA$ |
| $AsBr_3\cdot DMTF$ | 100.0 | 99.0 | 333– 713 | $-AsBr_3$, $-DMTF$ |
| $AsBr_3\cdot 2TU$ | 66.8 | 64.0 | 418– 643 | $-AsBr_3$ |
| | 16.6 | 18.0 | 643– 703 | $-TU$ |
| | 16.6 | 13.0 | 703– 893 | $-TU$ |
| $AsBr_3\cdot 2TA$ | 13.5 | 13.5 | 348– 428 | $-1/5AsBr_3$ |
| | 39.9 | 39.5 | 428– 558 | $-2/5AsBr_3$, $-2/5TA$ |
| | 46.6 | 46.0 | 558– 993 | $-2/5AsBr_3$, $-8/5TA$ |
| $AsBr_3\cdot A$ | 84.2 | 83.0 | 323– 463 | $-AsBr_3$ |
| | 15.8 | 14.0 | 463– 753 | $-A$ |
| $AsI_3\cdot TMTU$ | 100.0 | 100.0 | 543– 648 | $-AsI_3$, $-TMTU$ |
| $AsI_3\cdot DMTA$ | 100.0 | 100.0 | 368– 993 | $-AsI_3$, $-DMTA$ |
| $AsI_3\cdot DMTF$ | 100.0 | 99.0 | 373– 648 | $-AsI_3$, $-DMTF$ |
| $AsI_3\cdot TU$ | 85.7 | 86.0 | 348– 548 | $-AsI_3$ |
| | 14.3 | 13.5 | 548– 863 | $-TU$ |
| $AsI_3\cdot TA$ | 100.0 | 99.0 | 363– 948 | $-AsI_3$, $-TA$ |
| $AsI_3\cdot DMA$ | 100.0 | 99.0 | 349– 596 | $-AsI_3$, $-DMA$ |
| $AsI_3\cdot A$ | 100.0 | 98.5 | 358– 493 | $-AsI_3$, $-A$ |

TMTU, 110 °C: *m/e* 42, $C_2H_4N$; 43, $NC_2H_5$; 44, CS or $HNC_2H_5$ or $N(CH_3)_2$; 58, SCN; 59, SCNH; 60, $SCNH_2$; 73, $CH_3CSN$; 74, $CH_3CSNH$ or $CH_3CSCH_3$; 88, $CSN(CH_3)_2$; 89, $HCSN(CH_3)_2$; 103, $CH_3CSN(CH_3)_2$; 132, $(CH_3)_2NCSN(CH_3)_2$.

DMTA, 110 °C: *m/e* 42, HNCN; 43, NHCNH or $NH_2CN$; 44, $H_2NCNH$ or CS or $N(CH_3)_2$ or $HNC_2H_5$; 56, $CS_2$; 58, SCN; 60, $SCNH_2$; 71, $CH_3CN(CH_3)_2$; 89, $HCSN(CH_3)_2$; 103, parent ion plus 1; 104, parent ion plus 2; 105, parent ion plus 3.

DMTF, 110 °C: *m/e* 42, HNCN; 43, NHCNH or $NH_2CN$; 44, $C_2H_5NH$; 45, $HN(CH_3)_2$; 73, $SCNCH_3$; 74, $HSCNCH_3$; 88, $SCN(CH_3)_2$; 89, parent ion.

TA, 110 °C: *m/e* 38, CCN; 42, HNCN; 43, NHCNH; 44, $H_2NCNH$; 58, SCN; 59, HSCN; 60, $SCNH_2$; 74, $CH_3CSNH$; 75, parent ion.

TU, 110 °C: *m/e* 42, HNCN; 43, $NH_2CN$ or NHCNH; 44, $C_2H_5NH$; 58, SCN; 60, $SCNH_2$; 76, parent ion; 77, parent ion plus 1; 78, parent ion plus 2.

In addition to the peaks above, $AsX_3$ complexes yielded the following peaks:

$AsCl_3 \cdot$ DMA, 110 °C: *m/e* 145, $AsCl_2$; 180, $AsCl_3$.

