Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

Cerous sodium nitrate monohydrate, $Na_2Ce(NO_3)_5 \cdot H_2O$

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Received 15 March 2000
Accepted 25 April 2000

The title compound, disodium cerium pentanitrate monohydrate, was synthesized from a nitric acid solution of $Ce(NO_3)_3 \cdot 6H_2O$ and $NaNO_3$, and its structure has been determined from single-crystal X-ray diffraction data. The structure is built from isolated chains of irregular icosahedral $[Ce(NO_3)_6]^{3-}$ anions. Na atoms and water molecules are located between the chains. The Na coordination polyhedra, in the form of a square antiprism or a monocapped square antiprism, share common vertices and contribute to the formation of a three-dimensional network. Ten nitrate groups act as bridging ligands.

Comment

The present structure determination is part of a detailed study of the thermal behaviour of Ce^{III} and Ce^{IV} nitrate-based precursors of cerium oxide. The cerium(III) compounds $M^I_2Ce(NO_3)_5 \cdot 4H_2O$, with M^I = Rb (Audebrand *et al.*, 1996) or NH_4 (Audebrand *et al.*, 1997*a*), and the similar compound $Ag_2Ce(NO_3)_5 \cdot H_2O$ (Audebrand *et al.*, 1997*b*) have been thoroughly investigated. The family is here extended to include a new mixed Na-based precursor, the title compound, $Na_2Ce(NO_3)_5 \cdot H_2O$, (I).

Compound (I) was identified from powder X-ray diffraction, and pattern indexing suggested isostructural properties with $Ag_2Ce(NO_3)_5 \cdot H_2O$, $Na_2Nd(NO_3)_5 \cdot H_2O$ (Vigdorchik *et al.*, 1990) and $Ce(NO_3)_5(H_3O)_2 \cdot H_2O$ (Guillou *et al.*, 1993). Although the crystals were unstable under ambient conditions, the structure determination has been successful and has confirmed the chemical formula of (I).

The structure of (I) consists of isolated chains parallel to [100] formed by 12-coordinate Ce polyhedra connected by nitrate groups (Fig. 1), with the alternation Ce1–Ce2–Ce3–Ce2–Ce1. The mean distance between two Ce atoms within a chain is 5.349 (1) Å. The Ce atoms are bonded to six nitrate groups in the form of an irregular icosahedron (Table 1). The mean Ce—O distances [2.65 (5), 2.65 (6) and 2.64 (4) Å for Ce1, Ce2 and Ce3, respectively] are in agreement with the value of 2.65 Å calculated by the bond-valence method (Brown, 1981, 1996).

The Na atoms and the water molecules are located between the chains, with two kinds of alternation of Na atoms parallel to the *c* axis, *i.e.* Na2–Na4–Na2–Na4 and Na1–Na3–Na1–Na3. The Na atoms are surrounded by eight or nine O atoms, similar to the Ag atoms in $Ag_2Ce(NO_3)_5 \cdot H_2O$, whereas the environments are different in $Na_2Nd(NO_3)_5 \cdot H_2O$. The Na coordination polyhedra are in the form of a distorted monocapped square antiprism for Na1 and Na2 (Fig. 2*a*), which is less common than the tricapped trigonal prism generally described for a ninefold coordination. Na4 is eight-coordinate in the shape of a distorted square antiprism. For Na3, the coordination is 8+1 and the polyhedron can be described as a square antiprism or a monocapped square antiprism. Indeed, the Na3—O93 bond lengh of 3.104 (3) Å is greater than the other Na—O distances [mean value 2.6 (2) Å, Table 1]. Although such a distance is uncommon, the largest Na—O distance considered as a bond is 3.13 Å, according to Donnay & Allmann (1970). The mean Na—O distances [2.7 (2), 2.6 (2), 2.6 (2) and 2.6 (2) Å for Na1, Na2, Na3 and Na4, respectively] are in acceptable agreement with the values (2.62 and 2.57 Å) calculated using the bond-valence method (Brown, 1981, 1996) for Na bonded to nine or eight O atoms.

