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Two Polymorphic Forms of Ceric Potassium Nitrate, $K_2Ce(NO_3)_6$

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Abstract

Ceric potassium nitrate, $K_2Ce(NO_3)_6$, was synthesized from the dissolution in nitric acid of active hydrous ceria and potassium nitrate in stoichiometric quantities. Two forms, with hexagonal and monoclinic symmetries, have been isolated. The structures were solved by single-crystal X-ray diffraction analyses. They consist of discrete $[Ce(NO_3)_6]^{2-}$ anions in the form of irregular icosahedra, in which Ce atoms are twelvefold coordinated by six bidentate nitrate groups. The K atoms ensure the continuity of the structures by ionic contacts. Relationships between the two structures are described briefly.

Comment

The present structure investigations were performed as part of a detailed study into the mechanisms of thermal decomposition of precursors of cerium oxide, CeO_2, based on Ce^{IV} nitrates (Guillou, 1994; Guillou, Auffrédic & Louër, 1994). The high oxidation power of Ce^{IV} compounds is also one of the interesting properties of this kind of material. For instance, ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, has been used as an oxidant standard and in the conversion of some alcohols and toluenes in aldehydes (see Trahanovsky, Young & Brown, 1967). Its crystal structure has been determined by Beineke & Delgaudio (1968), and chemically related compounds with alkaline elements (K, Rb, Cs) were reported many years ago (Meyer & Jacoby, 1901). The determination of the unit-cell parameters from X-ray powder diffraction data of the mixed ceric caesium and ceric rubidium nitrates has suggested that these two compounds are isostructural with ceric ammonium nitrate (Guillou, Auffrédic & Louër, 1993).

In the case of ceric potassium nitrate, two crystalline $K_2Ce(NO_3)_6$ phases were identified in the system CeO_2–HNO_3–KNO_3–H_2O. From this study, single crystals of the two varieties could be isolated. One of them, (I), has hexagonal symmetry, while the other, (II), is monoclinic. Both structures comprise discrete $[Ce(NO_3)_6]^{2-}$ anions in the form of irregular icosahedra, in which Ce atoms are linked to six bidentate nitrate groups (Figs. 1 & 2). The mean Ce—O distances [2.506 (I), 2.507 Å (II)] are in agreement with the value (2.475 Å) calculated by the bond-valence method (Brown, 1981) for Ce^{IV} bonded to 12 O atoms. They are also close to the mean value (2.508 Å) found for the structure of $(NH_4)_2Ce(NO_3)_6$ (Beineke & Delgaudio, 1968).

As shown in Fig. 1, the $[Ce(NO_3)_6]^{2-}$ groups are located at the origin of the cell and along a threefold axis in the hexagonal phase, while they are in a body-

