

The Crystal Structure of Hydronium Cerium (III) Nitrate Hydrate, $Ce(NO_3)_5(H_3O)_2 \cdot H_2O$

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The crystal structure of $Ce(NO_3)_5(H_3O)_2 \cdot H_2O$ has been determined from three-dimensional single crystal X-ray diffraction data. Crystals are monoclinic, space group $P2_1/c$, with $a = 21.364(7)$, $b = 7.8990(7)$, $c = 15.133(2)$ Å, $\beta = 91.02(2)^\circ$, and $Z = 8$. Full matrix anisotropic least-squares techniques led to a conventional R factor of 0.049 for 4067 observed reflections. The structure consists of infinite and isolated chains running parallel to $[100]$. The cerium atoms are twelvefold coordinated by six bidentate nitrate groups. The chains are held together by hydrogen bonds through hydronium ions and water molecules located between the chains. © 1993 Academic Press, Inc.

Introduction

Studies of hydrated cerium sulfates have clearly shown that the coordination sphere about the cerium ion depends upon the oxidation state of the ion (I). Indeed, Ce is eightfold coordinated in Ce^{IV} sulfates, while it is ninefold coordinated in Ce^{III} sulfates. Although only a few crystal structures are known for the nitrates, it seems that this rule does not apply for this family; e.g., the Ce atoms are surrounded by twelve oxygen atoms in $Ce^{IV}(NH_4)_2(NO_3)_6 \cdot 2H_2O$ (2), as well as in $Ce^{III}_2Mg_3(NO_3)_{12} \cdot 24H_2O$ (3), and by eleven oxygen atoms in $Ce^{III}(NO_3)_3 \cdot 6H_2O$ (4). On the other hand, in the case of the twelvefold coordination, it appears that the average Ce–O distance is 2.51 Å for $Ce^{IV}(NO_3)_6^{2-}$ as opposed to 2.64 Å in $Ce^{III}(NO_3)_6^{3-}$. These values are in reasonable agreement with those calculated by the bond valence method introduced by Brown (5), i.e., 2.475 Å and 2.673 Å, respectively. Therefore, it can be said that, for nitrate compounds, where the Ce atom is twelvefold coordinated, the average distance Ce–O reflects more the oxidation state of the Ce ion than the coordination number.

In the course of studying the $CeO_2-HNO_3-H_2O$ system, crystals of a new phase have been obtained. The single crystal structure determination, reported here, demonstrates that this new compound is the acid cerium III nitrate salt, $Ce(NO_3)_5(H_3O)_2 \cdot H_2O$.

Experimental

Sample Preparation

Crystals of $Ce(NO_3)_5(H_3O)_2 \cdot H_2O$ were synthesized from a solution of ceria in concentrated nitric acid, partially evaporated at 40°C. The first step of this synthesis is related to the preparation of ceria soluble in concentrated nitric acid. By a slow reaction, at room temperature, of 1M sodium hydroxide solution with 0.2M cerous nitrate solution, an amorphous precipitate was obtained. This precipitate was decanted and washed with water and alcohol and then dried at 75°C for 2 days. Its composition, as found from a thermogravimetric analysis up to 1000°C, was $CeO_2 \cdot 1.5H_2O$. From X-ray diffraction line profile analysis, an estimation of the mean crystallite sizes of ceria

was obtained by using the Williamson–Hall method (6). The integral breadths of the observed diffraction lines 111, 200, 222, and 400 were corrected for instrumental contribution by means of the Langford method (7, 8). It was shown that the crystallites are strain free and isotropic with a mean apparent size of about 50 Å. This hydrated ceria was slowly soluble in boiling concentrated nitric acid. At 40°C, this solution becomes viscous and rod-shaped crystals appear on the surface. At room temperature these crystals become rapidly deliquescent. Taking into account the very small amount of the compound obtained and its instability, no chemical analysis could be carried out.

