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Trimethylamine Complexes of some Group VB Trihalides

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The white mono-adducts $AsBr_3 \cdot NMe_3$, $SbX_3 \cdot NMe_3$ (X = Cl, Br) and the pale yellow bis-adducts $SbX_3 \cdot 2NMe_3$ (X = Cl, Br) have been prepared. Characterisation follows from analytical and IR and NMR (^1H and ^{13}C) spectral data. Possible structures and their stereochemical implications are considered.

Introduction

The Group V trihalides react with a variety of donors to form complexes of which the majority assume a stereoactive lone pair [1]. With trimethylamine an early report [2] of the reactions with arsenic(III) and antimony(III) chlorides describes the white non-stoichiometric complexes $AsCl_3 \cdot 0.82 NMe_3$ and $SbCl_3 \cdot 1.10NMe_3$. Subsequent interest in the Group V trihalides–NMe_3 system indicates that the former is in fact the 1:1 complex with a pseudo-trigonal bipyramidal structure in which the ligand and lone pair occupy axial and equatorial positions respectively [3]. There is no further mention of the latter. In the case of phosphorus(III) halide complexes, thermally unstable under normal conditions [4, 5], low temperature ir and Raman studies of matrix isolated $PCl_3 \cdot NMe_3$ and $PBr_3 \cdot NMe_3$ support a similar AX_3LE structure. Formation of a second complex $PCl_3 \cdot 2NMe_3$ based on a *cis* pseudo-octahedral geometry is also suggested [6].

As part of a continuing interest in the donor–reducer properties of trimethylamine [7] we have studied its reactions with arsenic(III) and antimony(III) halides and herein report the 1:1 complexes $MX_3 \cdot NMe_3$ (M = As, Sb; X = Cl, Br) and the 1:2 complexes $SbX_3 \cdot 2NMe_3$ (X = Cl, Br).

Experimental

All preparations were carried out in a gloved box flushed with dry nitrogen. $AsCl_3$ (Hopkins and Williams) and $AsBr_3$ (Pfaltz and Bauer) were redistilled under reduced pressure prior to use. $SbCl_3$(BDH) and $SbBr_3$(BDH) were recrystallised from benzene solutions. Solvents were dried over CaH_2/P_2O_5 and distilled under nitrogen. NMe_3(BDH), dried over P_2O_5 at 196K, was distilled in an all-glass vacuum line system as required. Ir spectra were recorded on Perkin Elmer 621 and Fourier FS720 instruments with samples as nujol and HCB mulls held between CsI plates. Nmr spectra (^1H, 90 mHz; ^{13}C, 22.6 mHz) were recorded on a Bruker WH 90 spectrometer with deuterochloroform solutions. Microanalyses were performed commercially excepting halide which was evaluated by the Volhard titration.

Preparation of Complexes

In a typical reaction trimethylamine, calculated by volume on a closed section of the vacuum line, was distilled onto the frozen solution (90 K) of the metal halide in benzene contained in a single ampoule glass vessel. On warming to 273 K the solution was stirred for several hours to precipitate the appropriate product.

(a) As an example $AsCl_3$ (6.3 g, 34.7 mmol) and NMe_3 (775 cm^3, 34.6 mmol) gave the white *product* $AsCl_3 \cdot NMe_3$ [3] which was purified by sublimation under high vacuum (10^{-4} mm Hg) at room temperature. Yield 3.1 g (37%). *Anal.* Calcd for $C_3H_9NAsCl_3$: C, 15.0; H, 3.7; N, 5.8; Cl, 44.1. Found. C, 14.8; H, 3.4; N, 5.6; Cl, 44.0%. A repeat experiment using a three-fold excess of trimethylamine yielded an identical product.

(b) $AsBr_3$ (4.3 g, 13.6 mmol) and NMe_3 (306 cm^3, 13.6 mmol) gave the $AsBr_3 \cdot NMe_3$ as a white *product* which was purified by sublimation under high vacuum (10^{-4} mm Hg) at 318 K. Yield 1.1 g (22%). Mp 360–361 K (uncorr). *Anal.* Calcd. for $C_3H_9NAsBr_3$. C, 9.6; H, 2.4; N, 3.7; Br, 64.1. Found. C, 9.7; H, 2.3; N, 3.6; Br, 64.1%. Again a three-fold excess of trimethylamine provides an identical product.

(c) $SbCl_3$ (7.6 g, 33.3 mmol) and NMe_3 (745 cm^3, 33.3 mmol) gave white $SbCl_3 \cdot NMe_3$, which was purified by washing with benzene in vacuum, followed by pumping for several hours. Yield 4.1 g (42%). Mp 466–468 K (uncorr). *Anal.* Calcd. for $C_3H_9NSbCl_3$: C, 12.5; H, 3.5; N, 5.0; Cl, 37.1; Found. C, 12.5; H, 3.7; N, 5.1; Cl, 37.1%.

TABLE 1. Nmr Data for the $MX_3 \cdot NMe_3$ and $MX_3 \cdot 2NMe_3$ Complexes.

	^1H δ ppm (90 mHz)^a	^{13}C δ ppm (22.6 mHz)^a
$AsCl_3 \cdot NMe_3$	2.42	46.21
$AsBr_3 \cdot NMe_3$	2.51	47.18
$SbCl_3 \cdot NMe_3$	2.47	46.73
$SbBr_3 \cdot NMe_3$	2.50	b
$SbCl_3 \cdot 2NMe_3$	2.49	46.53
$SbBr_3 \cdot 2NMe_3$	2.51	47.83

^{a}CD_2Cl_2 and $CDCl_3$ solutions with reference TMS. ^{b}Insufficient solubility.

