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Trimethylamine Complexes of Zirconium(IV) Halides

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The zirconium(IV) derivatives $ZrX_4 \cdot 2NMe_3$ (X = Cl, Br and I) have been obtained from direct reaction of the appropriate metal halide with an excess of trimethylamine. Structural evidence for a monomeric formulation is provided specifically for the chloride and bromide complexes. Spectral evidence for a six co-ordinate cis-$ZrCl_4 \cdot 2NMe_3$, cis-$ZrBr_4 \cdot 2NMe_3$ and trans-$ZrI_4 \cdot 2NMe_3$ arrangement of ligands within the series is presented and discussed.

Introduction

The co-ordination behaviour of titanium and zirconium halides with trimethylamine offers interesting comparisons. Under controlled conditions titanium(IV) chloride and bromide give monomeric $TiX_4 \cdot NMe_3$ and, perhaps, traces of $TiX_4 \cdot 2NMe_3$; with an excess of amine the metal is reduced to the tervalent state with formation of monomeric $TiX_3 \cdot 2NMe_3$ [1, 2]. By contrast, zirconium(IV) chloride simply provides the white insoluble $ZrCl_4 \cdot 2NMe_3$ [3]; reactions with zirconium(IV) bromide and iodide are unreported. Titanium(III) chloride, bromide and iodide, which are all halogen bridged polymers [4], are degraded into mononuclear units and in what may be described as 'breaching' interactions give the five co-ordinate $TiX_3 \cdot 2NMe_3$ [1, 2]. The reactions with zirconium(III) chloride, bromide and iodide which are also polymeric materials [5], are less well-defined but do not appear to furnish the analogous $ZrX_3 \cdot 2NMe_3$ species [6]. To some extent these variations can be reconciled with the differing natures of the metal halides themselves, *e.g.* for the tetrachlorides, not only does $ZrCl_4(s)$ have a chain structure based on edge–edge fusion of $ZrCl_6$ octahedra [7], *cf.* monomeric tetrahedral $TiCl_4(liq)$ [8], but the relative ease of reduction M(IV) → M(III) is pre-eminently Zr < Ti. Our interest in the ZrX_4–NMe_3 system (X = Cl, Br and I) stemmed from two opposite considerations. Firstly, that such interactions might well be 'topochemical' [9]. In this event adduct formation, *e.g.* $ZrX_4 \cdot 2NMe_3$ without complete breakdown of the tetrahalide lattice structures would immediately jeopardise a six co-ordinate molecular assignment; here the ability of the metal to assume high co-ordination is well documented [10]. The alternative is that the halogen bridge bonds do not survive in the presence of such a powerful donor-reducer ligand, *e.g.* the reactions are breaching. That such breaching reactions might also, under certain circumstances, be accompanied by reduction thereby providing a synthetic route to discrete Zr(III) species heralded a further possibility. Reduction of zirconium(IV) chloride with the fluoroarsine ligand 1,2-bis(dimethylarsino)-3,3,4,4,tetrafluorocyclobutene (tfars) to give $[ZrCl_3(tfars)] \cdot MeCN$ [11] has set a precedent for this type of situation.

Experimental

All solvents (reagent grade) were heated at reflux over calcium hydride and distilled *in vacuo* as required. Commercial trimethylamine was stored over potassium hydroxide and distilled *in vacuo* prior to use. Zirconium(IV) chloride and bromide were obtained by hot tube sublimation of the commercial products in a stream of the appropriate halogen. Zirconium(IV) iodide was prepared by direct reaction of the elements using a high pressure sublimation tube. The initial red–brown product was resublimed over zirconium metal to ensure complete removal of unreacted iodine. Excellent elemental analyses were obtained in all three cases.

Microanalysis and molecular weight data was obtained by B.M.A.C. Teddington, Middlesex. Zirconium was estimated gravimetrically following ignition to the oxide and halide was evaluated by the Volhard method. Spectral measurements were obtained as follows: Infrared (4000–100) cm^{-1} (Perkin Elmer 621 and Fourier FS 720) with samples as nujol and fluorolube mulls between caesium iodide plates; ^1H nmr (90 MHz) (Bruker WH90) with deuterobenzene solutions; Electronic (Cary 14) with benzene solutions in 1 cm silica cells or as nujol mulls held between silica plates. Magnetic susceptibility measurements were made at room temperature by the Faraday method.

All manipulations were carried out in sections of an all-glass vacuum line system and in a gloved box flushed with dry oxygen-free nitrogen to avoid

TABLE I. Spectral and Magnetic Data of the $ZrX_4 \cdot 2NMe_3$ Complexes.