The distortions of each Na coordination polyhedron have been estimated by the calculation of the mean atomic deviations from the least-squares planes. In the case of the Na4 square antiprism, the mean atomic deviations from the two

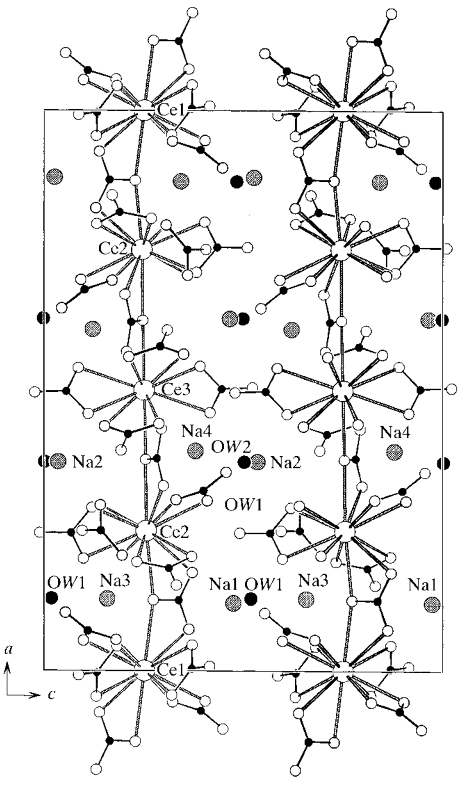

Figure 1
The projection of the structure of $Na_2Ce(NO_3)_5 \cdot H_2O$ along the *b* axis.

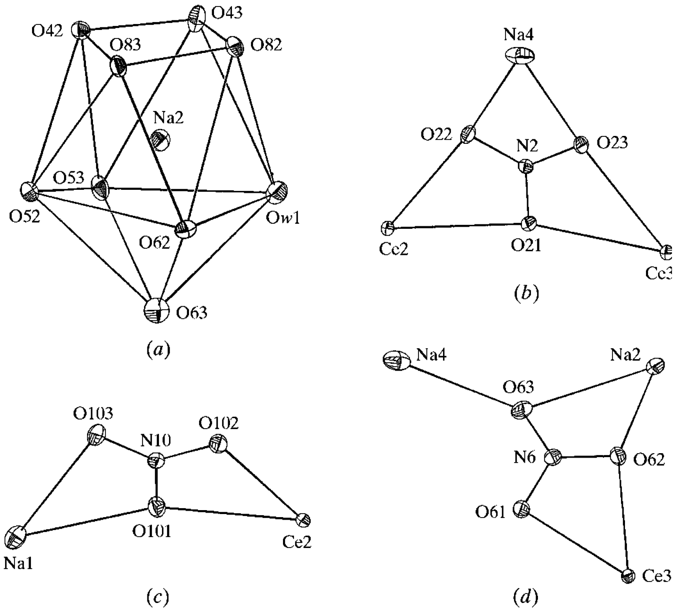

Figure 2
Views of (*a*) the environment in (I) of atom Na2, showing the distorted monocapped squared antiprism, and of the nitrate groups (*b*) N2, (*c*) N10 and (*d*) N6. Displacement ellipsoids are plotted at the 20% probability level.

planes are 0.1315 and 0.0795 Å. The angle between the two planes is 10.59 (9)°. The distances between Na4 and the two planes are 1.109 (3) and 1.369 (3) Å, which shows that Na4 is located near the centre of the square antiprism. For the Na1, Na2 and Na3 monocapped square antiprisms, the mean atomic deviations from the two planes are 0.1017 and 0.0826, 0.0358 and 0.0911, and 0.0080 and 0.0870 Å, respectively. The angles between the two planes are 15.98 (10), 4.71 (15) and 3.30 (14)°, respectively. As expected, the Na atoms are closer to the lower plane, which is close to the capped ninth O atom [distances 0.517 (2), 1.083 (2) and 1.215 (2) Å for Na1, Na2 and Na3, respectively], than to the upper plane [distances 1.687 (2), 1.724 (2) and 1.762 (2) Å for Na1, Na2 and Na3, respectively]. It can be noted that the equivalent isotropic atomic displacement parameter of Na4 is high [0.0473 (5) Å^2]. In fact, its displacement ellipsoid is significantly anisotropic in the direction of the chains of Ce icosahedra (Fig. 2). It is worthwhile noting that the equivalent Na atom in the structure of $Na_2Nd(NO_3)_5 \cdot H_2O$ and the Ag atom in $Ag_2Ce(NO_3)_5 \cdot H_2O$ also have high equivalent isotropic atomic displacement parameters.

