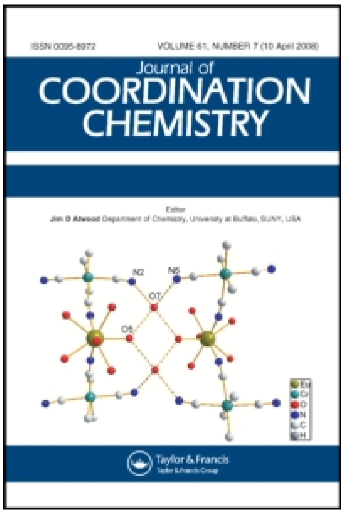

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Research note

Tetramethylammonium hexanitratoneodymiate(III). Structural variations of the $[Nd(NO_3)_6]^{3-}$ anion in a single crystal

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The structure of tetramethylammonium hexanitratoneodymiate(III) has been determined at 123 K in the suprisingly low symmetry space group $P\bar{1}$ considering the simplicity of the compound. The structure has $Z' = 4$ with seventeen distinct chemical fragments in the asymmetric unit (12 tetramethylammonium cations, three complete $[Nd(NO_3)_6]^{3-}$ anions and two half $[Nd(NO_3)_6]^{3-}$ species situated on special positions). This one structure contains five different coordination geometries of the $[Nd(NO_3)_6]^{3-}$ species.

Keywords: Lanthanoids; Nitrato complex; Z'

1. Introduction

There has been considerable recent interest in the study of crystal structures that contain a large number of crystallographically unique formula units, denoted by the Z' parameter [1–2]. It has recently been established that approximately 8.8% of structures in the Cambridge Structural Database possess values of $Z' > 1$ [3]. It is postulated that unusual packing is often a result of strong intermolecular interactions or awkwardly shaped molecules. However, some structures, such as the title compound, display high Z' values despite high molecular symmetry and lack of sites with the potential for any significant intermolecular association. Tetramethyl- and tetraethylammonium salts have been found to show no predisposition towards forming structures with $Z' > 1$. Searches of the Cambridge Structural Database (version 5.27, November 2005 + 3 updates) show no particular trend concerning high Z' structures of tetramethylammonium salts. There are 1405 Me_4N^+ structures in the database of which only 79 possess $Z' > 1$ and only 14 with $Z' > 2$. The most noteworthy structures containing $Z' > 2$ are of the simple salts $Me_4N(SO_4H)$ [4] and $[Me_4N]_2[ZnCl_4]$ [5–6] which both show temperature dependent phase transitions with varying values of Z' between 0.5 and 5. Tetraethylammonium salts show a similar frequency of high Z'

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structures (185 of 2690 have $Z' > 1$, 13 have $Z' > 2$). Out of these Et_4N^+ structures, four are of particular relevance to this current study as they are in the space group $P\bar{1}$ with $Z' = 4$. As with the high Z' Me_4N^+ structures, the Et_4N^+ compounds are relatively simple compounds with little potential for strong inter-species interaction; tungstate complexes [7], $[Cr(CN)_5]^{3-}$ [8] and bis(trifluoromethanesulfonyl)amide complexes [9]. Herein we report the simple tetramethylammonium salt of hexanitratoneodymiate(III) which contains five crystallographically unique and geometrically distinct $[Nd(NO_3)_6]^{3-}$ anions.

2. Experimental

2.1. *Synthesis*

$Nd(NO_3)_3 \cdot 6H_2O$ (43 mg, 98 mmol), tetramethylammonium dicyanonitrosomethanide (dicyanonitrosomethanide = $[C(NO)(CN)_2]^-$) (50 mg, 298 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (33 mg, 136 mmol) were dissolved in acetone (3 mL). The resultant solution was left to evaporate over the course of 2 weeks, resulting in small, pale purple crystals of the title compound.

2.2. *Crystallography*

Data were collected using a Nonius Kappa-CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A temperature of 123 K was maintained using an Oxford Cryostreams open-flow N_2 cryostat. Data were integrated using the DENZO [10] package and scaled using SORTAV [11]. An initial solution was obtained using Patterson synthesis with SHELXS-97 [12] before conventional least-squares refinement using F^2 in SHELXL-97 [12] using the program X-Seed [13] as a graphical interface. All hydrogen atoms were placed in calculated positions and refined with a riding model [C–H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$]. One of the tetramethylammonium cations (containing N36) shows minor signs of disorder that could not be satisfactorily modelled. The largest residual Fourier peak lies 1.12 Å from Nd5 and the largest hole lies 0.79 Å from C46 (part of the disordered Me_4N^+ residue).

