Three-co-ordinated Compounds of Titanium(III) and Vanadium(III)

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Summary The new compounds M[N(SiMe$_3$)$_2$]$_3$ (M = Ti, V) have been synthesised and characterised as authentic 3-co-ordinated complexes of these metals.

ALTHOUGH the monomeric nature of Cr(NPr$^i_2$)$_3$ and Cr[N(SiMe$_3$)$_2$]$_3$ was revealed by molecular weight determinations in solution,[1] a single-crystal *X*-ray structural determination on Fe[N(SiMe$_3$)$_2$]$_3$ was required to establish the trigonal configuration of the tris-silylamides.[2] This has stimulated renewed attempts to synthesise further examples of trigonally co-ordinated transition-metal complexes and the recent report of the e.s.r. spectra attributed to Ti(NPr$^i_2$)$_3$ and Ti(NPh$_2$)$_3$ [3] prompts us to report our results in this field. In view of the failure of previous attempts to isolate Ti(NPr$^i_2$)$_3$ (independently confirmed by Lappert and Sanger)[4] using essentially the same method as reported,[3] we are doubtful about the assignment of the e.s.r. spectrum to a compound Ti(NPr$^i_2$)$_3$ which has yet to be isolated and characterised. Previous work[4] showed that TiCl(NPr$^i_2$)$_2$ was preferentially formed under the same reaction conditions.

Nevertheless we have now found that both Ti[N(SiMe$_3$)$_2$]$_3$ (I) and V[N(SiMe$_3$)$_2$]$_3$ (II) may be isolated in reasonable yield by using a modified procedure. It was found essential to use the 5-co-ordinated complexes MCl$_3$(NMe$_3$)$_2$[5] in reactions with LiN(SiMe$_3$)$_2$.

The titanium compound (I) (bright blue crystals from pentane) could not be sublimed owing to thermal decomposition, but a mass spectrum was obtained (parent ion *m/e*, 528). A solution of (I) in toluene gave an e.s.r. signal at room temperature ($g = 1\cdot911$) consistent with a $^2A'$, ground state in a trigonal (D_{3h}) d^1 system and in frozen solution (135K) g-value anisotropy ($g_{\parallel} > g_{\perp}$) confirmed that the complex has axial symmetry.

The vanadium compound (II) (brown crystals) could be sublimed *in vacuo* and gave the parent ion (*m/e*, 531) in its mass spectrum. Although the compound is paramagnetic its solution in toluene gave no e.s.r. signals at room temperature or in frozen solution (135 K) and this behaviour can be reconciled with the requirements of a d^2 trigonal system. Both (I) and (II) are extremely reactive to water and oxygen and their reactivity with other small molecules is being studied.

X-Ray crystallography[6] has shown that (I) and (II) are isostructural with Cr[N(SiMe$_3$)$_2$]$_3$ and Fe[N(SiMe$_3$)$_2$]$_3$ so that a series of d^1, d^2, d^3, and d^5 trigonal complexes is available for study. We have attempted to prepare Mn[N(SiMe$_3$)$_2$]$_3$ and Co[N(SiMe$_3$)$_2$]$_3$ but so far without success. The electronic and vibrational spectra and magnetic properties of (I) and (II) are being determined and will be reported later elsewhere together with crystal-field calculations (with Dr. K. D. Sales) on d^n trigonal systems.

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