$AsCl_3 \cdot$ TMTU, 110 °C: *m/e* 145, $AsCl_2$; 180, $AsCl_3$.

$AsCl_3 \cdot$ DMTF, 110 °C: *m/e* 144, $AsClH_2S$; 181, $AsCl_3H$.

$2AsCl_3 \cdot$ 3DMTA, 110 °C: *m/e* 145, $AsCl_2$; 181, $AsCl_3H$.

$AsBr_3 \cdot$ DMA, 110 °C: *m/e* 235, $AsBr_2H_2$; 316, $AsBr_3H_2$.

$AsBr_3 \cdot$ 2TA, 110 °C: *m/e* 82, $BrH_3$.

$AsBr_3 \cdot$ TMTU, 110 °C: *m/e* 236, $AsBr_2H_3$; 314, $AsBr_3H_2$.

$AsBr_3 \cdot$ DMTF, 110 °C: *m/e* 234, $AsBr_2H$; 314, $AsBr_3H_2$.

$AsBr_3 \cdot$ DMTA, 110 °C: *m/e* 135, $AsSCNH_2$; 235, $AsBr_2H_2$; 314, $AsBr_3H_2$.

$AsI_3 \cdot$ A, 110 °C: *m/e* 127, I; 202, AsI; 254, $I_2$; 456, $AsI_3$.

$AsI_3 \cdot$ DMA, 110 °C: *m/e* 128, HI; 254, $I_2$; 456, $AsI_3$.

$AsI_3 \cdot$ TA, 110 °C: *m/e* 127, I; 202, AsI; 254, $I_2$; 329, $AsI_2$; 456, $AsI_3$.

$AsI_3 \cdot$ TMTU, 110 °C: *m/e* 202, AsI; 332, $AsI_2H_3$.

$AsI_3 \cdot$ TU, 110 °C: *m/e* 127, I; 202, AsI; 254, $I_2$; 331, $AsI_2H_2$; 456, $AsI_3$.

$AsI_3 \cdot$ DMTF, 110 °C: *m/e* 127, I; 202, AsI; 254, $I_2$; 329, $AsI_2$; 456, $AsI_3$.

$AsI_3 \cdot$ DMTA, 110 °C: *m/e* 127, I; 202, AsI; 254, $I_2$, 329, $AsI_2$; 456, $AsI_3$.

### *Calorimetric measurements*

The standard enthalpies of dissolution of arsenic trihalides, ligands and complexes ($\Delta_i H^{\ominus}$) were obtained as previously reported [1]. Table 5 gives these standard thermochemical values. Uncertainty intervals given in this table are twice the standard deviations of the means of about five replicate measurements on each compound. Combined errors were calculated from the square root of the sum of the squares of the component errors. From the standard enthalpies of dissolution, the standard enthalpies of the acid/base reaction ($\Delta_r H^{\ominus}$) can be determined [1]

$$\Delta_r H^{\ominus} = \Delta Dd1 H^{\ominus} + \Delta_2 H^{\ominus} - \Delta_3 H^{\ominus}$$

or

$$\Delta_r H^{\ominus} = \Delta_4 H^{\ominus} + \Delta_5 H^{\ominus} - \Delta_6 H^{\ominus}$$

Using appropriate thermochemical cycles and applying Hess's Law, the standard enthalpies of the following reactions were obtained

$$\mathrm{AsX_3 \cdot \mathit{n}L_{(s)} = AsX_3(g) + \mathit{n}L(g)};\ \Delta_D H^{\ominus} \tag{1}$$

$$\mathrm{AsX_3(g) + \mathit{n}L(g) = AsX_3 \cdot \mathit{n}L(s)};\ \Delta_M H^{\ominus} \tag{2}$$

$$\mathrm{AsX_3 \cdot \mathit{n}L(g) = AsX_3(g) + \mathit{n}L(g)};\ \Delta_r H^{\ominus}(\mathrm{g}) \tag{3}$$

The $\Delta_r H^{\ominus}(\mathrm{g})$ values obtained according to eqn. (3) can be used to calculate the standard enthalpy of the arsenic–sulphur [$\bar{D}$(As–S)] or arsenic–oxygen [$\bar{D}$(As–O)] bond (being equal to $-\Delta_r H^{\ominus}(\mathrm{g})/n$). Table 6 lists the values for all these parameters. For the determination of $\Delta_r H^{\ominus}(\mathrm{g})$, it was necessary to assume that the molar standard enthalpy of sublimation of each complex ($\Delta_s^g H^{\ominus}$) was equal to the enthalpy of vaporization or sublimation of 1 mol of ligand [1].

