Novel Co-ordination Numbers in Scandium(III) and Yttrium(III) Nitrato-complexes. *X*-Ray Crystal Structures of $Sc(NO_3)_3.2N_2O_4$ and $Y(NO_3)_3.2N_2O_4$

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Summary *X*-Ray crystallographic studies of the anions $[Sc(NO_3)_5]^{2-}$ and $[Y(NO_3)_5]^{2-}$, which have been prepared using liquid N_2O_4, have revealed novel co-ordination numbers of nine for scandium(III) and ten for yttrium(III), with geometries best described in terms of a pseudo-trigonal bipyramid.

SEVERAL N_2O_4 solvates, generally formulated as $Sc(NO_3)_3 \cdot xN_2O_4$ (x = 1·0—1·9), are reported[1] to be the products of the reaction of liquid N_2O_4 with anhydrous $ScCl_3$ at 303 K but repetition of the reaction in these laboratories, under a variety of conditions, resulted in only partial removal of chloride. The Russian authors[1] conducted the reaction 'in an ethyl acetate medium' and report the isolation of scandium(III) nitrate–ethyl acetate solvates from this system after evacuation. With certain metal chlorides, *e.g.*, $FeCl_3$[2] and $BeCl_2$,[3] however, it has been found necessary to evaporate dinitrogen tetroxide–ethyl acetate mixtures to a small bulk before addition of an excess of liquid N_2O_4 in order to obtain a pure, crystalline metal nitrate–dinitrogen tetroxide solvate. Following this procedure, colourless crystals of $Sc(NO_3)_3 \cdot 2N_2O_4$ (I) are readily isolated from the reaction of $ScCl_3$ with an equivolume mixture of N_2O_4 and ethyl acetate. In contrast to many reported solvates, *e.g.*, $Cu(NO_3)_2 \cdot N_2O_4$[4] and $Fe(NO_3)_3 \cdot 1{\cdot}5N_2O_4$,[2] the scandium compound retains its crystallinity even after evacuation at room temperature.

$Y(NO_3)_3$ is formed[5] by reaction of liquid N_2O_4 with Y_2O_3 in a sealed tube at 423 K, but no N_2O_4 solvate of this nitrate has been reported. The compound $Y(NO_3)_3 \cdot 2N_2O_4$ (II) has now been prepared, again as colourless crystals, after the reaction of yttrium metal with an equivolume mixture of N_2O_4 and ethyl acetate using the procedure described above. These crystals are also stable under reduced pressure at ambient temperatures.

A single crystal of each of the moisture-sensitive solvates was sealed into a 0·3 mm diameter capillary tube and unit cell parameters obtained initially from *X*-ray photographs were refined using a Hilger and Watts four-circle diffractometer.

Crystal data: $Sc(NO_3)_3 \cdot 2N_2O_4$, (I) M 414·6, monoclinic, space group $P2_1/c$, a = 8·074(5), b = 11·581(9), c = 14·128(8) Å, β = 102·15(8)°, Z = 4, D_c = 2·09 g cm^{-3}. $Y(NO_3)_3 \cdot 2N_2O_4$, (II) M 458·9, monoclinic, space group $P2_1/c$, a = 8·055(10), b = 11·981(10), c = 14·160(7) Å, β = 104·80(10)°, Z = 4, D_c = 2·16 g cm^{-3}.

In each case the structure was solved by the usual Patterson and Fourier methods. The analysis of the structure of (I) was based on 1597 independent, observed reflections collected in the range $0 \leqslant \theta \leqslant 25{\cdot}0°$ with Mo-K_α radiation (λ = 0·7107 Å). A conventional R value of 4·8% was achieved after weighted, block-diagonal, least-squares refinement had converged with anisotropic temperature factors for each atom. 2022 statistically observed reflections measured out to 27·5° were used in the refinement of the structure of (II). Weighted, full-matrix, least-squares refinement with anisotropic temperature factors gave a final R value of 6·0%.

As observed for other structurally characterised N_2O_4 solvates of metal nitrates,[6–8] the compounds are nitrosonium nitrato-metallates of composition $(NO^+)_2[Sc(NO_3)_5]^{2-}$

and $(NO^+)_2[Y(NO_3)_5]^{2-}$. Thus, in common with the N_2O_4 solvates of Fe^{III}[7] and Ho^{III}[8] nitrates, discrete nitrato-anions are present whereas in $Cu(NO_3)_2 \cdot N_2O_4$[6] bridging nitrate ligands are found and the anion is polymeric.