Structure Determination and Refinement

A single crystal (0.5 × 0.1 × 0.05 mm) was introduced into a capillary and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo K α radiation. A least-squares treatment of 25 reflections with 2 θ values between 12° and 20° indicated a monoclinic symmetry with the following cell parameters: $a = 21.364(7)$, $b = 7.8990(7)$, $c = 15.133(2)$ Å, and $\beta = 91.02(2)^\circ$. Systematic absences ($h0l$: l odd) are consistent with the monoclinic space group $P2_1/c$. One set of intensities (h : $0 \rightarrow 24$, k : $0 \rightarrow 10$, l : $\overline{18} \rightarrow 18$) was collected at room temperature by a θ – 2θ scanning technique to give 5608 unique reflections with $\sin \theta/\lambda \leq 0.6420 \text{ \AA}^{-1}$. Within this set, 4067 reflections were considered as observed by means of the criterion $I > 3\sigma(I)$. Data were corrected for Lorentz and polarization effects and absorption corrections were applied by means of the program DIFABS (9) (maximum and minimum transmission factors are, respectively, 0.829 and 0.154). Atomic scattering factors were taken from the "International Tables for X-ray Crystallography." All calculations were performed on a Microvax 3100 computer by means of the SDP programs (10).

The direct method (MULTAN) yielded the positions of three independent Ce

TABLE I
CRYSTALLOGRAPHIC DATA FOR
 $\text{Ce}(\text{NO}_3)_5(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$

Empirical formula	$\text{Ce}(\text{NO}_3)_5(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$
Formula weight	506.12
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	21.364(7)
b (Å)	7.8990(7)
c (Å)	15.133(2)
β (°)	91.02(2)
V (Å ³)	2553.4
Z	8
Radiation (Å)	0.71069
Data collection	$h, k, \pm l$
No. of observations	4067
No. of variables	415
R	0.049
R_w	0.082

atoms; these were also confirmed by the Patterson method. The positions of 46-remaining nonhydrogen atoms were obtained from a one-difference Fourier map. The list of interatomic distances showed that among them 40 corresponded to 10 independent nitrate groups. Taking into account the oxidation state III for cerium atoms (supported by the values of Ce–O contacts as shown below), it was assumed that the six remaining atoms corresponded to two water molecules and four hydronium cations in order to balance the negative charge of nitrate ions. Consequently, the chemical formula was found to be $\text{Ce}^{\text{III}}(\text{NO}_3)_5(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ with $Z = 8$. The R and R_w values, including anisotropic thermal parameters (except for four oxygen atoms for which the ellipsoids were not positively defined) were 0.049 and 0.082, respectively. At this stage, the height of the peaks observed on a final difference Fourier map ranged from 0.997 to $0.572 e \cdot \text{Å}^{-3}$, but none of them could correspond to hydrogen atoms. Crystallographic data and final atomic parameters with equivalent temperature factors are given in Tables I and II, respectively. O₁ to O₁₀ correspond to the oxygen atoms of nitrate groups, O₁–O₆ to the water mole-

