Anhydrous Cobalt(III) Nitrate

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THE remarkable feature of the reactions between cobalt compounds and either dinitrogen tetroxide or pentoxide, is the exclusive formation of nitrates[1] and nitrato-complexes[2] of cobalt(II), but not cobalt(III), even when complex ions such as hexanitrocobaltate(III) are employed. However, we can now report the synthesis of anhydrous cobalt(III) nitrate from the reaction between cobalt(III) fluoride and dinitrogen pentoxide. The pure pentoxide was condensed onto brown anhydrous cobalt(III) fluoride at −70°. The solids were mixed and allowed to warm to room temperature. Reaction proceeded with the development of a green colour (red or purple colours developed at this stage in reactions with hexanitrocobaltates[2]) and was complete in *ca.* 1 hr. Excess dinitrogen pentoxide and other gaseous products were removed in a stream of nitrogen. Vacuum sublimation of the residue at 40° produced hygroscopic green crystals. These were identified by analysis to be cobalt(III) nitrate. As expected, an initial green solution of the product in water rapidly evolved oxygen and changed to an acidic pink solution containing Co^{II} and NO_3^- in a 1 : 3 ratio. The iodide ion was oxidised quantitatively to iodine.

The physical properties of cobalt(III) nitrate are reminiscent of those of simple molecular covalent nitrates with bidentate nitrate ligands, *e.g.* $Ti(NO_3)_4$[3] and $Sn(NO_3)_4$,[4] and on this basis it seems probable that $Co(NO_3)_3$ involves cobalt(III) co-ordinated by bidentate nitrate ligands in an octahedral molecular complex.

To support this:

(i) The i.r. spectrum compares closely with those of $Ti(NO_3)_4$ and $Sn(NO_3)_4$ and is sufficiently simple to support three equivalent nitrate groups.[5] It is identical in gross features for either solutions (CCl_4, hexane), mulls (fluorube), or a sublimed solid film at $\sim$100° K. Principal band positions for solution spectra are: 499s, 761s, 965s sp, 1158s (1166sh), 1621vs, 1649m (cm.$^{-1}$). The complementary Raman spectrum[5] has not yet been obtained, so band assignments are deliberately omitted until this is available.

(ii) The compound is volatile at low temperature ($\sim$40° at 10^{-2} mm. Hg) and reacts vigorously with a range of organic solvents, *e.g.* ethers, ketones, nitriles, and some hydrocarbons. It is soluble in carbon tetrachloride and hexane with relatively slow decomposition of the solutions.

(iii) The visible spectrum (0·008 M in CCl_4) exhibits two broad peaks at 16,300 (ϵ_{max} 166) and 23,300 cm.$^{-1}$ (ϵ_{max} 240), qualitatively similar to the spectra of $[Co(C_2O_4)_3]^{3-}$ and $[Co(CO_3)_3]^{3-}$. The somewhat larger extinction coefficients arise because these bands are overlapped by the tail of an intense absorption band situated in the u.v. region.

(iv) The compound exhibits a magnetic moment, consistent with a low-spin t_{2g}^6 electronic arrangement for octahedrally co-ordinated Co(III). Several samples have been measured, and the results are variable presumably due to a degree of decomposition to cobalt(II) compounds. In no case was the value of χ_M greater than $\sim 400 \times 10^{-6}$ c.g.s. units, or $\mu_{eff} \sim 1\cdot0$ B.M.

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