The Na1 and Na4 coordination polyhedra share common vertices with four other polyhedra, whereas the Na2 and Na3 coordination polyhedra share only five vertices. Such connections generate infinite chains in the three crystallographic directions, leading to a three-dimensional network. In the *bc* plane, this network forms an irregular honeycomb generating tunnels along the *a* axis, which are filled by the chains of Ce coordination icosahedra. Ten nitrate groups act as bridging ligands. Two of them (N2 and N3) bridge two Ce coordination icosahedra and connect the two icosahedra to a polyhedron ($Na4O_8$ or $Na1O_9$ for N2 and N3, respectively). These nitrate groups (N2 and N3; Fig. 2*b*) belong to the class III6*b* proposed by Leclaire (1979). The nitrate group N10 (class II3*c*) bridges an icosahedron to the Na1 monocapped antiprism (Fig. 2*c*). All remaining nitrate groups ensure the connections between an icosahedron and two Na coordination polyhedra, generating infinite chains of Na polyhedra. They belong either to the class III6*b* (N1, N4, N5 and N8) or to the class III5 (N6, N7 and N9; Fig. 2*d*).

The water molecules, located between the chains of icosahedra, are bonded to the four Na atoms. Although attempts to locate the H atoms failed, it has been possible to distinguish some hydrogen bonds according to the criteria of Baur & Khan (1970). These bonds bridge the Ce coordination polyhedra, and Na atoms and water molecules contribute significantly to the structural framework.

Experimental

The title compound was obtained from the dissolution in boiling nitric acid of analytical grade $Ce(NO_3)_3 \cdot 6H_2O$ and $NaNO_3$ in the molar ratio 1:2. The solution was evaporated at 313 K until colourless rod-like crystals were formed. The crystals are hygroscopic. The single crystal used for structure analysis was mounted in a capillary containing dry oil to prevent its decomposition.

Crystal data

$Na_2Ce(NO_3)_5 \cdot H_2O$
$M_r = 512.15$
Monoclinic, $P2/c$
$a = 21.387$ (5) Å
$b = 7.9328$ (10) Å
$c = 15.184$ (3) Å
$\beta = 90.657$ (10)°
$V = 2575.9$ (10) Å^3
$Z = 8$

$D_x = 2.641$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.98$–13.65°
$\mu = 3.711$ mm^{-1}
$T = 293$ (2) K
Rod, colourless
0.25 × 0.23 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.860$, $T_{\max} = 0.999$
7649 measured reflections
7469 independent reflections
4530 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.013$
$\theta_{\max} = 29.97$°
$h = 0 \rightarrow 30$
$k = 0 \rightarrow 11$
$l = -21 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity decay: −1.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.062$
$S = 1.032$
7469 reflections
434 parameters
H atom parameters not defined

$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 2.1991P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.87$ e Å^{-3}
$\Delta\rho_{\min} = -1.85$ e Å^{-3}

Nitrate O atoms are denoted O11 to O103, and O*W*1 and O*W*2 correspond to water-O atoms. The magnitude of the minimal residual electron density corresponds to the deepest hole, located 0.19 Å from atom Ce3.

Table 1
Selected geometric parameters (Å, °).