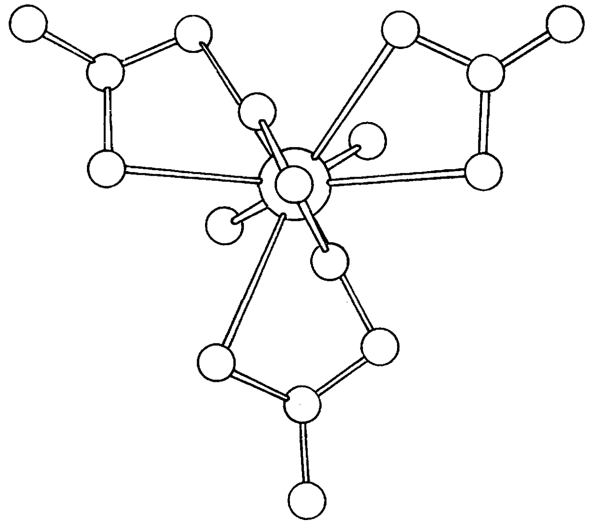

FIGURE 1. The $[Y(NO_3)_5]^{2-}$ anion viewed along the axial direction of the pseudo-trigonal bipyramid. The mean $Y-O_2NO$ bond length is 2·439(6) Å.

Although the unit cell dimensions in both crystals are similar, the stereochemistries of the yttrium and scandium pentanitrato-metallate(III) anions differ significantly, as is apparent from Figures 1 and 2. In the yttrium anion each nitrate group is symmetrically bidentate[9] and the overall co-ordination geometry closely resembles that reported for the lanthanide species $[Ce(NO_3)_5]^{2-}$[10] and $[Ho(NO_3)_5]^{2-}$.[8] The structure is most easily visualised following the structural principle enunciated by Bergman and Cotton[11] whereby the mean positions of the close pairs of ligand oxygen atoms lie at the vertices of a trigonal bipyramid.

In the nitrato-complexes, $M_2[Sc(NO_3)_5]$ (M = K, Rb, or Cs), i.r. spectroscopy was taken to indicate the presence of both unidentate and bidentate nitrate groups.[12] *X*-Ray analysis of the nitrosonium salt has now revealed four bidentate and one unidentate nitrate groups so that the Sc^{III} is nine-co-ordinate. The geometrical relationship between the co-ordination at the scandium atom of $[Sc(NO_3)_5]^{2-}$ and that at the yttrium centre of $[Y(NO_3)_5]^{2-}$ becomes apparent from the Figures in which both anions are viewed along the axial direction of the pseudo-trigonal bipyramid. The obvious difference is seen to be the presence of the unidentate nitrate group in the scandium anion presumably resulting from the smaller size of Sc^{3+} and its inability to achieve ten-co-ordination even with one of the most versatile ligands for the generation of high co-ordination numbers.

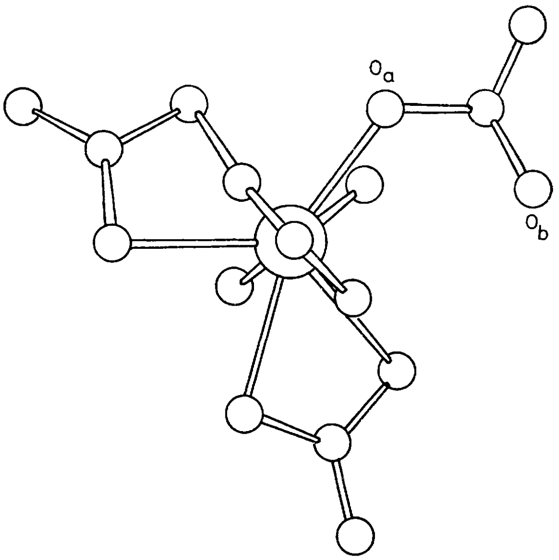

FIGURE 2. The $[Sc(NO_3)_5]^{2-}$ anion viewed in the same orientation as $[Y(NO_3)_5]^{2-}$ in Figure 1. Some bond lengths and distances are: $Sc-O_a$, 2·176(3); $Sc-O_b$, 3·231(4); and mean $Sc-O_2NO$, 2·283(4) Å.

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