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New Open-Framework Mixed-Valence Chromium(III) Cerium(III)/(IV) Sulfate: $CrCe^{III}_7Ce^{IV}_6(HSO_4)_6(SO_4)_{21}\cdot 75H_2O$

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Keywords: Mixed-valent compounds / Lanthanides / Cerium sulfate / X-ray diffraction

The title compound, synthesized from Cr^{VI} and Ce^{IV} species, crystallizes in the space group $P6_3$ with a = 19.3015(2), c = 25.2684(4) Å, and Z = 2. The structural design of the title compound differs essentially from structures of known mixed-valence cerium compounds which all form three-dimensional networks. In the title compound the cerium atoms, interlinked by sulfate groups, extend to form layers held together by hydrogen-bonding contacts. Perpendicular to these layers there are 10 Å wide channels. One third of the channels host solvent water only, while the other two thirds of the channels also host $[Cr(H_2O)_6]^{3+}$ and $[Ce(SO_4)_3(H_2O)_6]^{3-}$ units, blocking each of these channels once per unit cell, resulting in 14 Å long voids.

Introduction

Currently, there is interest in rare-earth compounds because of their important physical properties and advances achieved in the syntheses of new materials[1] with interesting applications.[2] Rare-earth materials are intriguing due to the complexity of their structural arrangements with high coordination numbers and a variety of coordination geometries. Structural investigations on hydrated rare-earth sulfates are quite numerous[3] and many of these compounds are isomorphic, with the ninefold coordinated rare-earth atoms interlinked by sulfate groups. There is structural information on anhydrous as well as hydrous ternary rare-earth sulfates with all alkaline ions for nearly all of the lanthanide series,[3] but not much work has been done combining transition metals with rare-earth metals to form double salts. Cerium compounds attract research attention owing to their applications as ion conductors, catalysts, magnetic and fluorescence materials. The existence of alterable oxidation states for the cerium ion will result in compounds with new structural frameworks and interesting properties.[4] There are six mixed-valence cerium compounds in the ICSD Database (version 2006-2):[5] $Ce_4O_4S_3$,[6] $Ce_3O_3S_2$,[7] $Ce_{10}(GeO_4)_3(Ge_2O_7)_2(Ge_3O_{10})$,[8] $(H_3O)[Ce_2(SeO_4)_4]$,[9] $KCe_2(SO_4)_4$,[10] and $Ce_{0.968}H_{10.432}O_{12.924}S_2$.[11] Here we present an open-framework structure of a new mixed-valence chromium(III) cerium(III)/(IV) sulfate.

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Results and Discussion

Synthesis of $CrCe^{III}_7Ce^{IV}_6(HSO_4)_6(SO_4)_{21}\cdot 75H_2O$

The title compound was synthesized from Cr^{VI} and Ce^{IV} species in diluted sulfuric acid. Cerium(IV) in acidic aqueous solutions is metastable with respect to the oxidation of water. The attainment of equilibrium is kinetically controlled, and the reaction is observed only in the presence of a catalyst.[12] Added ions or even the glass vessel may act as the catalytic agent.[12] Thus, in acidic aqueous media cerium(III) will be formed. Cerium(III) is known to inhibit chromium(VI) oxidation of organic compounds, and this effect is attributed to the chromic acid oxidation of the cerium(III) species[13] encountered also in our previous work.[14] The chromium system is able to produce a variety of transient and intermediate species, and several competing redox reactions can take place,[13,14] but the redox equilibria involved in this case can be written as the following total reactions:

$$2\ Ce^{4+} + H_2O \rightarrow 2\ Ce^{3+} + 2\ H^+ + 1/2\ O_2$$

$$[CrO_4]^{2-} + 3\ Ce^{3+} + 8\ H^+ \rightarrow Cr^{3+} + 3\ Ce^{4+} + 4\ H_2O$$

Purbaix diagrams on cerium and chromium species have been revised recently[15] showing that the first reaction occurs in acidic solutions, while the second reaction is dominant in neutral and basic solutions. Hence, in acidic aqueous solutions mixed-valence cerium species as well as mixed-valence chromium species may form.

Structural Description of $CrCe^{III}_7Ce^{IV}_6(HSO_4)_6(SO_4)_{21}\cdot 75H_2O$

The title compound crystallizes in the space group $P6_3$ with a = 19.3015(2), c = 25.2684(4) Å, and Z = 2. There

are two atoms, Cr^{III} and Ce^{III}, in special positions (on the threefold axis) while the remaining content of the asymmetric unit, two Ce^{III} atoms, two Ce^{IV} atoms, two HSO_4^- groups, seven SO_4^{2-} groups, and approximately 25 water molecules, are in general positions. The structure is noncentrosymmetric mainly due to $Ce1^{III}$ and Cr^{III} atoms that do not respect an additional mirror plane leading to space group $P6_3/m$. The crystal was centrosymmetrically twinned with the twin volume ratio refined to 0.692(10):0.308(10).