Ce1—O11	2.623 (3)	Na1—O31^{v}	2.655 (3)
Ce1—O11^{i}	2.623 (3)	Na1—O33^{v}	2.722 (3)
Ce1—O12	2.611 (3)	Na1—O73^{vi}	2.576 (3)
Ce1—O12^{i}	2.611 (3)	Na1—O93^{vii}	2.839 (3)
Ce1—O31	2.713 (3)	Na1—O101	2.543 (3)
Ce1—O31^{i}	2.713 (3)	Na1—O103	2.790 (4)
Ce1—O32	2.704 (2)	Na1—O*W*1	2.429 (3)
Ce1—O32^{i}	2.704 (2)	Na2—O42	2.590 (3)
Ce1—O91	2.646 (3)	Na2—O43	2.875 (4)
Ce1—O91^{i}	2.646 (3)	Na2—O52	2.447 (3)
Ce1—O92	2.578 (3)	Na2—O53	2.544 (3)
Ce1—O92^{i}	2.578 (3)	Na2—O62	2.637 (3)
Ce2—O21	2.721 (3)	Na2—O63	2.964 (4)
Ce2—O22	2.744 (3)	Na2—O82^{v}	2.459 (3)
Ce2—O32	2.667 (2)	Na2—O83	2.530 (3)
Ce2—O33	2.722 (3)	Na2—O*W*2	2.395 (3)
Ce2—O41	2.592 (3)	Na3—O11	2.535 (3)
Ce2—O42	2.609 (2)	Na3—O13	2.585 (3)
Ce2—O71	2.588 (2)	Na3—O41	2.510 (3)
Ce2—O72	2.654 (3)	Na3—O43	2.839 (3)
Ce2—O81	2.659 (3)	Na3—O71^{viii}	2.431 (3)
Ce2—O82	2.600 (3)	Na3—O73^{viii}	2.701 (3)
Ce2—O101	2.616 (3)	Na3—O91^{viii}	2.455 (3)
Ce2—O102	2.567 (3)	Na3—O93^{viii}	3.104 (3)
Ce3—O21	2.691 (2)	Na3—O*W*1^{viii}	2.351 (3)
Ce3—O21^{ii}	2.691 (2)	Na4—O22^{viii}	2.615 (3)
Ce3—O23	2.681 (3)	Na4—O23^{viii}	2.509 (3)
Ce3—O23^{ii}	2.681 (3)	Na4—O51	2.399 (3)
Ce3—O51	2.601 (3)	Na4—O53	2.869 (3)
Ce3—O51^{ii}	2.601 (3)	Na4—O63^{ii}	2.678 (4)
Ce3—O52	2.584 (2)	Na4—O81	2.756 (3)
Ce3—O52^{ii}	2.584 (2)	Na4—O83^{iii}	2.428 (3)
Ce3—O61^{iii}	2.624 (3)	Na4—O*W*2^{ix}	2.386 (3)
Ce3—O61^{iv}	2.624 (3)	O*W*1—O13^{x}	3.099 (4)
Ce3—O62^{iii}	2.663 (3)	O*W*1—O72^{vi}	2.873 (3)
Ce3—O62^{iv}	2.663 (3)	O*W*1—O92^{vi}	2.952 (4)
Na1—O12	2.511 (3)	O*W*2—O61^{xi}	2.964 (4)
Na1—O13	2.891 (3)	O*W*2—O102^{viii}	2.954 (4)
O13^{x}—O*W*1—O72^{vi}	90.70 (10)	O72^{vi}—O*W*1—O92^{vi}	70.85 (9)
O13^{x}—O*W*1—O92^{vi}	76.03 (10)	O61^{xi}—O*W*2—O102^{viii}	74.44 (10)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $1 - x, y, \frac{1}{2} - z$; (iii) $x, -y, \frac{1}{2} + z$; (iv) $1 - x, -y, -z$; (v) $x, -y, z - \frac{1}{2}$; (vi) $x, 1 - y, z - \frac{1}{2}$; (vii) $-x, 1 - y, -z$; (viii) $x, y - 1, z$; (ix) $x, -1 - y, \frac{1}{2} + z$; (x) $x, 1 + y, z$; (xi) $1 - x, -1 - y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1089). Services for accessing these data are described at the back of the journal.

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