Compound	Magnetic Susceptibility[a]	Electronic[b]	^1H nmr[c]	Ir (4000–100) cm^{-1}
$ZrCl_4 \cdot 2NMe_3$	-95×10^{-6}	28,560(sh)* 28,400(sh)** 39,520(sh) 46,200(sh)	2.38	3150(s), 3020(m), 2982(m), 2930(m), 2908(w), 2880(w), 2852(w), 2800(m), 2510(vw), 2450(w), 1412(m), 1260(w), 1230(s), 1106(s), 1040(vw), 1018(vw), 976(vs), 810(vs), 722(w), 520(vs), 430(w), 385(m), 358(sh), 345(vs), 233(s), 155(vs).
$ZrBr_4 \cdot 2NMe_3$	-140×10^{-6}	29,250(sh)* 35,300(sh)** 36,700(sh)	2.47	3116(s), 3010(m), 2978(w), 2910(s), 2850(w), 2790(m), 2725(m), 2510(vw), 2458(vw), 1418(m), 1260(vw), 1234(s), 1110(s), 1050(vw), 1026(vw), 980(vs), 812(vs), 730(w), 530(vs), 440(w), 390(w), 333(w), 268(vs), 228(s), 128(m).
$ZrI_4 \cdot 2NMe_3$	-176×10^{-6}	27,700* 22,900(sh)** 27,240(sh) 37,730(sh) 51,020(sh)	3.44	3120(s), 3015(m), 2940(m), 2910(w), 2870(sh), 2830(sh), 2740(s), 2510(sh), 2460(vw), 1409(m), 1245(m), 1220(vw), 1166(m), 1100(m), 1046(m), 1022(w), 970(vs), 805(vs), 720(m), 518(m), 425(vw), 186(vs).

[a] Room temperature, χ'_M values (cgsu) with diamagnetic corrections estimated from Pascal's constants.
[b] λ_{max} (cm^{-1}), *benzene solutions, **nujol mulls
[c] Absorption maxima (δ) recorded in C_6D_6 solutions with TMS as internal standard.

decomposition of the extremely air- and moisture-sensitive zirconium(IV) adducts.

Reaction of zirconium(IV) Halides with Trimethylamine

(i) Trimethylamine (~30 cm^3) was distilled *in vacuo* onto the white anhydrous zirconium tetrachloride (~3g) contained in a double ampoule glass vessel. On warming to room temperature and after several days standing reaction commenced as evidenced by the formation of a fringe of clear colourless crystals around the liquid meniscus. Extraction *via* repeated filtration and back-distillation across the sintered disc gave colourless chunky crystals of tetrachlorobis(trimethylamine)zirconium(IV) [A] leaving a small amount of white material apparently insoluble in trimethylamine. *Anal.* Calcd. for $C_6H_{18}N_2ZrCl_4$, mol. wt. 351.3, C, 20.5; H, 5.2; N, 8.0; Zr, 26.0; Cl, 40.4. Found: C, 20.4; H, 5.1; N, 7.9; Zr, 25.9; Cl, 40.2%; mol. wt. (osmometric in benzene solutions), 326. M.p., decomposes at T > 318 K to a brown solid. The small amount of insoluble material showed a high halide: amine ratio and on spectral evidence is essentially unreacted metal halide.

(ii) Addition of a trace of zinc dust to the reaction mixture as in (i) gave the same results. The only visible effect was that reaction was initiated much more quickly to give crystals of [A] after several hours.

(iii) A repeat of [i] now using the white anhydrous zirconium tetrabromide (~3g) gave tetrabromobis(trimethylamine)zirconium(IV) [B] as clear, colourless crystals. *Anal.* Calcd. for $C_6H_{18}N_2ZrBr_4$, C, 13.6; H, 3.4; N, 5.3; Zr, 17.2; Br, 60.4. Found: C, 13.8; H, 3.4; N, 5.0; Zr, 17.2; Br, 60.2%. M.p., decomposes at T > 414 K to a brown black solid. The small amount of residual insoluble cream material was discarded as unreacted metal halide.

(iv) The green–yellow semi-crystalline solid [C] obtained from the direct treatment as in [i] of the red–brown zirconium tetraiodide (~3g) analysed as tetraiodobis(trimethylamine)zirconium(IV). *Anal.* Calcd. for $C_6H_{18}N_2ZrI_4$, C, 10.1; H, 2.5; N, 4.0; Zr, 12.7; I, 70.8. Found: C, 9.9; H, 2.3; N, 3.9; Zr, 12.6; I, 70.6%. M.p., decomposes at T > 398 K to a brown–black solid.