The melting points, TG studies and mass spectra of the complexes showed that they decompose on heating and were not found in the gaseous phase. However, the correlation of $\Delta_M H^{\ominus}$ with $\bar{D}$ calculated according to four hypotheses [44]: $\Delta_s^g H^{\ominus}(\text{complex}) = \Delta_s^g H^{\ominus}(\text{ligand})$; $\Delta_s^g H^{\ominus}(\text{complex}) = \Delta_s^g H^{\ominus}(\mathrm{AsX_3})$; $\Delta_s^g H^{\ominus}(\text{complex}) = [n\Delta_s^g H^{\ominus}(\text{ligand}) + \Delta_s^g H^{\ominus}(\mathrm{AsX_3})]/(n+1)$; and $\Delta_s^g H^{\ominus}(\text{complex}) = \{[\Delta_s^g H^{\ominus}(\text{ligand})]^n \times [\Delta_s^g H^{\ominus}(\mathrm{AsX_3})]\}^{(1/n+1)}$, demonstrated that our assumption was the more consistent. Because $\bar{D} = \frac{1}{n}[\Delta_M H^{\ominus}(\text{complex})] - [\Delta_s^g H^{\ominus}(\text{complex})/n]$; the correlation of $\bar{D}$ with $\Delta_M H^{\ominus}$ must be a straight line. For complexes of the same type of donor atom, the first hypothesis showed the best correlation coefficient with a value of 0.9937 for thioamide complexes.

For calculation of the standard enthalpy of formation of the complexes, it was necessary to calculate the standard enthalpies of formation and vaporization or sublimation of the ligands DMTF and DMTA. Both decompose on heating and therefore these enthalpy values are not cited in the literature. We calculated them by a group contribution method [35–38], using a stabilization energy of 41 kJ $\mathrm{mol^{-1}}$ [35].

For a series of complexes with the same stoichiometry and the same ligand, if we relate the $\Delta_r H^{\ominus}$ values, the acidity order $\mathrm{AsCl_3 > AsBr_3 > AsI_3}$ is obtained as expected on the basis of an inductive effect. If the trihalide is fixed and the ligand changed, we obtain the basicity order DMTF > TA > DMA > TMTU > A (for $\mathrm{AsCl_3}$); A > DMA > DMTF > TMTU > DMTA (for $\mathrm{AsBr_3}$ mono-complexes); TA > TU (for $\mathrm{AsBr_3}$ bis-complexes) and DMTF > TA = TMTU > DMA > A > DMTA > TU (for $\mathrm{AsI_3}$ complexes). This means that DMTF is a better base for $\mathrm{AsCl_3}$ and $\mathrm{AsI_3}$, but that A is the better base for $\mathrm{AsBr_3}$. The expected sequence on the basis of an inductive effect would be that in which the amides are better than the thioamides. Among the amides or thioamides, those with greater substitution of hydrogen atoms by methyl groups would be the better bases.

