Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, -y, 1 - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

Data were corrected for Lorentz–polarization effects. The unit-cell dimensions were found by indexing the powder diffraction pattern with the program *DICVOL91* (Boultif & Louër, 1991). The final parameters were refined by the program *NBS*AIDS83* (Mighell, Hubbard & Stalick, 1981). The structure of (I) was solved by the Patterson method (Ce and K) and one subsequent difference Fourier synthesis (all other atoms). For (II), the atomic coordinates of the isostructural compound $(NH_4)_2Ce(NO_3)_6$ (Beineke & Delgaudio, 1968) were used as initial coordinates in the refinement. Calculations were performed with the *MolEN* (Fair, 1990) package on a MicroVAX 3100 computer. Diagrams were prepared using *ORTEPII* (Johnson, 1976).

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Cerous Potassium Nitrate, $K_3Ce_2(NO_3)_9$

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Abstract

The structure of cerous potassium nitrate, $K_3Ce_2(NO_3)_9$, which can be synthesized from an aqueous solution of cerous nitrate hexahydrate and potassium nitrate, or from a nitric acid solution of hydrated ceria and potassium nitrate, has been solved by single-crystal X-ray diffraction analysis. It comprises an anionic, $[Ce_2(NO_3)_9]^{3-}$, network of irregular icosahedra formed by bidentate nitrate groups around Ce atoms and linked to one another by bridging nitrate groups. The K atoms are located in the holes of the structure.

Comment

In a previous study (Guillou, Auffrédic, Louër & Louër, 1993), it was shown that Ce^{III} compounds could be obtained from a solution of hydrated ceria in nitric acid. In the course of the investigation of the system CeO_2–KNO_3–HNO_3–H_2O, a new cerium(III) nitrate compound was obtained. Indeed, from the dissolution in nitric acid of active hydrated ceria and potassium nitrate in stoichiometric quantities (ratio 1:2), colourless crystals appear at 313 K together with crystals of $K_2Ce(NO_3)_6$, the structures of two polymorphic phases of which have been reported (Guillou, Louër, Auffrédic & Louër, 1995). An alternative synthesis of the new compound is by the evaporation at 313 K of an aqueous solution of cerous nitrate hexahydrate and potassium nitrate (ratio 2:3). This reaction demonstrates that the new phase is a Ce^{III} compound. Furthermore, the crystal structure determination reported here shows that this compound is the tripotassium dicerium(III) nitrate, $K_3Ce_2(NO_3)_9$.

The structure of the title compound (Fig. 1) consists of a three-dimensional $[Ce_2(NO_3)_9]^{3-}$ network of irregular icosahedra in which Ce atoms are twelvefold coordinated (Fig. 2). The coordination of the Ce atoms involves six bidentate nitrate groups. Three of these nitrate groups each bridge two icosahedra. This network can also be described as spirals running along the *c* axis (Fig. 3). As a result of the cubic symmetry, these spirals also run along the *a* and *b* axes, from which the three-dimensional network arises. The mean Ce—O distance (2.649 Å) is similar to the value (2.649 Å) calculated by the bond-valence method (Brown, 1981) for

Ce^{III} bonded to 12 O atoms. This value is in agreement with those found for $Ce(NO_3)_5(H_3O)_2.H_2O$ (mean value 2.638 Å; Guillou, Auffrédic, Louër & Louër, 1993) and $Ce_2Mg_3(NO_3)_{12}.24H_2O$ (mean value 2.64 Å; Zalkin, Forrester & Templeton, 1963).

The first nitrate group (N1) is symmetrically bidentate and belongs to the class I_{2b}, proposed by Leclaire (1979). As found for this class of nitrate compounds, the distance from the N atom to the non-coordinated O atom [1.217 (8) Å] is significantly shorter than the other N—O distances (mean value 1.265 Å). The displacement parameter of the free O atom of the nitrate group is higher than those of the coordinated O atoms, and the O—N—O angle between the two coordinated O atoms is smaller than the O—N—O angles involv-
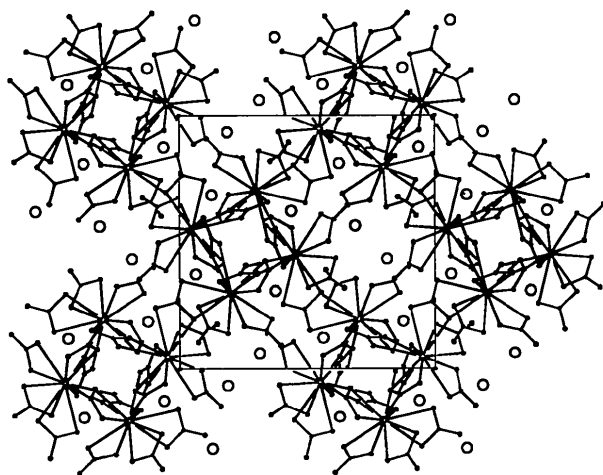

Fig. 3. Stereoscopic view of one spiral in the unit cell of $K_3Ce_2(NO_3)_9$.