Results and Discussion

The reactions between zirconium(IV) chloride, bromide and iodide and trimethylamine (in excess) were studied in sealed double-ampoule systems and over a period of several weeks, and were found to provide the extremely air-sensitive bis-adducts $ZrX_4 \cdot 2NMe_3$ (Table I). Their solubility in the parent amine facilitated extraction and crystalline materials were obtained in each case. On pumping *in vacuo* at room temperature or washing with benzene both the chloride and bromide adducts show loss of crystallinity and revert to off-white solids. In anticipation of enhanced lattice breakdown with, perhaps, reduction, the reaction using zirconium(IV) chloride was repeated several times in the presence of trace amounts of zinc dust. Certainly, there was some catalytic effect(s), the reaction starting almost immediately, but there was no evidence to support reduction *via* electron exchange in this or, indeed, in any of the other cases. All the complexes are diamagnetic (Table I) and excepting trimethylamine and to a lesser extent, benzene, are virtually insoluble in the common organic solvents. The electronic spectra (Table I) show no absorptions in the visible or near ir regions to confirm a general d^0 classification; the intense uv bands are assigned as charge-transfer transitions of the type zirconium(d) $\leftarrow$ halogen(π) [12]. Support for a monomeric formulation for the chloride adduct is two-fold, *viz.* the molecular weight determination and initial results of a crystal structure analysis [13]. Crystals of $ZrCl_4 \cdot 2NMe_3$ are tetragonal, $a = 15.640$ (12), $c = 24.588$ (16)Å, Laue Group 4/mmm, systematic absences $h + k + l = 2n + 1$, $d_m = 1.54$, $d_c = 1.55$ for $Z = 16$. Intensity data have been measured but no satisfactory solution has so far been obtained possibly because of merohedral twinning. It would appear, however, from the Patterson function that no $Zr \cdots Zr$ contact is less than 6Å which effectively rules out a polymeric structure. $ZrBr_4 \cdot 2NMe_3$ which is equally beset with twinning problems is found to be isomorphous. In the wide context of $ZrX_4 \cdot 2L$ complexes (X = Cl, Br, I; L = monodentate with either nitrogen-, phosphorus-, arsenic-, oxygen- or sulphur-donors) where a six-co-ordinate molecular structure is usually assumed [14] a *cis* C_{2v} rather than a *trans*-D_{4h} arrangement is normally assigned on the basis of ir correlations of ν(ZrX) modes [15]. A recent example where the reverse is favoured is provided by the $ZrX_4 \cdot 2L$ derivatives [16] (X = Cl, Br, I; L = 2,4- and 3,5-lutidines); here the steric effects of the methyl groups are believed to be the predominant factor. The ir spectra (4000–400) cm^{-1} in the present instance (Table I) are all very similar and contain bands at ~1230 (ν_{as} CN), ~975 (ρCH_3), ~810 (ν_s CN), ~520 (δ_{as} CN) and ~430 (δ_s CN) cm^{-1} respectively associated with co-ordinated trimethylamine [17]. Significant variations do occur in the far ir region (400–100) cm^{-1}. For the chloride adduct the broad asymmetric absorption based at 330–340 cm^{-1} was resolved into discrete bands associated with ν(ZrCl) vibrations at 385 (m), 358 (sh), 345 (vs), 233 (s), and 155 (vs) cm^{-1} respectively. Equally the broad absorption at ~270 cm^{-1} observed for the bromide adduct was resolved into bands assigned as ν(ZrBr) modes at 390 (w), 333 (w), 268 (vs), 228 (s) and 128 (m) cm^{-1} respectively. Only the one intense absorption at 186 cm^{-1} ν(ZrI) was obtained for the iodide adduct. These patterns allow a clear distinction between the three species and are consistent [18] with a *cis*-$ZrCl_4 \cdot 2NMe_3$, *cis*-$ZrBr_4 \cdot 2NMe_3$ and *trans*-$ZrI_4 \cdot 2NMe_3$ arrangement of ligands. Although the differences in total inter-ligand repulsions between the *cis*- and *trans*-stereochemistries of such compounds are likely to be fairly small [19], the present situation with only the iodide complex evidently favouring the *trans*-juxtaposition of ligands is not unexpected from the steric viewpoint. The proton nmr spectra (Table I) confirm the methyl groups in equivalent stereochemical positions throughout with only slight deshielding for the chloride and bromide complexes (δ_{NMe_3} 2.13). With the iodide complex the increase is much more dramatic and reflects an increased transfer of electron density to the metal ($\delta_{NMe_4^+}$ 3.33) commensurate with a much stronger Zr–N bonded species.

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