Considering $\bar{D}$ values of the complexes of the same stoichiometry and the

TABLE 5

Enthalpies of dissolution at 298.15 K

| Compound | Calorimetric solvent [a] | Number of experiments | $\Delta_i H^{\ominus}$ (kJ mol$^{-1}$) |
|---|---|---|---|
| AsCl$_3$(l) | 25 % aq. EA | 5 | $(i=1)-250.47\pm0.46$ |
| TMTU(s) | 1:1 AsCl$_3$–25% EA | 5 | $(i=2)\ \ 14.30\pm0.21$ |
| AsCl$_3$·TMTU(s) | 25% aq. EA | 5 | $(i=3)-189.01\pm0.04$ |
| 3DMTA(s) | 25% eth. EA | 5 | $(i=4)\ \ 40.65\pm0.25$ |
| AsCl$_3$(l) | 2:3 DMTA–25% eth. EA | 5 | $(i=5)-288.69\pm0.16$ |
| 2AsCl$_3$·3DMTA(s) | 25% eth. EA | 5 | $(i=6)-197.56\pm0.01$ |
| AsCl$_3$(l) | 10% DEA in acet. | 5 | $(i=1)-268.65\pm0.25$ |
| DMTF(l) | 1:1 AsCl$_3$–10% DEA in acet. | 5 | $(i=2)\ \ 17.46\pm0.14$ |
| AsCl$_3$·DMTF(s) | 10% DEA in acet. | 5 | $(i=3)\ \ 95.11\pm0.60$ |
| 2TU(s) | 25% eth. EA | 5 | $(i=4)\ \ 14.12\pm0.08$ |
| AsCl$_3$(l) | 1:2 TU–25% eth. EA | 5 | $(i=5)-285.43\pm0.60$ |
| AsCl$_3$·2TU(s) | 25% eth. EA | 5 | $(i=6)-223.80\pm0.36$ |
| AsCl$_3$(l) | 10% aq. EA | 5 | $(i=1)-267.58\pm0.21$ |
| TA(s) | 1:1 AsCl$_3$–10% aq. EA | 5 | $(i=2)\ \ 13.81\pm0.02$ |
| AsCl$_3$·TA | 10% aq. EA | 5 | $(i=3)\ \ -71.79\pm0.25$ |
| DMA(l) | acet. | 5 | $(i=4)\ \ 6.81\pm0.06$ |
| AsCl$_3$(l) | 1:1 DMA–acet. | 5 | $(i=5)\ \ -32.72\pm0.07$ |
| AsCl$_3$·DMA | acet. | 5 | $(i=6)\ \ 75.06\pm0.21$ |
| A(s) | EtOH | 5 | $(i=4)\ \ 14.95\pm0.01$ |
| AsCl$_3$(l) | 1:1 A–EtOH | 5 | $(i=5)\ \ -76.23\pm0.08$ |
| AsCl$_3$·A(s) | EtOH | 5 | $(i=6)\ \ -15.56\pm0.04$ |
| TMTU(s) | 20% eth. DEA | 5 | $(i=4)\ \ 25.87\pm0.05$ |
| AsBr$_3$(s) | 1:1 TMTU–20% eth. DEA | 5 | $(i=5)-253.08\pm0.23$ |
| AsBr$_3$·TMTU(s) | 20% eth. DEA | 5 | $(i=6)-190.45\pm0.23$ |
| AsBr$_3$(s) | 25% eth. EA | 5 | $(i=1)-329.44\pm0.24$ |
| DMTA(s) | 1:1 AsBr$_3$–25% eth. EA | 5 | $(i=2)\ \ 24.22\pm0.04$ |
| AsBr$_3$·DMTA | 25% eth. EA | 5 | $(i=3)-283.11\pm0.23$ |
| DMTF(l) | 25% aq. EA | 5 | $(i=4)\ \ 8.51\pm0.02$ |
| AsBr$_3$(s) | 1:1 DMTF–25% aq. EA | 5 | $(i=5)-272.80\pm0.15$ |
| AsBr$_3$·DMTF(s) | 25% aq. EA | 5 | $(i=6)-187.50\pm0.18$ |
| 2TU(s) | 10% eth. EA | 5 | $(i=4)\ \ 12.51\pm0.07$ |
| AsBr$_3$(s) | 1:2 TU–10% eth. EA | 5 | $(i=5)-294.77\pm0.25$ |
| AsBr$_3$·2TU(s) | 10% Ea | 5 | $(i=6)-268.49\pm0.42$ |
| 2TA(s) | 10% aq. EA | 5 | $(i=4)\ \ 38.00\pm0.09$ |
| AsBr$_3$(s) | 1:2TA–10% aq. EA | 5 | $(i=5)-276.02\pm0.50$ |
| AsBr$_3$·2TA | 10% aq. EA | 5 | $(i=6)\ \ -81.57\pm0.19$ |
| DMA(l) | acet. | 5 | $(i=4)\ \ 6.91\pm0.00$ |
| AsBr$_3$(s) | 1:1 DMA–acet. | 5 | $(i=5)\ \ -26.81\pm0.05$ |
| AsBr$_3$·DMA | acet. | 5 | $(i=6)\ \ 62.88\pm0.09$ |
| A(s) | 15% aq. EA | 5 | $(i=4)\ \ 16.86\pm0.02$ |
| AsBr$_3$(s) | 1:1 A–15% aq. EA | 5 | $(i=5)-259.00\pm0.02$ |
| AsBr$_3$·A(s) | 15% aq. EA | 5 | $(i=6)-133.84\pm0.08$ |
| AsI$_3$(s) | 10% aq. EA | 5 | $(i=1)-230.27\pm0.30$ |
| TMTU(s) | 1:1 AsI$_3$–10% aq. EA | 5 | $(i=2)\ \ 11.98\pm0.05$ |
| AsI$_3$·TMTU(s) | 10% aq. EA | 5 | $(i=3)-183.74\pm0.23$ |
| AsI$_3$(s) | 20% aq. DEA | 5 | $(i=1)-159.13\pm0.43$ |
| DMTA(s) | 1:1 AsI$_3$–20% aq. DEA | 5 | $(i=2)\ \ 20.43\pm0.38$ |