The Cr^{III} atom is sixfold coordinated to water molecules, as in known structures of chromium alums.[16] The Ce^{III} atoms are in contact with nine oxygen atoms belonging to three corner-sharing sulfate groups and six water molecules. The Ce^{III} coordination polyhedra are best described as tricapped trigonal prisms for the Ce^{III} atom in a special position and as singly capped tetragonal antiprisms for the two Ce^{III} atoms in general positions. The Ce^{IV} atoms are ninefold coordinated to oxygen atoms belonging to three edge-sharing and three corner-sharing sulfate groups. The Ce^{VI} coordination polyhedra are slightly distorted tricapped trigonal prisms. Coordination numbers such as nine are expected for the large Ce^{III} ion but are rarely encountered for the smaller Ce^{IV} ion.[17] The Cr^{III}–O, Ce^{III}–O, and Ce^{IV}–O distances average to 1.97(1), 2.53(4), and 2.39(9) Å, respectively (Table 1) as in known Cr^{III}, Ce^{III}, and Ce^{IV} compounds.[16,17] The bond-valence sums for Cr^{III}, $Ce1^{III}$, $Ce2^{III}$, $Ce3^{IV}$, $Ce4^{IV}$, and $Ce5^{III}$ are 3.13, 2.85, 2.95, 4.00, 3.98, and 2.95 valence units, respectively (using parameters from Brese and O'Keefe[18] for Cr and Trzesowska et al.[19] for Ce). The S–O distances within the nine sulfate groups average to 1.48(2) Å (Table 1), and as expected, due to the restrained bite angle, the edge-sharing sulfate groups (S6, S7, S8, S12, S13, and S14) show a departure from the ideal tetrahedral symmetry, the angles ranging from 102.4(2) to 111.7(2)°. One of the sulfate groups is partly disordered (S9A, O91A, O92A and S9B, O91B, O92B) occupying 0.563(7) and 0.437(7) of two sets in a general position. All the sulfate groups link two cerium atoms, except for the S3 sulfate unit that is bridging by corner sharing from $Ce1^{III}$ to $Ce3^{IV}$ and $Ce4^{IV}$. It is difficult to distinguish by analyzing the terminal S–O bond length which two of the nine sulfate groups may be protonated to give hydrogen sulfate groups. Hence, the location of these protons may be disordered.

Table 1. Bond lengths [Å].

Ce1–O11	2.511(4)	Cr–O1	1.975(5)
Ce1–O11^{ii}	2.511(4)	Cr–O1^{iv}	1.975(5)
Ce1–O12	2.492(4)	Cr–O1^{v}	1.975(5)
Ce1–O12^{i}	2.492(4)	Cr–O2	1.955(5)
Ce1–O12^{ii}	2.492(4)	Cr–O2^{iv}	1.955(5)
Ce1–O11^{i}	2.511(4)	Cr–O2^{v}	1.955(5)
Ce1–O101^{i}	2.636(4)	S6–O61	1.463(4)
Ce1–O101	2.636(4)	S6–O62	1.461(4)
Ce1–O101^{ii}	2.636(4)	S6–O63	1.497(4)
Ce2–O21	2.512(4)	S6–O64	1.502(4)
Ce2–O22	2.522(4)	S7–O71	1.447(4)
Ce2–O23	2.559(4)	S7–O72	1.476(4)
Ce2–O24	2.521(4)	S7–O73	1.509(4)
Ce2–O25	2.547(4)	S7–O74	1.496(4)
Ce2–O26	2.541(4)	S8–O81	1.465(4)
Ce2–O62	2.492(4)	S8–O82	1.457(4)
Ce2–O72^{ii}	2.530(4)	S8–O83	1.492(4)
Ce2–O81^{iii}	2.540(4)	S8–O84	1.495(4)
Ce3–O63	2.383(4)	S9A–O91A	1.480(8)
Ce3–O64	2.519(4)	S9A–O92A	1.449(8)
Ce3–O73	2.391(4)	S9A–O93	1.516(5)
Ce3–O74	2.455(4)	S9A–O94	1.513(5)
Ce3–O83	2.409(4)	S9B–O91B	1.458(10)
Ce3–O84	2.478(4)	S9B–O92B	1.453(10)
Ce3–O94	2.267(4)	S9B–O93	1.459(5)
Ce3–O111	2.270(4)	S9B–O94	1.472(5)
Ce3–O104	2.330(4)	S10–O101	1.456(4)
Ce4–O93	2.272(4)	S10–O102	1.498(4)
Ce4–O102	2.255(4)	S10–O103	1.469(3)
Ce4–O114	2.294(4)	S10–O104	1.484(4)
Ce4–O122	2.503(4)	S11–O111	1.490(4)
Ce4–O124	2.409(4)	S11–O112	1.460(3)
Ce4–O133	2.431(4)	S11–O113	1.462(3)
Ce4–O134	2.509(4)	S11–O114	1.500(4)
Ce4–O143	2.385(4)	S12–O121	1.460(4)
Ce4–O144	2.490(4)	S12–O122	1.482(4)
Ce5–O51	2.519(5)	S12–O123	1.475(4)
Ce5–O52	2.508(4)	S12–O124	1.500(4)
Ce5–O53	2.529(4)	S13–O131	1.460(4)
Ce5–O54	2.488(4)	S13–O132	1.461(4)
Ce5–O55	2.587(4)	S13–O133	1.505(4)
Ce5–O56	2.534(4)	S13–O134	1.491(4)
Ce5–O121^{ii}	2.528(4)	S14–O141	1.460(4)
Ce5–O132^{iii}	2.541(4)	S14–O142	1.463(4)
Ce5–O141	2.509(4)	S14–O143	1.504(4)
		S14–O144	1.486(4)