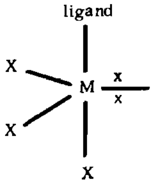
(d) $SbBr_3$ (8.2 g, 22.7 mmol) and NMe_3 (508 cm^3, 22.7 mmol) gave white $SbBr_3 \cdot NMe_3$, which was purified by washing with benzene in vacuum, then pumping dry. Yield 4.6 g (48%). Mp (decomp.) 477–480 K. *Anal.* Calcd. for $C_3H_9NSbBr_3$: C, 8.5; H, 2.1; N, 3.3; Br, 56.9; Found. C, 8.7; H, 2.1; N, 3.5; Br, 56.9%.

(e) $SbCl_3$ (6.0 g, 26.3 mmol) and NMe_3 (1310 cm^3, 58.5 mmol) gave pale yellow $SbCl_3 \cdot 2NMe_3$, which was washed and dried as above. Mp (decomp.) 359 K. *Anal.* Calcd. for $C_6H_{18}N_2SbCl_3$: C, 20.8; H, 5.2; N, 8.0; Cl, 30.7. Found C, 20.4; H, 5.1; N, 7.9; Cl, 30.6%.

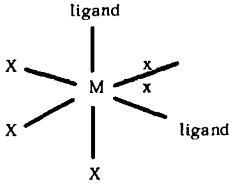
(f) $SbBr_3$ (5.9 g, 16.3 mmol) and NMe_3 (764 cm^3, 34.1 mmol) gave pale yellow $SbBr_3 \cdot 2NMe_3$, which was washed and dried as above. Mp (decomp.) 380 K. *Anal.* Calc for $C_6H_{18}N_2SbBr_3$: C, 15.0; H, 3.8; N, 5.8; Br, 50.0. Found. C, 14.7; H, 3.6; N, 5.9; Br, 50.0%.

Results and Discussion

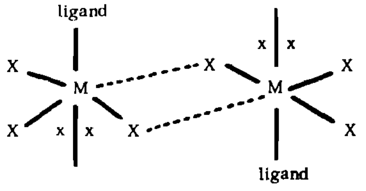
Reaction of MX_3 (M = As, Sb; X = Cl, Br) and trimethylamine at 273 K in benzene gives two series of products: the white $MX_3 \cdot NMe_3$ (M = As, Sb; X = Cl, Br) and the pale yellow $SbX_3 \cdot 2NMe_3$ (X = Cl, Br) adducts. All are moisture sensitive ranging in extent from $AsCl_3 \cdot NMe_3$ which fumes immediately in air to $SbBr_3 \cdot 2NMe_3$ which decolourises only after several hours exposure. Thermal stability was of the order Sb > As, Br > Cl. Pyrolysis of $SbCl_3 \cdot 2NMe_3$ in high vacuum at 359 K gave the mono-adduct as a white sublimate in ~10% yield but no such reaction was observed for the bromo-analogue. No evidence could be found for the existence of $AsX_3 \cdot 2NMe_3$ (X = Cl, Br). The existence of $PCl_3 \cdot 2NMe_3$ only at very low temperature, suggests a general thermal instability of these bis-adducts. The products are soluble to varying extents in the general organic solvents but decomposition occurs in the chlorinated solvents (CH_2Cl_2, $CHCl_3$) after ~25 min. This is possibly the result of solvent attack on the amine to initially give quaternary ammonium salts in a Menshutkin type reaction [8].



I (a)



I (b)



I (c)

Proton and ^{13}C nmr spectra (Table 1) show one sharp singlet in all cases indicating stereochemically equivalent CH_3 groups. Strong bands in the ir spectra at 1247–1259 $\nu_{as}(CN)$, 998–1004 $\rho(CH_3)$, 794–803 $\nu_s(CN)$ and 456–474 $\delta(NMe_3)$ cm^{-1} respectively are associated with co-ordinated amine. In the low ir region broad intense bands at 387, 356 cm^{-1} ($AsCl_3 \cdot NMe_3$), 285 cm^{-1} ($AsBr_3 \cdot NMe_3$), 185 cm^{-1} ($SbCl_3 \cdot NMe_3$), 180 cm^{-1} ($SbBr_3 \cdot NMe_3$), 195 cm^{-1} ($SbCl_3 \cdot 2NMe_3$) and 176 cm^{-1} ($SbBr_3 \cdot 2NMe_3$) are tentatively assigned to metal–halogen stretching modes [6, 9]. Single crystal X-ray studies of $AsCl_3 \cdot NMe_3$ [3] and $SbCl_3 \cdot PhNH_2$ [10] and vibrational analysis of $PX_3 \cdot NMe_3$ (X = Cl, Br) [6] point to the pseudo trigonal bipyramidal structure I(a) and it seems reasonable to propose the same for $AsBr_3 \cdot NMe_3$. Similarly by analogy with $SbCl_3 \cdot 2PhNH_2$ [11] and $SbCl_3 \cdot 2Ph_3AsO$ [12] the bis-adducts $SbX_3 \cdot 2NMe_3$ (X = Cl, Br) are proposed to have structure I(b). The same pseudo-octahedral configuration is presumed for the recent bis-amine complex $SbCl_3 \cdot 2NH_3$ [13]. In the case of $SbX_3 \cdot NMe_3$ (X = Cl, Br), however, the close similarity in terms of low ir spectra with the corresponding bis-adducts suggests another structure than I(a). We propose the pseudo square-based pyramidal structure I (c) in which the SbX_3 unit is realigned to give a long range Sb–X interaction leading to weak halogen bridging. This type of secondary bonding to give loosely joined dimeric molecules has been established for $AsCl_3 \cdot$ dmit (dmit = 1,3-dimethyl-2(3H)-imidazolethione) [14].

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