TABLE II
POSITIONAL PARAMETERS AND THEIR ESTIMATED
STANDARD DEVIATIONS

Atom	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Ce1	0.500	0.32932 (8)	0.250	1.41 (1)
Ce2	0.000	0.35287 (9)	0.250	1.51 (1)
Ce3	0.25088 (2)	0.33275 (6)	0.24473 (3)	1.389 (9)
N1	-0.0021 (4)	0.249 (1)	0.0554 (5)	2.2 (2)
N2	0.1797 (3)	0.5201 (9)	0.1014 (4)	2.0 (1)
N3	0.3172 (3)	0.0126 (9)	0.1886 (4)	1.7 (1)
N4	0.3752 (4)	0.4535 (9)	0.1635 (4)	1.8 (1)
N5	0.4296 (3)	0.5184 (9)	0.3913 (4)	1.9 (1)
N6	0.2546 (3)	0.214 (1)	0.4329 (4)	2.1 (1)
N7	0.0776 (4)	0.6601 (9)	0.2901 (5)	2.1 (2)
N8	0.1217 (3)	0.1503 (9)	0.2170 (5)	1.8 (1)
N9	0.2507 (4)	0.6474 (9)	0.3575 (4)	1.9 (1)
N10	0.5032 (3)	0.020 (1)	0.3693 (5)	2.1 (2)
O1 ₁	0.0430 (3)	0.1956 (9)	0.3905 (4)	2.6 (1)
O1 ₂	0.0401 (3)	0.3436 (8)	0.0844 (4)	2.6 (1)
O1 ₃	-0.0045 (4)	0.207 (1)	-0.0224 (4)	3.4 (2)
O2 ₁	0.1969 (3)	0.3696 (8)	0.0909 (4)	2.3 (1)
O2 ₂	0.1956 (3)	0.5969 (8)	0.1699 (4)	2.2 (1)
O2 ₃	0.1470 (3)	0.5861 (9)	0.0438 (4)	2.7 (1)
O3 ₁	0.2965 (3)	0.1147 (8)	0.1307 (4)	2.0 (1)
O3 ₂	0.3065 (3)	0.0456 (8)	0.2676 (4)	2.1 (1)
O3 ₃	0.3468 (3)	-0.1130 (9)	0.1701 (4)	2.8 (1)
O4 ₁	0.3744 (3)	0.3498 (7)	0.2284 (3)	1.7 (1)
O4 ₂	0.3251 (3)	0.4982 (8)	0.1295 (4)	2.2 (1)
O4 ₃	0.5735 (3)	0.5104 (8)	0.3619 (4)	2.1 (1)
O5 ₁	0.4448 (3)	0.5916 (8)	0.3210 (4)	2.2 (1)
O5 ₂	0.4466 (3)	0.3680 (8)	0.4024 (4)	2.4 (1)
O5 ₃	0.3978 (3)	0.5900 (9)	0.4461 (4)	3.0 (1)
O6 ₁	0.3004 (3)	0.2963 (9)	0.4020 (4)	2.4 (1)
O6 ₂	0.2103 (3)	0.1814 (8)	0.3814 (4)	2.4 (1)
O6 ₃	0.2550 (4)	0.170 (1)	0.5092 (4)	3.5 (2)
O7 ₁	0.0650 (3)	0.5545 (8)	0.3493 (4)	2.0 (1)
O7 ₂	0.0604 (3)	-0.3737 (9)	0.2119 (4)	2.4 (1)
O7 ₃	0.1075 (3)	0.7870 (9)	0.3066 (4)	3.1 (1)
O8 ₁	0.1239 (3)	0.2997 (8)	0.2456 (3)	1.7 (1)
O8 ₂	0.0698 (3)	0.0853 (8)	0.2055 (4)	2.2 (1)
O8 ₃	0.1705 (3)	0.0747 (8)	0.2011 (4)	2.2 (1)
O9 ₁	0.2053 (3)	0.5442 (8)	0.3593 (4)	2.1 (1)
O9 ₂	0.2947 (3)	0.6168 (8)	0.3056 (4)	2.1 (1)
O9 ₃	0.2518 (4)	0.2277 (9)	-0.0950 (4)	3.6 (2)
O10 ₁	0.5457 (3)	0.1336 (8)	0.3705 (4)	2.2 (1)
O10 ₂	0.4561 (3)	0.0465 (8)	0.3189 (4)	2.3 (1)
O10 ₃	0.5077 (3)	0.8933 (9)	0.4136 (4)	3.0 (1)
O1	0.3726 (2)	0.8413 (5)	0.3423 (3)	0.02 (7) *
O2	0.1280 (2)	0.3123 (6)	-0.0352 (3)	0.25 (7) *
O3	0.6199 (2)	0.7363 (6)	0.4735 (3)	0.34 (7) *
O4	0.1082 (2)	-0.1642 (6)	0.1203 (3)	0.72 (8) *
O5	0.6277 (3)	0.0308 (9)	0.5172 (4)	2.6 (1)
O6	0.1280 (3)	0.0155 (8)	-0.0030 (4)	2.8 (1)

* Atoms were refined isotropically.

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

cules or H_3O^+ . Bond distances are listed in Table III and angles of nitrate groups in Table IV.

Description and Discussion

The crystal structure of the title compound can be described as consisting of isolated chains running parallel to [100], formed by twelfold Ce polyhedra connected by nitrate groups, as shown in Figs.

1 and 2. Hydronium ions and water molecules are located between the chains.

Cerium Polyhedra

The cerium atoms are bonded to six bidentate nitrate groups in order to form an irregular icosahedron (Fig. 3). As reported above, this twelfold coordination is found in the Ce^{III} salt $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ as well as in the Ce^{IV} salt $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$. In the present study, the Ce–O distances range

TABLE III
BOND DISTANCES IN ANGSTROMS

Ce1	O4 ₁	(x2)	2.703(3)	Ce2	O1 ₁	(x2)	2.614(3)	Ce3	O2 ₁	2.596(3)
Ce1	O4 ₃	(x2)	2.700(3)	Ce2	O1 ₂	(x2)	2.663(3)	Ce3	O2 ₂	2.643(3)
Ce1	O5 ₁	(x2)	2.623(3)	Ce2	O7 ₁	(x2)	2.578(3)	Ce3	O3 ₁	2.637(3)
Ce1	O5 ₂	(x2)	2.610(3)	Ce2	O7 ₂	(x2)	2.586(3)	Ce3	O3 ₂	2.581(3)
Ce1	O10 ₁	(x2)	2.570(3)	Ce2	O8 ₁	(x2)	2.681(3)	Ce3	O4 ₁	2.657(3)
Ce1	O10 ₂	(x2)	2.644(3)	Ce2	O8 ₂	(x2)	2.680(3)	Ce3	O4 ₂	2.713(3)
								Ce3	O6 ₁	2.603(3)
								Ce3	O6 ₂	2.554(3)
								Ce3	O8 ₁	2.727(3)
								Ce3	O8 ₃	2.739(3)
								Ce3	O9 ₁	2.608(3)
								Ce3	O9 ₂	2.594(3)

