# A Five-co-ordinate Complex of Chromium(III)

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TRIMETHYLAMINE forms complexes of the type $MX_3,2NMe_3$ where M = Ti and V, and X = Cl and Br.[1–4] The vanadium complexes have been shown to be monomers in solution with *trans*-trigonal-bipyramidal structures, and infrared studies[5] have shown a similar structure for the solid. A chlorine-bridged six-co-ordinate structure was originally suggested[3] for $TiCl_3,2NMe_3$, but a single-crystal study[6] of the bromine analogue shows the complex to be five-co-ordinate (approximately $D_{3h}$).

We have now prepared the analogous chromium(III) chloride complex by the direct reaction of the anhydrous halide with dry trimethylamine in the

presence of a catalytic amount of zinc dust, by using a double-ampoule technique.[3] The trimethylamine-soluble compound was extracted with benzene to yield a blue–purple solid which hydrolysed very readily. Analysis shows the complex to have the empirical formula $CrCl_3,2NMe_3$, and a variety of physical data indicates that it is five-co-ordinate both in solution and in the solid state with the same structure as $VCl_3,2NMe_3$. The tervalency of chromium in the compound is confirmed by the magnetic moment of 3·77 B.M. Cryoscopic measurements on benzene solutions show the compound to be monomeric, and hence five-co-ordinate. Evidence for a similar structure in the solid is provided by the electronic spectra which are identical for the benzene solution and the solid (*cf.*, Table).

The *trans*-trigonal-bipyramidal structure is also supported by the far-infrared spectrum (Nujol mull), which shows a single strong band at 392 cm.$^{-1}$ that can be assigned to a Cr–Cl stretching frequency. The analogous band for $VCl_3,2NMe_3$ occurs[5] at 409 cm.$^{-1}$. The position of this band effectively rules out a six-co-ordinate species with bridging chlorines; a second peak of medium intensity observed at 274 cm.$^{-1}$ is tentatively assigned to a Cr–N stretching mode.

The compound is particularly interesting since all previously reported complexes of tervalent chromium are six co-ordinate, with the possible exception of $[PCl_4][CrCl_4]$ which may contain a four-co-ordinate anion.[8]

The analogous reaction of chromium(III) bromide with trimethylamine is being studied.

TABLE

*Electronic spectra of* $CrCl_3,2NMe_3$

| | Peaks (cm.$^{-1}$) ($\epsilon_{max}$ in parentheses) | | | | | | |
|---|---|---|---|---|---|---|---|
| Benzene solution | 10,100 (23) | 13,000 w, sh | 17,600 (130) | 23,200 w, sh | 30,200 sh (1000) | | |
| Solid | ~10,000 | 12,900 sh | 17,600 br | ~23,000 sh | 30,000 | 37,500 | 45,600 |

The detailed assignments of these peaks and those obtained[7] for $VCl_3,2NMe_3$ will be published later.

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