TABLE 5 (continued)

| Compound | Calorimetric solvent [a] | Number of experiments | $\Delta_i H^\ominus$ (kJ mol$^{-1}$) |
|---|---|---|---|
| $AsI_3 \cdot DMTA(s)$ | 20% aq. DEA | 5 | $(i=3)\ -113.60 \pm 0.02$ |
| $AsI_3(s)$ | 20% aq. EA | 5 | $(i=1)\ -157.97 \pm 0.38$ |
| DMTF(l) | 1:1 $AsI_3$–20% aq. EA | 5 | $(i=2)\ 7.98 \pm 0.00$ |
| $AsI_3 \cdot DMTF(s)$ | 20% aq. EA | 5 | $(i=3)\ -93.69 \pm 0.25$ |
| TU(s) | 10% aq. DEA | 5 | $(i=4)\ 22.27 \pm 0.10$ |
| $AsI_3(s)$ | 1:1 TU–10% aq. DEA | 5 | $(i=5)\ -175.58 \pm 0.25$ |
| $AsI_3 \cdot TU(s)$ | 10% aq. DEA | 5 | $(i=6)\ -135.80 \pm 0.17$ |
| TA(s) | 20% eth. EA | 5 | $(i=4)\ 14.13 \pm 0.08$ |
| $AsI_3(s)$ | 1:1 TA–20% eth. EA | 5 | $(i=5)\ -273.68 \pm 0.36$ |
| $AsI_3 \cdot TA(s)$ | 20% eth. EA | 5 | $(i=6)\ -225.05 \pm 0.32$ |
| $AsI_3(s)$ | 10% aq. DEA | 5 | $(i=1)\ -138.45 \pm 0.06$ |
| DMA(l) | 1:1 $AsI_3$–10% aq. DEA | 5 | $(i=2)\ 23.20 \pm 0.11$ |
| $AsI_3 \cdot DMA(s)$ | 10% aq. DEA | 5 | $(i=3)\ -83.08 \pm 0.83$ |
| A(s) | 10% aq. EA | 5 | $(i=4)\ 25.87 \pm 0.08$ |
| $AsI_3(s)$ | 1:1 A–10% aq. EA | 5 | $(i=5)\ -170.34 \pm 0.30$ |
| $AsI_3 \cdot A(s)$ | 10% aq. EA | 5 | $(i=6)\ -118.13 \pm 0.19$ |

[a] EA, Ethanolamine; DEA, diethanolamine; eth., ethanolic; aq., aqueous; acet., acetone.