Nitrate groups

N1	O1 ₁	1.280(5)	N2	O2 ₁	1.255(5)	N3	O3 ₁	1.264(4)
N1	O1 ₂	1.247(5)	N2	O2 ₂	1.243(4)	N3	O3 ₂	1.249(4)
N1	O1 ₃	1.223(4)	N2	O2 ₃	1.224(4)	N3	O3 ₃	1.212(5)
N4	O4 ₁	1.279(4)	N5	O5 ₁	1.259(4)	N6	O6 ₁	1.272(5)
N4	O4 ₂	1.232(4)	N5	O5 ₂	1.253(5)	N6	O6 ₂	1.241(5)
N4	O4 ₃	1.251(5)	N5	O5 ₃	1.220(4)	N6	O6 ₃	1.205(4)
N7	O7 ₁	1.258(4)	N8	O8 ₁	1.258(5)	N9	O9 ₁	1.267(4)
N7	O7 ₂	1.261(4)	N8	O8 ₂	1.230(5)	N9	O9 ₂	1.260(5)
N7	O7 ₃	1.213(5)	N8	O8 ₃	1.229(4)	N9	O9 ₃	1.221(5)
N10	O10 ₁	1.275(5)						
N10	O10 ₂	1.268(4)						
N10	O10 ₃	1.209(5)						

Possible hydrogen bonds

O1	O3 ₂	2.414(4)	O2	O1 ₂	2.643(4)	O3	O3 ₃	2.588(4)
O1	O3 ₃	2.679(4)	O2	O1 ₁	2.961(4)	O3	O4 ₂	2.723(4)
O1	O5 ₁	2.527(4)	O2	O2 ₁	2.431(4)	O3	O4 ₃	2.637(4)
O1	O5 ₂	2.582(4)	O2	O2 ₂	2.501(4)	O3	O5 ₂	2.514(4)
O1	O9 ₂	2.488(4)	O2	O7 ₁	2.427(4)	O3	O5 ₃	2.878(4)
O1	O9 ₃	2.820(5)	O2	O7 ₂	2.550(4)	O3	O6 ₁	2.530(4)
O1	O10 ₂	2.441(4)	O2	O9 ₁	2.579(4)	O3	O6 ₂	2.782(5)
O1	O10 ₃	3.091(4)	O2	O9 ₂	2.888(5)	O3	O10 ₁	2.833(4)
O4	O1 ₃	2.664(4)	O5	O3 ₁	2.865(4)	O6	O1 ₁	2.928(5)
O4	O2 ₂	2.749(4)	O5	O5 ₁	3.097(5)	O6	O6 ₂	2.947(4)
O4	O2 ₃	2.439(4)	O5	O6 ₁	2.999(5)	O6	O6 ₃	3.085(5)
O4	O7 ₂	2.399(4)	O5	O10 ₁	2.918(4)			
O4	O7 ₃	2.846(4)						
O4	O8 ₂	2.501(4)						
O4	O8 ₃	2.602(4)						

Note. Numbers in parentheses are estimated standard deviations in the last significant digits.

from 2.554 to 2.739 Å (mean values are 2.642(3), 2.634(3), and 2.638(3) Å for Ce1, Ce2, and Ce3, respectively). These distances are very close to that calculated by Brown's method for the twelfold coordinated Ce^{III} (2.675 Å) and to that found in Ce₂Mg₃(NO₃)₁₂ · 24H₂O (2.635 Å). This re-

sult is consistent with an oxidation state of three for cerium.

