Low Co-ordination Numbers for Chromium in Chromium(III) Compounds

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THE only previously reported examples of chromium(III) compounds not involving octahedrally co-ordinated chromium were the 12-tungstochromic(III) acid[1] and tetrachlorophosphonium tetrachlorochromate(III),[2] which were both believed to contain tetrahedrally co-ordinated chromium, and trichloro(bistrimethylamine)-chromium(III), which contains 5-co-ordinated chromium.[3,4] Following our earlier work[5] which established that tetrahedral chromium(IV) was stabilized by the presence of certain bulky ligands we now report the isolation of 3- and 4-co-ordinated chromium(III) compounds.

Trisdi-isopropylamidochromium(III) $[\mathrm{Cr(NPr^i_2)_3}]$ was obtained as a red–brown solid from lithium di-isopropylamide and chromium trichloride in tetrahydrofuran. It was highly reactive to air and water, sublimed *in vacuo*, and was soluble in common organic solvents. Traces of oxygen immediately generated the blue colour of $\mathrm{Cr^{IV}}$ (broad band at 17700 cm.$^{-1}$).[5] Under rigorously moisture- and oxygen-free conditions pentane solutions of $\mathrm{Cr(NPr^i_2)_3}$ gave two absorption bands in the visible region at 6900 cm.$^{-1}$ (br; $\epsilon_{\max} \sim 170$) and 23200 cm.$^{-1}$ (sh; $\epsilon_{\max} \sim 2800$). These spectra are incompatible with tetrahedral or octahedral $\mathrm{Cr^{III}}$, and very careful molecular weight measurements (cryoscopically in cyclohexane and nitrobenzene) over a wide concentration range showed that the compound is monomeric and thus contains 3-co-ordinated $\mathrm{Cr^{III}}$. Magnetic susceptibility determinations over the range 298–123° K gave a temperature independent effective magnetic moment of 3·80 B.M. confirming that a 3-co-ordinated species is also present in the solid. Doubtless the bulky ligands prevent the attainment of a higher co-ordination by the chromium but the ligand-field stabilization energy of the d^3 configuration in a trigonal field may well be significant. Other sterically hindered secondary amines also give 3-co-ordinated chromium(III) dialkylamides and we have shown that tris(bis-trimethylsilylamido)chromium(III)[6] $\{\mathrm{Cr[N(SiMe_3)_2]_3}\}$ is monomeric in solution (cryoscopy) and in the solid state (magnetic susceptibility).

Treatment of chromium trichloride in tetrahydrofuran with excess of lithium diethylamide followed by excess t-butyl alcohol gave an insoluble compound $\mathrm{LiCr(OBu^t)_4}$. Lack of solubility precluded molecular weight or conductance measurements and it is assumed to be a highly polymeric compound. Apart from the presence of lithium–oxygen bands the i.r. spectrum (Nujol mull) resembled that of $\mathrm{Cr(OBu^t)_4}$.[7] The electronic absorption spectrum (Nujol mull between silica plates) gave an intense band in the region 20000–50000 cm.$^{-1}$ and three broad bands of moderate and near equal intensity. The latter can be assigned to the transitions for a d^3 configuration in a tetrahedral complex[8,9] as follows: ${}^4T_1(F) \rightarrow {}^4T_2(F)$, 10100; ${}^4T_1(F) \rightarrow {}^4T_1(P)$, 17400; ${}^4T_1(F) \rightarrow {}^4A_2(F)$, 19400 cm.$^{-1}$. These data correspond to $10Dq = 11200$ and $B = 560$ cm.$^{-1}$. Magnetic susceptibility measurements showed that the effective magnetic moment decreased from 3·58 B.M. at 298° K to 3·43 B.M. at 98° K which confirms the tervalency of the chromium and is consistent with the ${}^4T_1$ ground term in tetrahedral chromium.[8] The compound was oxidized to $\mathrm{Cr(OBu^t)_4}$[5] in 85% yield by cuprous chloride whilst treatment with acetylacetone gave tris-acetylacetonatochromium-(III) and lithium acetylacetonate.

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