Crystal data for $[Me_4N]_3[Nd(NO_3)_6]$: $C_{12}H_{36}N_9Nd_1O_{18}$, $M = 738.74$, pale purple block, $0.10 \times 0.10 \times 0.06$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 17.7787(2)$, $b = 18.3664(2)$, $c = 19.2285(2)$ Å, $\alpha = 106.736(1)$, $\beta = 90.442(1)$, $\gamma = 97.531(1)^\circ$, $V = 5954.04(11)$ Å^3, $Z = 8$, $D_c = 1.648$ g cm^{-3}, $F_{000} = 3000$, $2\theta_{max} = 55.0^\circ$, 93409 reflections collected, 27286 unique ($R_{int} = 0.0560$). Final GoF = 1.032, $R_1 = 0.0392$, $wR_2 = 0.0806$, R indices based on 20166 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1493 parameters, 0 restraints, $\mu = 1.830$ mm^{-1}.

3. Results and discussion

The title compound, $[Me_4N]_3[Nd(NO_3)_6]$, was serendipitously obtained during the course of research into metal complexes of the dicyanonitrosomethanide anion [14].

The presence of nitrate in the reaction mixture instead led to the formation of the hexanitrato complex. We previously reported a similar product, $[Me_4N]_3[La(NO_3)_6]$, that was obtained as a methanol solvate [15] although in this case the crystals grew in the space group $P2_1/c$ and contained only one formula unit per asymmetric unit. The present use of acetone as a reaction medium instead yields solvent-free crystals with the composition $[Me_4N]_3[Nd(NO_3)_6]$.

$[Me_4N]_3[Nd(NO_3)_6]$ crystallizes in the low symmetry space group $P\bar{1}$ with $Z' = 4$, figure 1. The Addsym routine in PLATON [16] does not suggest any higher symmetry and there are no large matrix correlations. Unit cell measurements at room temperature show the same dimensions (allowing for thermal expansion) and upon slow cooling no phase change is observed. The Z' value of four is misleading as the unit cell contains two $[Nd(NO_3)_6]^{3-}$ anions that are situated on special positions. Therefore the contents of the asymmetric unit are three complete anions and two half anions (giving five unique anions) and twelve tetramethylammonium cations ($Z'' = 17$) [17]. That the compound crystallises with such low symmetry is surprising considering that the tetrabutylammonium analogue, $[nBu_4N]_3[Nd(NO_3)_6]$, crystallises in the space group $P2_1/n$ [18].

The coordination of the nitrate ligands around the neodymium atoms does not vary significantly in terms of either the Nd–O distances or O–Nd–O angles in the structure. The average Nd–O bond length is 2.603 Å and all 24 unique Nd–O bonds occur within a