Nitrate Groups

The 10 nitrate groups act as bidentate ligands. Two of them (N4 and N8) bridge two icosahedra (Fig. 1). Indeed, O4₁ is bonded

TABLE IV
BOND ANGLES (°) IN NITRATE GROUPS

O1 ₁	N1	O1 ₂	118.0(4)	O2 ₁	N2	O2 ₂	119.5(4)	O3 ₁	N3	O3 ₂	117.5(3)
O1 ₁	N1	O1 ₃	120.7(4)	O2 ₁	N2	O2 ₃	118.5(4)	O3 ₁	N3	O3 ₃	122.7(3)
O1 ₂	N1	O1 ₃	121.3(4)	O2 ₂	N2	O2 ₃	122.0(4)	O3 ₂	N3	O3 ₃	119.8(4)
O4 ₁	N4	O4 ₂	118.6(4)	O5 ₁	N5	O5 ₂	118.1(3)	O6 ₁	N6	O6 ₂	117.2(3)
O4 ₁	N4	O4 ₃	119.5(3)	O5 ₁	N5	O5 ₃	121.1(4)	O6 ₁	N6	O6 ₃	120.5(4)
O4 ₂	N4	O4 ₃	121.9(4)	O5 ₂	N5	O5 ₃	120.8(4)	O6 ₂	N6	O6 ₃	122.3(4)
O7 ₁	N7	O7 ₂	117.8(4)	O8 ₁	N8	O8 ₂	117.9(4)	O9 ₁	N9	O9 ₂	118.1(3)
O7 ₁	N7	O7 ₃	121.3(4)	O8 ₁	N8	O8 ₃	119.8(4)	O9 ₁	N9	O9 ₃	120.9(4)
O7 ₂	N7	O7 ₃	120.8(4)	O8 ₂	N8	O8 ₃	122.3(4)	O9 ₂	N9	O9 ₃	121.0(4)
O10 ₁	N10	O10 ₂	116.8(4)								
O10 ₁	N10	O10 ₃	121.6(4)								
O10 ₂	N10	O10 ₃	121.6(4)								

Note. Numbers in parentheses are estimated standard deviations in the last significant digits.

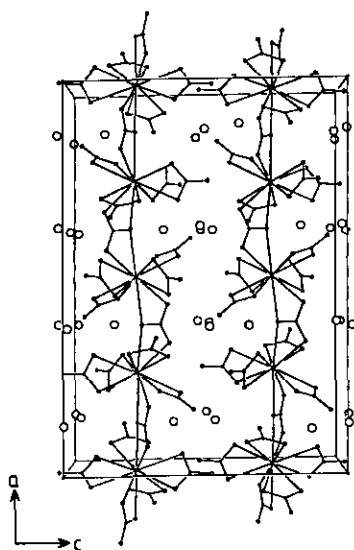


FIG. 1. View of the unit cell of $\text{Ce}(\text{NO}_3)_3(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ along b , with c horizontal and a vertical. Large circles correspond to water and hydronium.

to Ce1 and Ce3, and O8₁ to Ce2 and Ce3. Their three oxygen atoms are bonded to cerium atoms as in the class II_{3b} reported by Leclaire (11). The bond distance from the nitrogen to the twofold coordinated oxygen (mean value, 1.268(5) Å) is significantly longer than the other N–O distances (mean value, 1.235(5) Å), and the isotropic thermal parameters of O4₁ and O8₁ are also lower. These two nitrate groups ensure the continuity of the chains parallel to [100]. (It can be noted that in $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ icosahedra

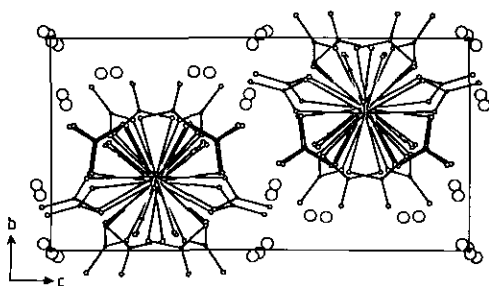


FIG. 2. Projection of the unit cell of $\text{Ce}(\text{NO}_3)_3(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ along a , with c horizontal and b vertical. Large circles correspond to water and hydronium.

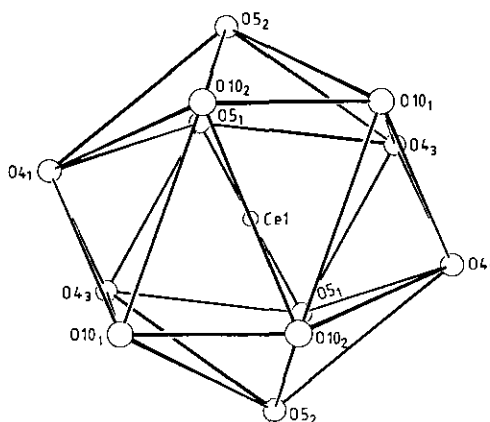


FIG. 3. The environment of Ce1.

are linked together by the NH_4^+ ions and not by bridging NO_3^- groups). The eight remaining nitrate groups are bidentate symmetric (class I_{2b} (11)). The bond distance from the nitrogen to the third oxygen (mean value, 1.216(5) Å) is significantly shorter than the other N–O distances (mean value, 1.259(5) Å) and the isotropic thermal parameter of that oxygen atom is also higher.

