Crystal Structure of the Cerium(III) Pentanitrate Ion: a Ten-co-ordinate Stereochemistry based on a Trigonal Bipyramid

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Summary The structure of the cerium(III) pentanitrate ion is described: the anion has ten-co-ordinate stereochemistry based on a trigonal bipyramid.

SEVERAL crystal structure analyses of complexes containing ten-co-ordinate metal atoms have been reported recently,[1,2] but in only one instance,[2] does the co-ordination geometry appear to closely approach the shape of one of the two "idealised" polyhedra suggested for ten-co-ordination, *viz.*, the bicapped square antiprism of D_{4d} point symmetry and the bicapped dodecahedron of D_2 symmetry.[3]

Since ligand–ligand repulsion calculations have shown the D_{4d} geometry to be appreciably more stable than D_2 polyhedron,[4] we felt it of interest to examine one of the lanthanide nitrate complexes formulated as $M(NO_3)_3$-$2(R_4PNO_3)$ since it seemed that these might contain $M(NO_3)_5{}^{2-}$ ions.[5] In addition to giving further information on ten-co-ordination stereochemistry, such an ion should afford the opportunity to test further the principle postulated by Cotton and Bergman in describing the structures of the $Co(NO_3)_4{}^{2-}$ and $Ce(NO_3)_6{}^{3-}$ ions,[6] namely that if the nitrate ion ligands are viewed as occupying one co-ordination position around a central atom, then the resulting polyhedron has one of the accepted geometries appropriate to the lower co-ordination number.

We have carried out a structure analysis of the $Ce(NO_3)_5{}^{2-}$ ion, in the form of its triphenylethylphosphonium salt, and find that this principle appears to work well, since the mid-points of the five nitrate ligands define an almost perfect trigonal bipyramid around the cerium atom. The complex crystallises in space group $C2/c$ and the anion has crystallographically-required C_2 point symmetry. The analysis was carried out using *ca.* 2000 photometrically measured intensities collected by the precession method, and the residual at the present level of refinement is 10·5%. The anion is ten-co-ordinate as expected and all metal oxygen distances are equivalent to within the standard deviations, the average being 2·58(2) Å.

The structure as a whole bears a close resemblance to the tetraphenylarsonium tetranitratocobaltate[6] and manganate[7] salts, the unit cells being almost isodimensional. A fairly small rearrangement of the four nitrate groups in the anions is all that is necessary in order to accommodate the fifth nitrate on the twofold axis and this similarity is thus readily understood.

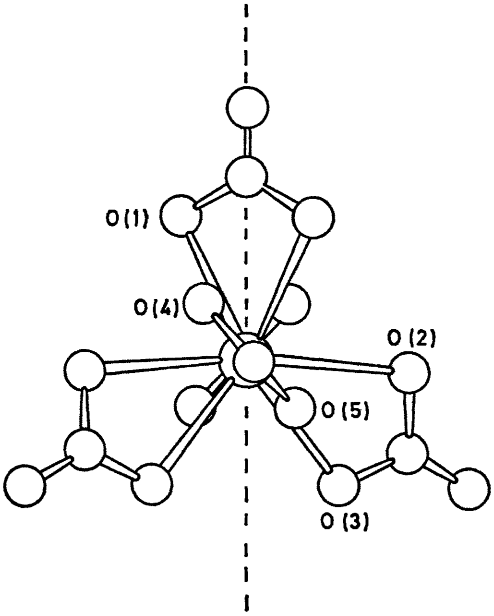

FIGURE. *The cerium*(III) *pentanitrate ion projected on to the* (001) *plane. The location of the crystallographic twofold axis is indicated.*

The structure of the pentanitrate ion projected on to (001) is illustrated in the Figure and this view which is almost along the principal axis of the trigonal bipyramid, clearly shows the nitrate ions approximately related by a threefold axis. These three ions, which thus constitute the equatorial set of ligands, are almost coplanar with one another and with the cerium atom, while the two axial nitrate ions whose terminal N–O bonds lie very close to a line through the central atom and normal to the equatorial plane, have a dihedral angle of *ca.* 80° between their planes.

If the polyhedron is described in terms of one of the idealised ten-co-ordination geometries, then the bicapped dodecahedron would seem preferable to the energetically more favourable bicapped square antiprism, since atoms O(1), O(4), O(5), and O(3), together with their twofold related set, define the two trapezoidal planes of the dodecahedron, rather better than this group of eight atoms defines the square antiprism. However, as might be anticipated, the constraints resulting from the short 'bite' of the nitrate ligand introduce large angular deviations from either of the calculated polyhedra,[4] so that reference to them is not very meaningful. In any event, the resemblance to the five-co-ordination geometry of the trigonal bipyramid is so clear, that we feel such a description is to be preferred.

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