Fig. 1. Projection of the structure of $K_3Ce_2(NO_3)_9$ along the c axis. Large circles represent K atoms.

ing the free O atom. The second nitrate group (N2) bridges two icosahedra and ensures the continuity of the structure. The O atoms are thus bonded to Ce atoms as in the class II_{3b} (Leclaire, 1979). The bond length from the N atom to the twofold-coordinated O atom [1.275 (5) Å] is significantly longer than the other N—O distances [1.234 (7) Å] and the displacement parameter of the twofold-coordinated O atom is also lower. It can be noted that this class of nitrate groups was also found in the structure of the hydronium cerium(III) nitrate hydrate, $Ce(NO_3)_5(H_3O)_2.H_2O$ (Guillou, Auffrédic, Louër & Louër, 1993).

The K atoms, located in the holes of the structure, are surrounded by ten O atoms and are linked by ionic contacts.

Experimental

An aqueous solution of cerium(III) nitrate hexahydrate, $Ce(NO_3)_6.6H_2O$, and potassium nitrate, KNO_3, (ratio 2:3) was evaporated at 313 K. Colourless crystals of $K_3Ce_2(NO_3)_9$ were formed after a few days.
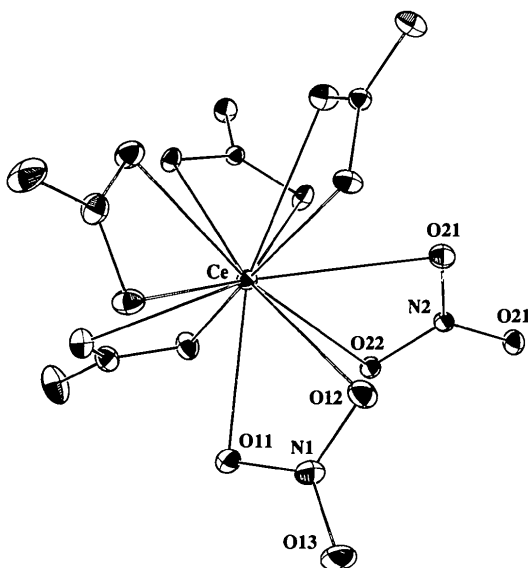

Fig. 2. View of the environment of the independent Ce atom showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 20% probability level.
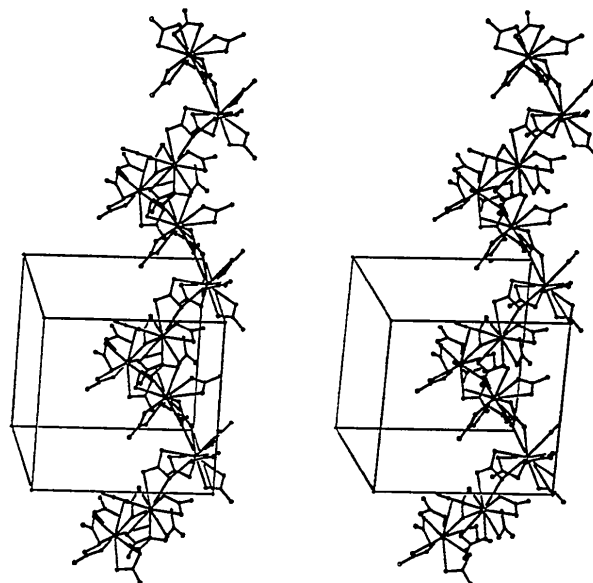
Crystal data

$K_3Ce_2(NO_3)_9$	Mo $K\alpha$ radiation
$M_r = 955.6$	$\lambda = 0.71073$ Å
Cubic	Cell parameters from 24
$P4_132$	reflections
$a = 13.5975$ (8) Å	$\theta = 7.3–12.7°$
$V = 2514.1$ (4) Å^3	$\mu = 4.255$ mm^{-1}
$Z = 4$	$T = 293$ K
$D_x = 2.525$ Mg m^{-3}	Block
	$0.25 \times 0.25 \times 0.12$ mm
	Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer	1857 observed reflections [$I > 3\sigma(I)$]
$\theta/2\theta$ scans	$R_{int} = 0.081$
Absorption correction:	$\theta_{max} = 30°$
ψ scan (North, Philips & Mathews, 1968)	$h = 0 \rightarrow 19$
	$k = 0 \rightarrow 19$
$T_{min} = 0.5299$, $T_{max} = 0.9549$	$l = 0 \rightarrow 19$
4064 measured reflections	2 standard reflections frequency: 60 min
2910 independent reflections	intensity decay: 2.2%

