

Nitrato-complexes of Cobalt-(II) and -(III)

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No example is known in which reaction of a metal compound with dinitrogen pentoxide leads to a reduction in the oxidation state of the metal. We were therefore surprised to observe that the reaction of sodium or potassium hexanitrocobaltates(III) with dinitrogen pentoxide yields exclusively the new cobalt(II) compounds $\text{Na}_2\text{Co}(\text{NO}_3)_4$ and $\text{K}_2\text{Co}(\text{NO}_3)_4$ and not the expected cobalt(III) complexes, *e.g.*, $\text{Na}_3[\text{Co}(\text{NO}_3)_6]$. Tetranitrocobaltates(II) have been reported previously¹⁻³ for large cations $(\text{Me}_4\text{N})^+$, $(\text{MePh}_3\text{As})^+$, and $(\text{Ph}_4\text{As})^+$, but nitratocobaltates(III) remain unknown.

In a typical preparation, pure dinitrogen pentoxide was condensed on to anhydrous sodium hexanitrocobaltate(III) at -70° . Dinitrogen tetroxide was evolved, and the colour of the remaining solid changed from yellow-brown to red. The infrared spectrum of the red product at this stage, after removal of the gaseous products, showed bands due to sodium nitrate, together with a pattern indicative of a nitrato-complex. The pure pale red complex was isolated by treatment with anhydrous ethyl acetate, filtration from insoluble sodium nitrate, and precipitation with anhydrous carbon tetrachloride. The infrared spectrum of the recovered complex (see below) was identical

with that of the crude mixture after subtracting bands due to sodium nitrate. The nitrate/cobalt(II) ratio was confirmed from the intensities of the $302\text{ m}\mu$ (NO_3^-) and $516\text{ m}\mu$ (Co^{2+}) peaks in the ultraviolet absorption spectrum of an aqueous solution.

Two possible potential reducing agents, nitrite ion and dinitrogen tetroxide are present in this system, but separate experiments showed that negligible reduction of the low-spin hexanitrocobaltate(III) ion occurs in contact with either. It is therefore concluded that cobalt(III) must be reduced in a complex in which some, or all, of the nitro-groups have been replaced by nitrate. Because of the very low position of nitrate in the spectrochemical series (it occurs just above fluoride) such replacement will lower the value of Dq and hence the ligand field stabilization of the low spin t_{2g}^6 configuration, and thus facilitate reduction to cobalt(II). For the hypothetical $[\text{Co}(\text{NO}_3)_6]^{3-}$ ion, we have calculated that $Dq = 1780\text{ cm}^{-1}$, by application of the average environment rule using Dq -values for $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{2+}$ derived from their absorption spectra and the relevant Tanabe-Sugano diagram. This value is higher than the value ($Dq = 1300$

cm.⁻¹) for the high-spin fluoro-complex $[\text{CoF}_6]^{3-}$, but it is difficult to predict whether the nitrate-complex would also be high-spin because the value of the interelectronic parameter B for the nitrate complex is uncertain. There does, however, seem to be no reason for expecting nitrate-complexes of cobalt(III) to be unstable if prepared in fully oxidising conditions, and we are examining this aspect further.

The infrared spectrum (and probably the structure) of the potassium compound is virtually identical with that of $(\text{Ph}_4\text{As})_2[\text{Co}(\text{NO}_3)_4]$ for which a discrete complex anion consisting of an eight-coordinate cobalt ion co-ordinated by four bidentate nitrate ions has been shown by *X*-rays;³ there are five main bands at approximately 1470, 1300, 1030,

810, and 750 cm.⁻¹ The sodium salt, however, exhibits a spectrum for which overall positions are similar, but which is different in detail. The bands are split, most strikingly in the 1000 cm.⁻¹ region where now two strong bands appear, and in the 800 cm.⁻¹ region where there are three sharp bands close together; the prominent bands in the spectrum (4000—3000 cm.⁻¹) are 2070 w, 1742 w, 1525 vs, 1486 vs. b, 1335 vs. b, 1287 s, 1042 s. sp., 1025 s. sp., 812s. sp, 808 s. sp, 804 s. sp, 759 s. sp. (cm.⁻¹). This indicates that a change in crystal structure may occur as the cation size is decreased to that of Na^+ , and may extend to the $[\text{Co}(\text{NO}_3)_4]^{2-}$ anion itself.

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¹ D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, 1962, **1**, 848.

² F. A. Cotton and T. G. Dunne, *J. Amer. Chem. Soc.*, 1962, **84**, 2013.

³ F. A. Cotton and J. G. Bergman, *J. Amer. Chem. Soc.*, 1964, **86**, 2941.