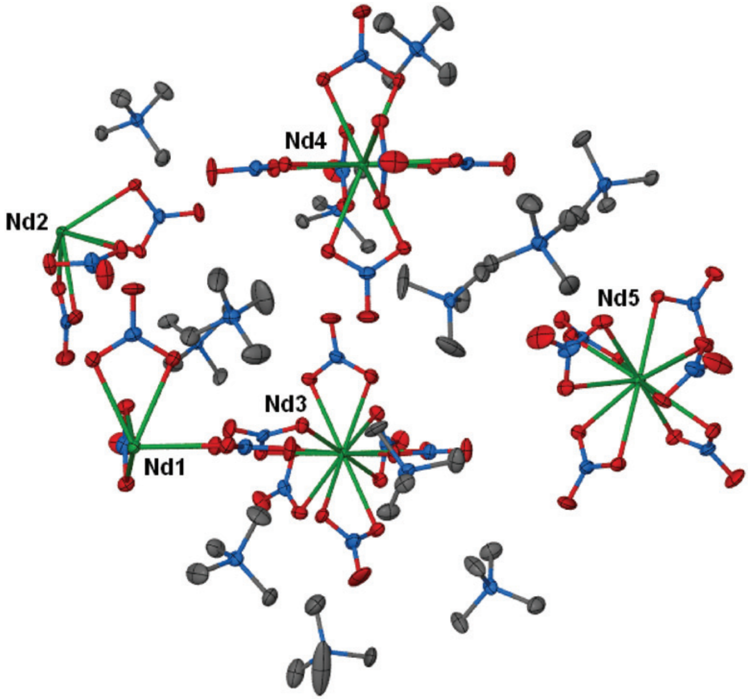

Figure 1. The asymmetric unit of $[Me_4N]_3[Nd(NO_3)_6]$ contains three complete $[Nd(NO_3)_6]^{3-}$ anions (Nd3, Nd4, Nd5), two anions situated over special positions (Nd1, Nd2) and twelve tetramethylammonium countercations giving $Z' = 4$ and $Z'' = 17$. Displacement ellipsoids shown at 50% probability, hydrogen atoms not shown for clarity.