same trihalide, we obtain the order TA > DMTF > DMA > TMTU > A (for $AsCl_3$); A > DMA > DMTF > TMTU > DMTA (for $AsBr_3$ mono-complexes); TA > TU (for $AsBr_3$ bis-complexes) and DMTF > TA = TMTU > DMA > A > DMTA > TU (for $AsI_3$). Fixing the ligand we obtain $AsCl_3 > AsI_3 > AsBr_3$ or $AsI_3 > AsBr_3 > AsCl_3$ (for thioamides) and $AsBr_3 > AsI_3 > AsCl_3$ or $AsBr_3 > AsCl_3 > AsI_3$ (for amides). The donicity order obtained on the basis of $\bar{D}$ values DMA > A, is the same as is found in the literature [45]. Only in the $AsBr_3$ complexes is the order inverted. This means that for $AsBr_3$, the ligand A is a better base than DMA.

According to hard/soft acid/base (HSAB) [46–48], we expect the amides to be hard and the thioamides to be soft. Substitution of hydrogen atoms by methyl groups will lead to a relative softness of the amide or thioamide with respect to the non-substituted amide or thioamide. The expected hardness order in the trihalides is $AsI_3 < AsBr_3 < AsCl_3$. Considering the order of $\bar{D}$ values mentioned above, we see that in the thioamide complexes the expected hardness order is not observed except in TMTU and DMTA complexes. In most complexes there are inversions between members of the series. Thus, $AsI_3$ does not form the strongest bond with all the thioamides. The same is true for the amide complexes. They do not form the strongest bond with $AsCl_3$. It seems that the type of bonding formed between the donor and the acceptor atoms, is important in determining the relative strength of the interaction [49].

Correlation of the $\bar{D}$ values with the number of methyl groups substituting hydrogen atoms in the amide or thioamide, showed in general a

TABLE 6

Summary of the thermochemical results (kJ mol$^{-1}$)

