First Case of an Eleven-co-ordinated Trivalent Lanthanoid: X-Ray Crystal Structure of Penta-aquatri(nitrato)lanthanum(III) Monohydrate

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Summary In the structure of $[La(NO_3)_3(H_2O)_5]\cdot H_2O$ (determined by *X*-ray crystallography) the lanthanum atom is surrounded by three bidentate nitrate ligands and five water molecules; this result indicates a hitherto unknown co-ordination number of eleven for a trivalent lanthanoid.

MAINLY owing to their large size the trivalent lanthanoids are capable of acquiring high co-ordination numbers, nine or higher being quite common.[1] This is the case especially with the first members of the lanthanoid series in combination with suitable ligands, such as the bidentate nitrato group, which have a short 'bite'. To our knowledge, however, a co-ordination number of eleven has not been encountered in any of these or other lanthanoid(III) structures studied so far, but it has been found in the tetravalent $Th(NO_3)_4\cdot 5H_2O$.[2,3]

During our systematic investigation into nitrato-complexes of La^{III} we have found that in the structure of $La(NO_3)_3\cdot 6H_2O$ there are eleven oxygen atoms around La^{III} at distances $<2{\cdot}9$Å .

Well formed crystals of lanthanum nitrate hexahydrate were produced at room temperature by dissolving lanthanum oxide in aqueous nitric acid and recrystallizing

twice from the aqueous solution. The crystals were not completely stable in air at room temperature, and they were therefore covered with shellac before the data collection. Intensities of reference reflections showed, however, that decomposition had occurred during data collection, and an appropriate correction had to be applied to the data.

Crystal data: $La(NO_3)_3(H_2O)_5 \cdot H_2O$, $M = 433{\cdot}01$, triclinic, $a = 8{\cdot}933(5)$, $b = 10{\cdot}732(4)$, $c = 6{\cdot}664(2)$ Å, $\alpha = 78{\cdot}86(3)$, $\beta = 77{\cdot}92(4)$, $\gamma = 87{\cdot}91(4)°$, $U = 612{\cdot}4$ Å^3, $D_m = 2{\cdot}35(1)$ g cm^{-3}, $Z = 2$, $D_c = 2{\cdot}347$ g cm^{-3}, space group $P\bar{1}$, μ(Mo-K_α) = 34·9 cm^{-1} (no correction applied), λ(Mo-K_α) = 0·71069 Å. All reflections in the range $5° < 2\theta < 60°$ were measured using a Syntex $P2_1$ diffractometer with graphite-monochromated Mo-K_α-radiation; a θ–2θ scan technique was used. Intensities of 3048 reflections, corrected for Lorentz and polarizing effects, and satisfying the criterion $I > 3\sigma(I)$, were used in subsequent calculations. The La position was obtained from a Patterson map and the other nonhydrogen atoms from electron density calculations. Full-matrix least-squares refinement of the structure (Figure) with anisotropic temperature factors has given the present R-value of 0·033 based on 2918 reflections.

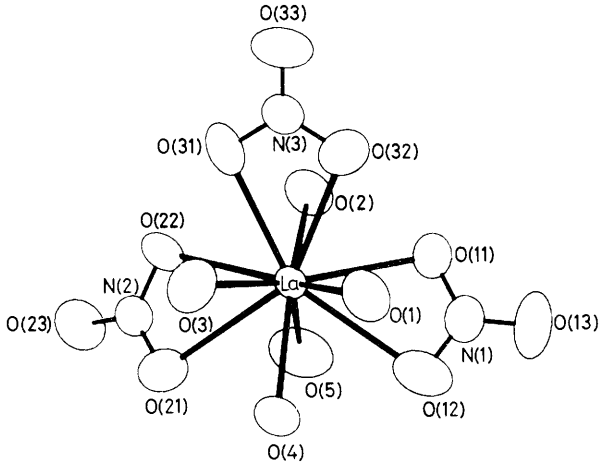

FIGURE. Structure of $[La(NO_3)_3(H_2O)_5]$.

The lanthanum atom is surrounded by eleven oxygen atoms at distances of 2·524—2·877 Å. Of these, five belong to water molecules [O(1)—O(5)] at distances of 2·662, 2·587, 2·560, 2·560, and 2·524 Å, respectively. The average value of La–O(water) is 2·579 Å: the estimated standard deviations of the La–O distances are, on the average, 0·005 Å. The sixth water molecule, located outside the co-ordination sphere of lanthanum, is held in the structure by hydrogen bonds.

All three nitrato-groups are bidentately bound to the central atom. Two of them seem to be, probably for steric reasons, unsymmetrically bound: the distances vary by more than 0·2 Å [La–O(11) 2·622, La–O(12) 2·845 Å; La–O(22) 2·663, La–O(21) 2·877 Å]. The third nitrate group shows symmetrical bond lengths of 2·689 and 2·697 Å for La–O(31) and La–O(32), respectively. The N–O distances are in the range 1·209—1·282 Å; the shortest distances are those involving the non-co-ordinated nitrate oxygen atoms. The La–O(12) and La–O(21) distances exceed the sum of the corresponding ionic radii by some 0·15 Å;[4] the distances are, however, less than the reported maximum distance in some other high-co-ordination polyhedra, *e.g.*, in $[Ho(HCO_3)_3(H_2O)_4]H_2O$.[5] However, the two oxygen atoms involved belong to nitrato-groups, and should thus be included in the co-ordination sphere.

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