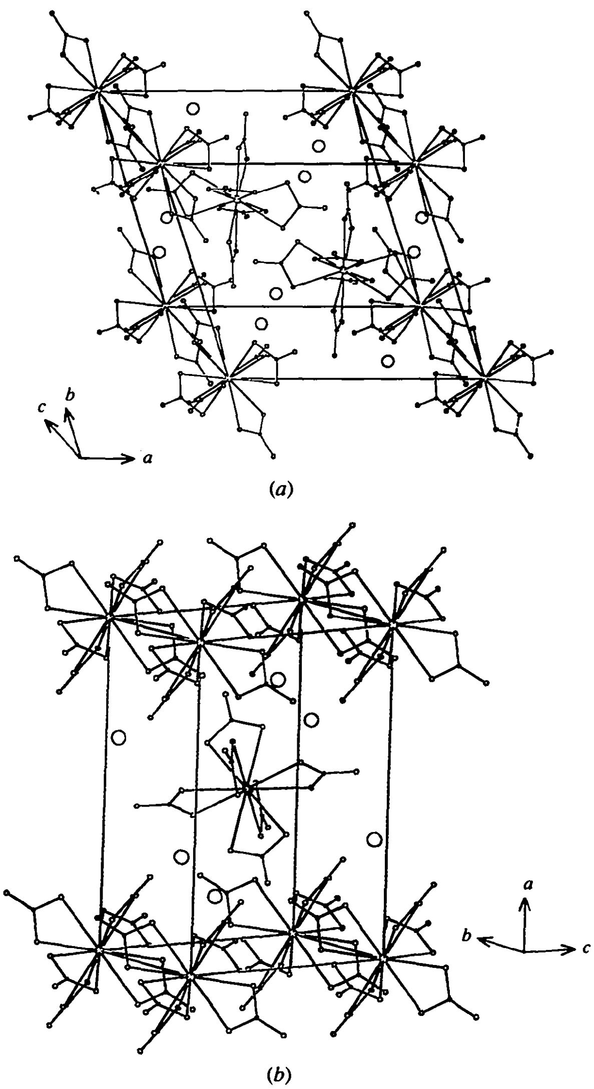
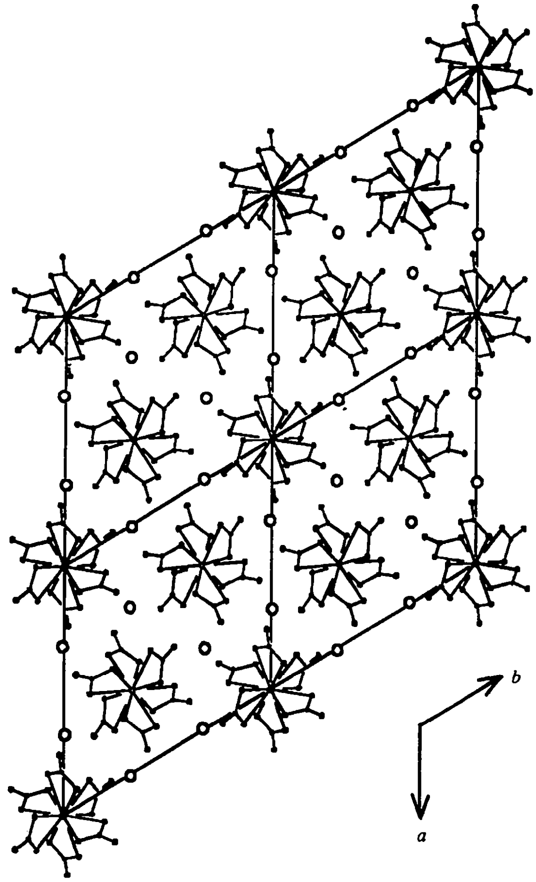


Fig. 1. View of the unit cell of the two polymorphic (*a*) hexagonal and (*b*) monoclinic forms of $K_2Ce(NO_3)_6$. Large circles correspond to K atoms.



(a)

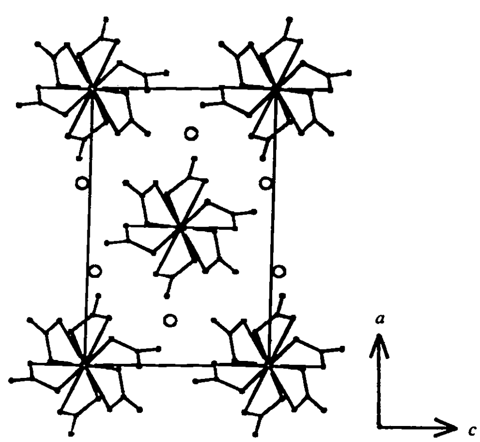


Fig. 2. Projections of the two structures of $K_2Ce(NO_3)_6$ (*a*) along **c** for the hexagonal form and (*b*) along **b** for the monoclinic form.

centred arrangement in the monoclinic phase. For the two compounds, the three independent nitrate groups are symmetrically bidentate and belong to the class I_{2b}, proposed by Leclaire (1979). As found for this class of nitrate compounds, the distances from the N atom to the non-coordinated O atom are significantly shorter [mean values: 1.210 (I), 1.211 Å (II)] than the other N—O distances [mean values: 1.274 (I), 1.272 Å (II)]. The displacement parameters of these free O atoms are greater than those of the coordinated O atoms, and the O—N—O angles between the two coordinated O atoms are smaller than the O—N—O angles involving a free O atom.

The K atoms located between the $[Ce(NO_3)_6]^{2-}$ anions ensure the continuity of the structure by ionic contacts. They are surrounded by nine and ten O atoms for compounds (I) and (II), respectively. It may be noted that the *c* parameter for (I) is similar to the *b* axis of the monoclinic form. Projections of the structures along [001] and [010] for (I) and (II), respectively, are shown in Fig. 2, from which the structural relationships between the two varieties can be seen. Indeed, if we consider four hexagonal cells (Fig. 2*a*), an arrangement like that in the monoclinic cell (Fig. 2*b*) is found at the intersection of these four hexagonal cells with a translation of $\frac{1}{2}$ along the projection axis. The $\bar{3}$ axis clearly reproduces the monoclinic cell every 60°.

