The Molecular Structure of Bistrimethylaminetitanium Tribromide; an Example of the Jahn–Teller Effect in Pentaco-ordinate Molecules

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ALTHOUGH on the basis of dipole-moment and molecular-weight measurements,[1] and far-infrared studies,[2] the compounds $VCl_3,2NMe_3$ and $VBr_3,2NMe_3$ are believed to exhibit trigonal-bipyramidal co-ordination of the metal atom, it has been suggested[3,4] that the corresponding titanium compounds may exist in the solid state as dimeric species with halogen bridges, the metal atom being octahedrally co-ordinated. This suggestion was put forward to account for the marked difference in

solubility and volatility found for the titanium compounds compared to their vanadium analogues. However, comparison of the unit cell dimensions of $VCl_3,2NMe_3$ and $TiCl_3,2NMe_3$ [5] suggests that the two compounds are isomorphous although the crystal densities, which are reported as 2·9 g.cm.$^{-3}$,[5] and 1·33 g. cm.$^{-3}$,[4] respectively, would seem to refute this idea.

In order to clarify the situation regarding the stereochemistry of these molecules it was thought worthwhile to determine the crystal structures of $VCl_3,2NMe_3$ and $TiBr_3,2NMe_3$ and here we report preliminary results obtained for the titanium complex.

Crystals of $TiBr_3,2NMe_3$ are orthorhombic, space group *Pnma*, and have unit cell dimensions very near to the values reported for the two chloride compounds. Using approximately 600 independent $F(hkl)$'s, measured photometrically from integrated Weissenberg photographs we have found that the crystal contains four monomeric molecules possessing, basically, trigonal bipyramidal geometry. The residual, R, is at present 15% and refinement is continuing.

Although, crystallographically, the molecule is only required to possess a mirror plane, which passes through the titanium atom, one of the bromine atoms, and the two trimethylamine groups, to within the present standard deviations it possesses C_{2v} symmetry. The distortion away from the idealised D_{3h} symmetry of the trigonal bipyramid is significant and it occurs within the equatorial $TiBr_3$ group of atoms; the relevant dimensions being as follows (s.d.'s in parentheses): (*a*) Ti–Br, 2·442 Å (0·006) 2 values and 2·404 Å (0·010), (b) Br–Ti–Br angles, 121·25° (0·20) (2 values) and 117·5° (0·35), (c) Ti–N, 2·27 Å (0·04) and 2·30 Å (0·06) and (d) Br–Ti–N angles, 89·25° (1·5) and 90·20° (1·0). The $TiBr_3$ group is planar and there is no statistical disorder of the trimethylamine groups about their three-fold axes.[6] There are no short intermolecular contacts involving the bromine atoms (the shortest distance being to a methyl group at 4·2 Å) and we therefore believe the observed deviation from D_{3h} symmetry to be significant in terms of the electronic structure of the molecule.

Assuming D_{3h} symmetry, pentaco-ordinate molecules with $n\,d^1$ configurations should in theory be subject to a Jahn–Teller distortion since the one electron would otherwise occupy a doubly degenerate e'' m.o. In the present instance, with bromine atoms as ligands, this m.o. will be π-antibonding and the molecule might therefore be expected to show a larger deviation from D_{3h} symmetry than if it were mainly nonbonding.

Although we believe this configurational instability to be the origin of the observed molecular symmetry, it should be pointed out that on taking spin–orbit coupling into account the orbitally doubly degenerate ground state $^2E''$ is split into two doubly-degenerate states, $\Gamma_4 + \Gamma_5$ and Γ_6, neither of which can be split further. However, since the spin–orbit coupling constant for titanium is fairly small it might not be large enough to render the Jahn–Teller effect inoperative, so that the above argument would still hold.

Further structural details on this compound, together with those for $VCl_3,2NMe_3$, which in the absence of crystal forces should not show significant deviations from D_{3h} symmetry, will be published elsewhere.

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