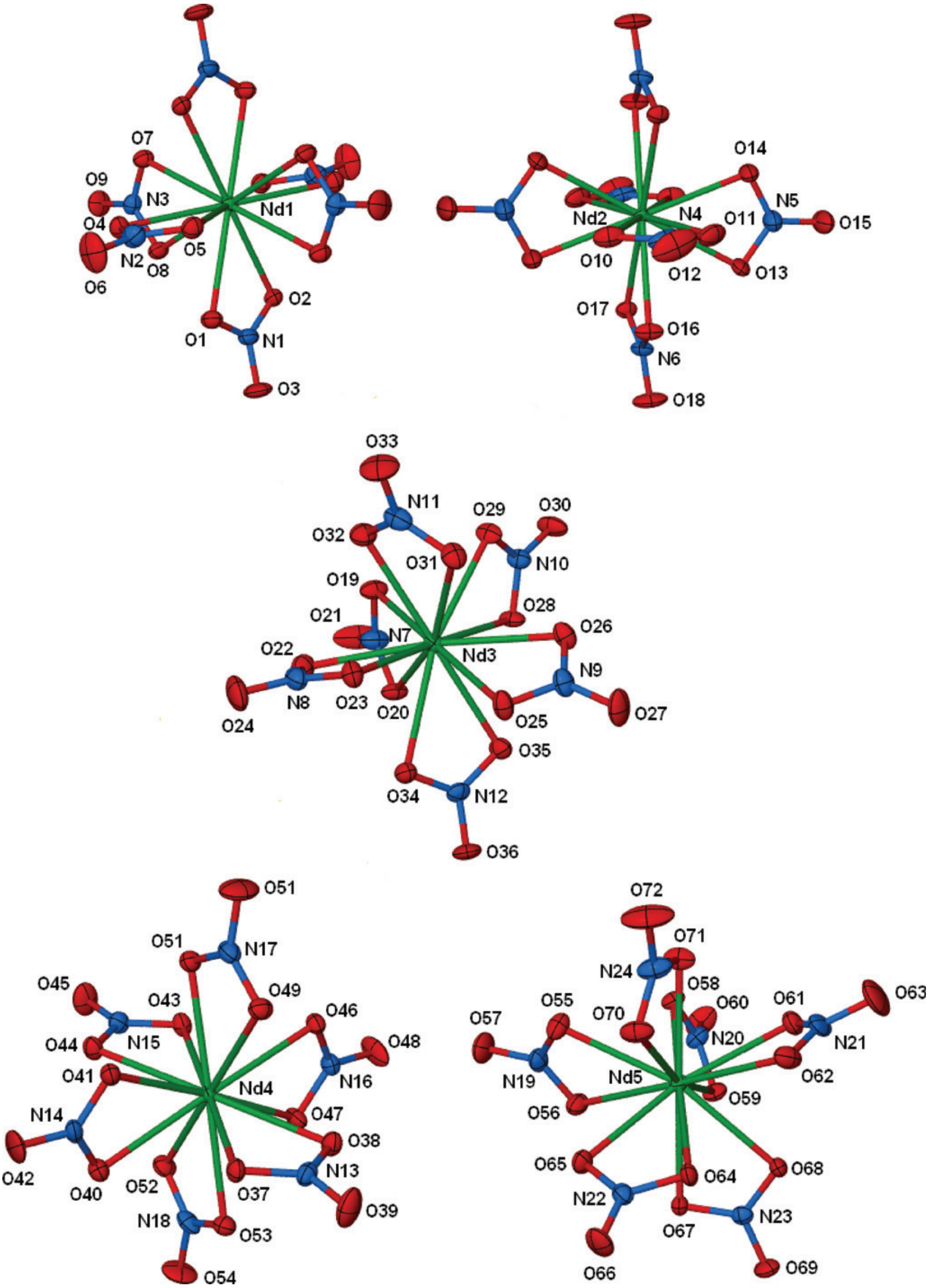

Figure 2. The coordination geometries of the five unique $[Nd(NO_3)_6]^{3-}$ anions are different. The anions based around Nd3 and Nd5 are substantially different from the symmetrical pseudo-octahedral geometries that are expected. Only half of the each of the Nd1 and Nd2 anions is unique due to the metal atoms residing on special positions.

Table 1. Interplanar nitrato angles in the $[Nd3(NO_3)_6]^{3-}$ anion.

	N8	N9	N10	N11	N12
N7	89.0	82.6	61.5	36.3	82.0
N8	–	36.4	76.6	60.9	89.9
N9	–	–	76.7	85.8	56.5
N10	–	–	–	88.3	25.4
N11	–	–	–	–	76.2

Table 2. Interplanar nitrato angles in the $[Nd5(NO_3)_6]^{3-}$ anion.

	N20	N21	N22	N23	N24
N19	61.4	77.5	89.8	33.4	87.3
N20	–	84.6	76.8	87.6	32.2
N21	–	–	31.0	85.6	58.2
N22	–	–	–	62.3	85.1
N23	–	–	–	–	77.4

range of less than 0.1 Å (2.555(3)–2.642(2) Å). The average O–Nd–O angle is 49.09° within the narrow range 48.64(7)–49.63(8)°. Within $[Ln(NO_3)_6]^{3-}$ anions the nitrato ligands are usually positioned pseudo-octahedrally around the metal atom in an arrangement that minimizes repulsion between ligands [15]. The nitrate ligands are also usually oriented so as to be mutually perpendicular to one another with opposing ligands being close to co-planar. The structure of $[Me_4N]_3[Nd(NO_3)_6]$ contains only three out of five unique anions that adopt the expected coordination geometry (those containing Nd1, Nd2 and Nd4), Figure 2. In the cases of the Nd1 and Nd2 anions the geometry is enforced by symmetry restraints due to the metal atoms being positioned on the inversion centres (0, 0, 0) and (0, 0, 1/2), respectively. The anions containing Nd1 and Nd4 all contain opposing nitrate ligand pairs that are coplanar and all adjacent ligands are perpendicular. The orientations of these ligands are such that three mutually perpendicular planes intersect at the central metal atom. The Nd2 anion has a slight distortion in the coordination geometry with the N6-nitrate ligands (opposite each other) slightly out of position so that their planes are parallel and not coplanar.

The Nd3 and Nd5 centred anions show significant distortions of the pseudo-octahedral coordination geometry and a change in the relative orientations of the nitrate ligands (Tables 1 and 2). The Nd3 anion has N ··· Nd ··· N angles in the range 73–116° with the Nd5 anion showing a similar range of angles, 72–116°, both of which ranges are far from the octahedral ideal. In both cases there are instances where adjacent ligands are not perpendicular, such as the N10/N12 and N21/21 pairs of adjacent ligands, which are nearing a co-planar orientation (angles between planes = 25.4 and 31.0°, respectively). In some cases opposing ligands are close to perpendicular (e.g., the N23/24 ligands, angle between planes = 77.4°).

The tetramethylammonium cations, with one exception, are well ordered in the structure despite the lack of strong hydrogen bonding. Weak CH ··· O hydrogen bonding is observed between the cations and anions with distances in the range 2.4 to 3.0 Å. There are 155 unique CH ··· O interactions within the sum of the van der Waals radii of the two atoms plus 0.1 Å. The cations surround the $[Nd(NO_3)_6]^{3-}$ anions and separate them from each other.

4. Conclusion

The simple salt $[Me_4N]_3[Nd(NO_3)_6]$ crystallises in the low symmetry space group $P\bar{1}$ and contains five crystallographically unique $[Nd(NO_3)_6]^{3-}$ anions. The coordination geometries of three of the anions are as expected for a $[Ln(NO_3)_6]^{3-}$ anion, however, the remaining two show significant deviations from the ideal pseudo-octahedral geometry.

Supplementary data

Full crystallographic data have been deposited with the CCDC (ref. 622524). These data may be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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