Experimental

Crystals of $K_2Ce(NO_3)_6$ were synthesized by evaporation at 313 K of a solution of 0.94 g of potassium nitrate and 1 g of cerium oxide, $CeO_2.2.4H_2O$, previously dissolved in boiled concentrated nitric acid in a closed vessel. This synthesis requires a finely divided oxide (Guillou, Auffrédic & Louër, 1994). The hexagonal and monoclinic forms appear simultaneously when the evaporation is fast. The monoclinic form dominates when the crystallization is slow.

Form (I)

Crystal data

$K_2Ce(NO_3)_6$
$M_r = 590.3$
Hexagonal
$P\bar{3}$
$a = 13.5737\ (4)$ Å
$c = 6.6624\ (3)$ Å
$V = 1063.06\ (6)$ Å^3
$Z = 3$
$D_x = 2.767$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–$12°$
$\mu = 4.0$ mm^{-1}
$T = 293$ K
Hexagonal plate
0.20 × 0.17 × 0.05 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.6746$, $T_{max} = 0.9983$
5201 measured reflections
3148 independent reflections

2748 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.04$
$\theta_{max} = 35°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F
$R = 0.045$

Extinction correction: Stout & Jensen (1968)

$wR = 0.051$
$S = 1.7$
2748 reflections
124 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.38$
$\Delta\rho_{max} = 1.2$ e Å^{-3}
$\Delta\rho_{min} = -1.3$ e Å^{-3}
Extinction coefficient: 7.4×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	B_{eq}
Ce1	0	0	0	1.367 (3)
Ce2	1/3	2/3	0.51053 (3)	1.339 (2)
K	0.00696 (6)	0.32616 (6)	0.2227 (1)	3.40 (1)
N1	0.1691 (2)	0.1788 (2)	0.2676 (3)	1.87 (3)
O11	0.1381 (1)	0.0735 (1)	0.2871 (3)	2.16 (3)
O12	0.1283 (2)	0.2017 (1)	0.1127 (3)	2.27 (3)
O13	0.2311 (2)	0.2509 (2)	0.3839 (3)	2.97 (4)
N2	0.5268 (2)	0.7240 (2)	0.7768 (3)	2.02 (3)
O21	0.4324 (2)	0.6351 (2)	0.8021 (3)	2.27 (3)
O22	0.5354 (2)	0.7824 (2)	0.6211 (3)	2.48 (4)
O23	0.6067 (2)	0.7567 (2)	0.8933 (3)	2.82 (4)
N3	0.3835 (2)	0.5223 (2)	0.2518 (3)	2.23 (4)
O31	0.2965 (2)	0.5331 (2)	0.2295 (3)	2.43 (3)
O32	0.4474 (2)	0.5774 (2)	0.4005 (3)	2.58 (4)
O33	0.4075 (2)	0.4666 (2)	0.1421 (4)	3.73 (4)

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

Ce1—O11	2.510 (2)	K—O13^{viii}	2.864 (2)
Ce1—O12	2.515 (2)	K—O22^{ix}	2.873 (2)
Ce2—O21	2.518 (2)	K—O23^{ix}	3.120 (3)
Ce2—O22	2.495 (2)	K—O23^{x}	2.765 (2)
Ce2—O31	2.477 (2)	K—O32^{vii}	2.917 (2)
Ce2—O32	2.506 (3)	K—O33^{v}	2.986 (2)
Ce1—O11^{i,ii,iii,iv,v}	2.510 (2)	N1—O11	1.278 (3)
Ce1—O12^{i,ii,iii,iv,v}	2.515 (2)	N1—O12	1.281 (3)
Ce2—O21^{vi,vii}	2.518 (2)	N1—O13	1.201 (3)
Ce2—O22^{vi,vii}	2.495 (2)	N2—O21	1.257 (2)
Ce2—O31^{vi,vii}	2.477 (2)	N2—O22	1.275 (3)
Ce2—O32^{vi,vii}	2.506 (3)	N2—O23	1.222 (3)
K—O11^{ii}	3.178 (2)	N3—O31	1.269 (3)
K—O12	2.981 (3)	N3—O32	1.283 (3)
K—O12^{v}	3.235 (2)	N3—O33	1.207 (4)
O11—N1—O12	114.4 (2)	O22—N2—O23	120.1 (2)
O11—N1—O13	123.4 (2)	O31—N3—O32	114.8 (2)
O12—N1—O13	122.2 (2)	O31—N3—O33	124.0 (2)
O21—N2—O22	116.0 (2)	O32—N3—O33	121.2 (3)
O21—N2—O23	123.9 (2)		