Water Molecules and Hydronium Ions

These lie between the chains and are not directly bonded to the cations. Attempts to locate hydrogen atoms failed, but an examination of possible hydrogen bonds (Table III) is in favor of O1 to O4 being an oxygen of hydronium ions. Indeed, there are more possible hydrogen bonds around these four oxygen atoms, with the shortest O–O contacts. The anisotropic temperature factors were not definite for these four oxygen atoms. This fact could be regarded as a different chemical behavior with respect to the other two oxygen atoms O5 and O6, which could correspond to the water molecules. Nevertheless, this feature could also be explained by the experimental conditions and instability of the crystal inside the capillary.

It is surprising that such a Ce^{III} compound can be obtained from a solution of hydrated ceria in nitric acid. However, this phenomenon of the higher valency being less stable

in the ionic, but more stable in the covalent state, as in hydroxides, is not uncommon. The instability of the higher valency is due to the magnitude of the charge of the cation, and this is diminished or spread by covalency formation. For example, it is well known that a solution of ceric hydroxide in hydrochloric acid evolves chlorine and goes over into cerous chloride CeCl_3 . More recently, double cerium III cerium IV sulfate $\text{K}_5\text{Ce}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$ (12) was synthesized under hydrothermal conditions in the $\text{Ce}(\text{SO}_4)_2\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ system, involving the reduction $\text{Ce}^{\text{IV}} \rightarrow \text{Ce}^{\text{III}}$ in sulfuric acid. With regard to the system $\text{CeO}_2\text{-HNO}_3\text{-H}_2\text{O}$ used, reduction of species such as $\text{Ce}(\text{H}_2\text{O})_{6-q}(\text{NO}_3)_q^{4-q}$ and $\text{Ce}(\text{OH})_p(\text{H}_2\text{O})_{6-(p+q)}(\text{NO}_3)_q^{4-p-q}$ by water with the evolution of O_2 could be assumed in boiling concentrated nitric acid. The presence of H_3O^+ ions in the structure is probably due to the hydrolysis of such ions.

Finally, the crystal structure of the hydronium cerium nitrate hydrate confirms that the coordination number of cerium does not reflect the oxidation state of the rare earth in this kind of compound. On the other hand, in the case of twelfefold

coordinated cerium, the average distances Ce-O are significantly different in nitrate compounds, to be a characteristic more representative of the oxidation state III or IV of the cerium.

References

1. B. M. GATEHOUSE AND A. PRING, *J. Solid State Chem.* **38**, 116 (1981).
2. T. A. BEINEKE AND J. DELGAUDIO, *Inorg. Chem.* **7**, 715 (1968).
3. A. ZALKIN, J. D. FORRESTER, AND D. H. TEMPLETON, *J. Chem. Phys.* **39**, 2881 (1963).
4. N. MILINSKI, B. RIBAR, AND M. SATARIĆ, *Cryst. Struct. Commun.* **9**, 473 (1980).
5. I. D. BROWN AND K. K. WU, *Acta Crystallogr. Sect. B* **32**, 1957 (1976).
6. G. K. WILLIAMSON AND W. H. HALL, *Acta Metall.* **1**, 22 (1953).
7. J. I. LANGFORD, *J. Appl. Crystallogr.* **11**, 10 (1978).
8. J. I. LANGFORD, R. DELHEZ, TH. H. DE KEIJSER, AND E. J. MITTEMEIJER, *Aust. J. Phys.* **41**, 173 (1988).
9. N. WALKER AND D. STUART, *Acta Crystallogr. Sect. A* **39**, 158 (1983).
10. B. A. FRENZ, "The Enraf-Nonius CAD-4 SDP," Frenz and Assoc., College Station, TX, and Enraf-Nonius, Delft (1986).
11. A. LECLAIRE, *J. Solid State Chem.* **28**, 235 (1979).
12. A. I. TURSINA AND L. D. ISKNAKOVA, *J. Struct. Chem.* **30**, 114 (1989).