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Cis-Tetrachlorobis(trimethylamine)hafnium(IV): Synthesis and Characterisation

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One of the interesting aspects concerning reactions of trimethylamine with halides of the early transition series is that normal adduct formation can be accompanied by redox [1]. This is especially so with titanium where the tetrahalides are readily reduced to the tervalent species $TiX_3 \cdot 2NMe_3$ [2]. Vanadium(IV) halides show similar behaviour [3]. Reaction with bi(cyclopentadienyl)titanium dichloride also involves reduction and gives Cp_2TiCl as one of the products [4]. The situation with zirconium(IV) has recently been described [5]; the tetrahalides simply provide the monomeric six coordinate complexes $ZrX_4 \cdot 2NMe_3$ where X = Cl (*cis*), Br (*cis*) and I (*trans*) with no trace of reduced species. Bis(cyclopentadienyl)zirconium dichloride dissolves unchanged in an excess of neat trimethylamine [4]. To complete comparisons within the Group IVA series we now report the reaction with hafnium(IV) chloride.

Direct interaction with excess trimethylamine in a sealed double ampoule is fairly rapid (~30 min) and gives a white solid which, by virtue of its solubility in the parent amine, was obtained as white needle-shaped crystals [6] following continued filtration and back-distillation *in situ*. *Anal.* Calcd. for $C_6H_{18}N_2HfCl_4$, C, 16.4; H, 4.1; N, 6.4; Hf, 40.7; Cl, 32.3%. Mol. wt. 439. Found: C, 16.4; H, 4.0; N, 6.3; Hf, 40.6; Cl, 32.1%. Mol. wt. (osmometric in benzene), 450. The white crystals melt at 462–463 K (uncorr) to a brown liquid. The product which is very air-moisture sensitive shows limited solubility in benzene and dichloromethane. One sharp singlet in the proton nmr spectrum (C_6D_6, δ 2.43 ppm (TMS)) establishes stereochemically equivalent methyl groups for the monomeric species. Diagnostic ir bands associated with co-ordinated trimethylamine and metal–halogen vibrations are observed at 1227 (ν_{as} CN), 972 (ρ CH_3), 804 (ν_s CN), 523 (δ_{as} CN) and at 280–300 cm^{-1} respectively. Resolution of the latter gave separate intense bands ν(HfCl) at 332, 310, 290 and 150 cm^{-1} in support of the proposed *cis* $HfCl_4 \cdot 2NMe_3$ (C_{2v}) formulation [7].

Although the co-ordination chemistry of hafnium (IV) is sparse in comparison to that of zirconium(IV) little difference between the two is expected [8]. In the present instance the possibilities of co-ordination > 6 and reduction have evidently not been realised [9] and *cis* $HfCl_4 \cdot 2NMe_3$ [10] forms a direct parallel with the zirconium counterpart. Other similar hafnium species have been recently recorded, *e.g.* *cis* $HfCl_4 \cdot 2L$ where L = pyridine [7], 2,6-lutidine N-oxide [11] and 3-cyanopyridine [12].

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