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

Form (II)

Crystal data

$K_2Ce(NO_3)_6$
$M_r = 590.3$
Monoclinic
$P2_1/n$
$a = 12.707$ (4) Å
$b = 6.6858$ (6) Å
$c = 8.2535$ (7) Å
$\beta = 91.547$ (8)°
$V = 700.95$ (8) Å^3
$Z = 2$
$D_x = 2.798$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–12°
$\mu = 4.0$ mm^{-1}
$T = 293$ K
Irregular
$0.50 \times 0.25 \times 0.20$ mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.552$, $T_{max} = 0.720$
1866 measured reflections
1530 independent reflections
1354 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.028$
$\theta_{max} = 27°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: 2.9%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.061$
$S = 2.2$
1354 reflections
125 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 1.6$ e Å^{-3}
$\Delta\rho_{min} = -1.8$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: 1.9×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

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

	x	y	z	B_{eq}
Ce	1/2	1/2	1/2	1.164 (8)
K	0.1602 (1)	0.2758 (2)	0.5417 (2)	2.96 (2)
N1	0.6819 (3)	0.2328 (6)	0.4627 (5)	1.76 (7)
O11	0.6196 (3)	0.2162 (5)	0.5766 (4)	2.11 (6)
O12	0.6696 (3)	0.3876 (5)	0.3735 (4)	1.97 (6)
O13	0.7496 (3)	0.1095 (6)	0.4363 (6)	2.97 (8)
N2	0.3872 (3)	0.2195 (6)	0.2832 (5)	1.52 (6)
O21	0.4848 (3)	0.2061 (5)	0.3142 (4)	2.02 (6)
O22	0.3412 (3)	0.3647 (5)	0.3570 (4)	2.02 (6)
O23	0.3394 (3)	0.1075 (5)	0.1948 (5)	2.43 (7)
N3	0.4504 (3)	0.2546 (6)	0.7834 (5)	1.90 (7)
O31	0.4072 (3)	0.2222 (5)	0.6448 (4)	2.07 (6)
O32	0.5048 (3)	0.4140 (5)	0.7960 (4)	2.27 (7)
O33	0.4418 (3)	0.1398 (5)	0.8968 (5)	2.75 (7)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

Ce—O11	2.501 (4)	K—O22	2.856 (4)
Ce—O12	2.535 (4)	K—O23^{iv}	2.954 (4)
Ce—O21	2.497 (4)	K—O31	3.250 (4)
Ce—O22	2.481 (4)	K—O32^{v}	3.067 (4)
Ce—O31	2.518 (4)	K—O33^{v}	3.045 (5)
Ce—O32	2.509 (4)	K—O33^{vi}	2.809 (4)
Ce—O11^{i}	2.501 (4)	N1—O11	1.250 (6)
Ce—O12^{i}	2.535 (4)	N1—O12	1.277 (5)
Ce—O21^{i}	2.497 (4)	N1—O13	1.216 (5)
Ce—O22^{i}	2.481 (4)	N2—O21	1.263 (5)
Ce—O31^{i}	2.518 (4)	N2—O22	1.294 (5)
Ce—O32^{i}	2.509 (4)	N2—O23	1.199 (6)
K—O12^{i}	3.186 (4)	N3—O31	1.274 (6)
K—O12^{ii}	2.948 (4)	N3—O32	1.273 (5)
K—O13^{iii}	2.824 (4)	N3—O33	1.218 (6)
K—O21^{ii}	3.211 (4)		
O11—N1—O12	115.8 (4)	O22—N2—O23	121.8 (4)
O11—N1—O13	122.7 (4)	O31—N3—O32	115.8 (4)
O12—N1—O13	121.4 (4)	O31—N3—O33	122.5 (4)
O21—N2—O22	114.3 (4)	O32—N3—O33	121.6 (5)
O21—N2—O23	123.9 (4)		

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 *DICVOL*91 (Boultif & Louër, 1991). The final parameters were refined by the program *NBS*AIDS*83 (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 *ORTEP*II (Johnson, 1976).

The authors are grateful to Dr L. Toupet for his assistance in the collection of the single-crystal X-ray diffraction data.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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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