| Compound | $\Delta_r H^\ominus$ | $\Delta_f H^\ominus$ | $\Delta_s^g H^\ominus$ or $\Delta_l^g H^\ominus$ | $\Delta_M H^\ominus$ | $\Delta_D H^\ominus$ | $\Delta_r H^\ominus$(g) | $\overline{D}$(As–S) or $\overline{D}$(As–O) |
|---|---|---|---|---|---|---|---|
| $AsCl_3$(l) | | −305.0 [a] | 43.5 [a] | | | | |
| $AsBr_3$(s) | | −197.5 [a] | 67.5 [a] | | | | |
| $AsI_3$(s) | | −58.2 [a] | 95.0 [a] | | | | |
| TMTU(s) | | −38.3 ± 2.3 [b] | 83.26 ± 0.2 [b] | | | | |
| DMTA(s) | | −66.6 [c,d,e,f] | 78.62 [c,d,e,f] | | | | |
| DMTF(l) | | −16.0 [c,d,e,f] | 76.1 [c,d,e,f] | | | | |
| TU(s) | | −89.15 ± 0.5 [g,h] | 112.0 ± 1.5 [g,h] | | | | |
| TA(s) | | −70.6 ± 1.1 [c,f] | 83.26 ± 0.34 [c,f] | | | | |
| DMA(l) | | −278.32 ± 1.5 [i] | 50.0 ± 0.2 [j] | | | | |
| A(s) | | −317.0 ± 0.7 [b] | 78.7 ± 0.8 [b] | | | | |
| $AsCl_3 \cdot$ TMTU | −47.16 ± 0.51 | −390.3 | | −173.7 | 130.4 | 90.7 | 90.7 |
| $2AsCl_3 \cdot$ 3DMTA | −50.48 ± 0.30 | −455.4 | | −211.9 | 168.4 | 133.3 | 89.2 |
| $AsCl_3$DMTF | −156.08 ± 0.67 | −477.1 | | −275.7 | 232.2 | 199.6 | 199.6 |
| $AsCl_3 \cdot$ 2TU | −47.51 ± 0.70 | −530.8 | | −315.0 | 271.5 | 203.0 | 115.9 |
| $AsCl_3 \cdot$ TA | −181.98 ± 0.33 | −557.6 | | −308.7 | 265.2 | 225.5 | 225.4 |
| $AsCl_3 \cdot$ DMA | −100.98 ± 0.23 | −684.3 | | −194.6 | 151.0 | 144.5 | 144.5 |
| $AsCl_3 \cdot$ A | −45.72 ± 0.04 | −667.7 | | −167.9 | 124.4 | 89.2 | 89.2 |
| $AsBr_3 \cdot$ TMTU | −36.76 ± 0.32 | −272.6 | | −187.3 | 120.0 | 104.3 | 104.3 |
| $AsBr_3 \cdot$ DMTA | −22.11 ± 0.33 | −286.2 | | −168.2 | 100.7 | 89.6 | 89.6 |
| $AsBr_3 \cdot$ DMTF | −76.79 ± 0.24 | −290.3 | | −220.4 | 152.9 | 144.3 | 144.3 |
| $AsBr_3 \cdot$ 2TU | −13.77 ± 0.45 | −389.6 | | −305.3 | 237.8 | 193.3 | 96.7 |
| $AsBr_3 \cdot$ 2TA | −156.45 ± 0.30 | −495.2 | | −390.5 | 323.0 | 307.2 | 154.7 |
| $AsBr_3 \cdot$ DMA | −82.78 ± 0.10 | −558.6 | | −200.4 | 132.8 | 150.3 | 150.3 |
| $AsBr_3 \cdot$ A | −109.00 ± 0.09 | −623.5 | | −255.2 | 187.7 | 176.5 | 176.5 |
| $AsI_3 \cdot$ TMTU | −34.55 ± 0.38 | −131.1 | | −212.6 | 117.8 | 129.6 | 129.6 |
| $AsI_3 \cdot$ DMTA | −25.10 ± 0.57 | −150.0 | | −198.7 | 103.7 | 120.1 | 120.1 |
| $AsI_3 \cdot$ DMTF | −56.30 ± 0.46 | −130.5 | | −227.4 | 132.4 | 151.3 | 151.3 |
| $AsI_3 \cdot$ TU | −17.51 ± 0.32 | −164.8 | | −224.5 | 129.5 | 112.5 | 112.5 |
| $AsI_3 \cdot$ TA | −34.50 ± 0.49 | −163.3 | | −212.8 | 117.8 | 129.5 | 129.5 |
| $AsI_3 \cdot$ DMA | −32.17 ± 0.84 | −368.7 | | −177.3 | 82.2 | 127.2 | 127.2 |
| $AsI_3 \cdot$ A | −26.34 ± 0.36 | −401.5 | | −200.0 | 105.0 | 121.3 | 121.3 |

[a] Ref. 1. [b] Ref. 35. [c] Ref. 36. [d] Ref. 37. [e] Ref. 38. [f] Ref. 39. [g] Ref. 40. [h] Ref. 41. [i] Ref. 42. [j] Ref. 43.

diminution in the intensity of the interaction between donor and acceptor atoms with an increase in the number of methyl groups. This is contrary to the behaviour expected on the basis of HSAB and also contrary to what is expected on the basis of an inductive effect. Correlation of $\bar{D}$ values with the type of donor atom for complexes of the same stoichiometry and the same trihalide and ligands in which the only change is the donor atom, shows, in general, a decrease in the induction from the oxygen to the sulphur atom. This is the opposite of what is expected on the bases of HSAB and also contrary to the decrease in the electronegativity value of the sulphur atom with respect to the oxygen atom. Correlation of $\Delta_f H^\ominus$ (complexes) values with $\Delta_f H^\ominus$ (ligand) values in their reference states gives a straight line for the complexes of the same stoichiometry. A correlation coefficient of 0.9653 is obtained for the thioamide complexes. This same behaviour was found by Dias et al. for a series of complexes [50]. This result confirms our estimate of $\Delta_f H^\ominus$ for DMTA and DMTF.

The mean arsenic–oxygen coordinate bond dissociation energies for $AsCl_3$ and $AsI_3$ amide complexes are weaker than the As–S bonds in comparable thioamide complexes, although they are stronger in the $AsBr_3$ complexes.

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