Refinement

Refinement on F	Extinction correction: Stout
$R = 0.044$	& Jensen (1968)
$wR = 0.055$	Extinction coefficient:
$S = 1.25$	6.8×10^{-8}
1857 reflections	Atomic scattering factors
65 parameters	from *International Tables*
$w = 1/\sigma^2(F)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} < 0.01$	(1974, Vol. IV)
$\Delta\rho_{max} = 1.6$ e Å^{-3}	
$\Delta\rho_{min} = -0.5$ e Å^{-3}	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ce	0.54899 (3)	x	x	1.472 (2)
K	3/8	0.1875 (1)	$\bar{y}+3/4$	3.05 (3)
N1	0.3995 (5)	0.4124 (5)	0.6397 (5)	2.5 (1)
O11	0.4440 (4)	0.3900 (3)	0.5610 (4)	2.47 (9)
O12	0.4170 (4)	0.4964 (4)	0.6753 (4)	2.7 (1)
O13	0.3419 (5)	0.3555 (5)	0.6778 (4)	4.2 (1)
N2	5/8	0.5127 (4)	$y+1/4$	1.57 (9)
O21	0.5934 (4)	0.5952 (4)	0.7418 (4)	2.36 (9)
O22	5/8	0.4463 (3)	$y+1/4$	1.92 (8)

Table 2. *Selected geometric parameters* (Å, °)

Ce—O11	2.596 (5)	K—O13	2.807 (7)
Ce—O12	2.585 (5)	K—O13^{iv,v}	2.931 (6)
Ce—O21	2.763 (5)	K—O13^{iii}	2.807 (7)
Ce—O22	2.652 (4)	K—O21^{vi,vii}	2.973 (6)
Ce—O11^{i,ii}	2.596 (5)	N1—O11	1.266 (8)
Ce—O12^{i,ii}	2.585 (5)	N1—O12	1.264 (8)
Ce—O21^{i,ii}	2.763 (5)	N1—O13	1.217 (8)
Ce—O22^{i,ii}	2.652 (4)	N2—O21	1.234 (7)
K—O11	2.909 (5)	N2—O21^{viii}	1.234 (7)
K—O11^{iii}	2.909 (5)	N2—O22	1.275 (5)
K—O12^{iv,v}	3.168 (6)		
O11—N1—O12	116.9 (6)	O21—N2—O21^{viii}	122.6 (6)
O11—N1—O13	120.9 (7)	O21—N2—O22	118.7 (5)
O12—N1—O13	122.2 (7)	O21^{viii}—N2—O22	118.7 (5)

Symmetry codes: (i) z, x, y; (ii) y, z, x; (iii) $\frac{3}{4} - x, \frac{3}{4} - z, \frac{3}{4} - y$; (iv) $z - \frac{1}{4}, \frac{1}{4} - x, 1 - y$; (v) $\frac{3}{4} - z, y - \frac{1}{4}, \frac{1}{4} + x$; (vi) $1 - x, y - \frac{1}{4}, \frac{3}{4} - z$; (vii) $x - \frac{1}{4}, z - \frac{3}{4}, \frac{3}{4} - y$; (viii) $\frac{3}{4} - x, z - \frac{1}{4}, \frac{1}{4} + y$.

Data were corrected for Lorentz–polarization effects. The unit-cell dimensions were found by indexing the powder diffraction pattern with the program *DICVOL91* (Boultif & Louër, 1991). The final parameters were refined by the program *NBS*AIDS83* (Mighell, Hubbard & Stalick, 1981). The structure was solved in the $P4_132$ space group. The position of the Ce atom was determined by direct methods (*MUL-TAN80*; Main *et al.*, 1980) and confirmed by interpretation

of a Patterson map. The remaining atoms were located by one subsequent difference Fourier synthesis. Calculations were performed with the *MolEN* (Fair, 1990) package on a MicroVAX 3100 computer. Diagrams were prepared using *OR-TEPII* (Johnson, 1976).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Barium Perrhenate Monohydrate

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Abstract

The triclinic lattice of barium perrhenate monohydrate, $Ba(ReO_4)_2.H_2O$, is metrically pseudomonoclinic. The