Crystal Structure and Electron Spin Resonance Spectrum of Tris-di-isopropylaminatochromium(III)

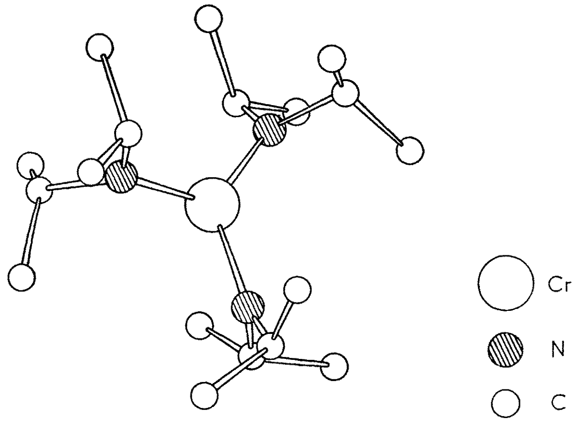
By D. C. BRADLEY,* M. B. HURSTHOUSE, and C. W. NEWING
(*Department of Chemistry, Queen Mary College, Mile End Road, London, E.*1)

Summary An *X*-ray crystal structure analysis on $Cr(NPr^i_2)_3$ has shown that it is a trigonal complex of Cr^{III} with near D_3 symmetry for the $Cr(NC_2)_3$ unit; an authentic e.s.r. spectrum has also been obtained which confirms this structure in solution.

THE crystal structures of $M[N(SiMe_3)_2]_3$ ($M = Cr$, Fe) showed that these trigonally co-ordinated transition-metal complexes had an interesting configuration corresponding to D_3 symmetry of the $M(NSi_2)_3$ unit with planar $MNSi_2$ groups.[1] Since the planarity of the $MNSi_2$ unit could be due to metal–nitrogen and/or nitrogen–silicon π-bonding it was particularly important to determine the configuration of $Cr(NPr^i_2)_3$, which was shown to be monomeric in solution,[2] since planarity of $CrNC_2$ units could only involve metal–nitrogen π-bonding. Single crystals of this highly reactive compound were obtained from pentane and sealed under vacuum in Lindemann capillaries.

Crystal data: $CrN_3C_{18}H_{42}$, M = 352·55, triclinic, a = 8·393 (2), b = 9·442(2), c = 14·629(2) Å, α = 91·28(3), β = 99·03(2), γ = 98·72(2)°, Z = 2, D_c = 1·06, space group $P\bar{1}$.

Intensity data were recorded on a G.E. XRD6 manual diffractometer using the stationary crystal–stationary counter technique. Of a total of 2017 reflections measured out to a value of 2θ = 95°, 1897 had intensities significantly above background. The structure was solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares. R is currently 0·084.



FIGURE

The structure found, which is shown in the Figure—a view down the crystallographic a axis—confirms the monomeric, three-co-ordinate nature of the compound. The CrN_3 system is planar to within the limits of experimental error, as are the $CrNC_2$ system of each of the amide ligands. The dihedral angles between the CrN_3 plane and the three amide planes are very similar at 68, 72, and 73°.

The Cr–N bonds, at *ca.* 1·87 Å are somewhat shorter (*ca.* 0·1 Å) than might be expected This, together with the planarity of the $CrNC_2$ units, is indicative of ligand-to-metal π-bonding.

In continuation of our e.s.r. studies on trigonally co-ordinated transition-metal complexes we have found that solutions of $Cr[N(SiMe_3)_2]_3$ do not give an e.s.r. signal at room temperature but do so in frozen solutions at low temperatures with g-value anisotropy corresponding to a d^3 system with axial symmetry and a zero-field splitting.[3] Therefore, we suspected that the room temperature signal previously attributed to $Cr(NPr^i_2)_3$[4,5] in solution must be due to a trace of an oxygen complex. A solution of $Cr(NPr^i_2)_3$ in toluene which at room temperature gave a strong signal (g = 1·975) was kept in a sealed sample tube for several weeks and the signal decayed to zero due to instability of the trace of oxygen complex However, on freezing this solution to 130 K a signal due to $Cr(NPr^i_2)_3$ was detected, $g_{\parallel} = 2{\cdot}0$; $g_{\perp} = 4{\cdot}0$, as expected for a trigonal chromium(III) complex. On being warmed to room temperature the solution still gave no e.s.r. signal but on opening the tube and exposing it momentarily to the air an intense e.s.r. signal (g = 1·975) immediately developed. These results demonstrate the inherent problems involved in obtaining reliable e.s.r. spectra of highly reactive species in solution and the need for independent confirmation of the identity of species giving rise to signals in such systems.

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