Symmetry transformations for equivalent atoms: (i): $-x + y + 1$, $-x + 1$, z; (ii): $-y + 1$, $x - y$, z; (iii): $x + y + 1$, $-x + 2$, z; (iv): $-x + y$, $-x + 1$, z; (v): $-y + 1$, $x - y + 1$, z.

The structural design of the title compound differs from structures of known mixed-valence cerium compounds, all of which form three-dimensional networks.[6–11] In the title compound the cerium atoms, interlinked by sulfate groups, extend to form layers parallel to the *ab* plane (Figure 1a). These layers (ca. 11.5 Å thick) are held together by hydrogen-bonding contacts (Figure 1b). Perpendicular to the layers, in the *c* direction, there are channels (ca. 9.7 Å in diameter), shown in Figure 1a. One of the channels, at (0,0,*z*), hosts solvent water only, while the other two channels, at (1/3,2/3,*z*) and (2/3,1/3,*z*), also host $[Cr(H_2O)_6]^{3+}$ and $[Ce(SO_4)_3(H_2O)_6]^{3-}$ units, blocking each of these channels once per unit cell. Thus, there are voids in the latter two channels, approximately 14 Å long. The $[Cr(H_2O)_6]^{3+}$ cations, located in the channels (Figure 2), are situated between the layers participating in the hydrogen-bonding network that are connecting one layer to an adjacent layer, shown in Figures 1b and 2.

There are four crystallographically different water molecules inside the voids, OW1–OW4. We believe that the OW1 water molecule acts as a hydrogen-bond donor towards O122 (S12 sulfate oxygen atom) and towards O53 (a water molecule attached to Ce5), the OW2 molecule acts as a hydrogen-bond donor towards O72 (S7 sulfate oxygen atom) and towards O11 (a water molecule attached to Ce1), the OW3 water molecule acts as a hydrogen-bond donor towards O12 and O55 (water molecules attached to Ce1 and Ce5, respectively), and that the OW4 water molecule acts

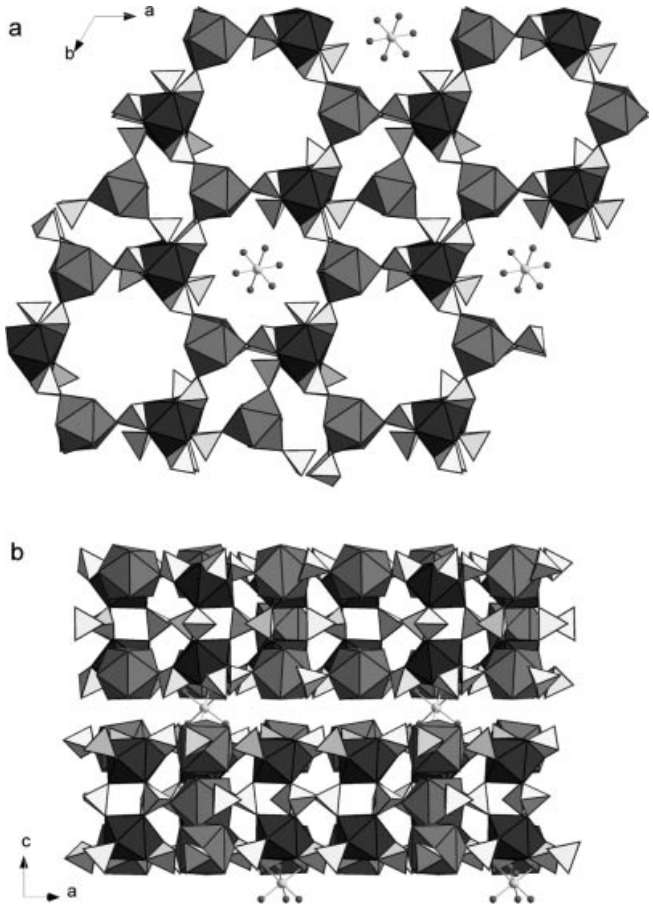

Figure 1. Packing diagrams of the title compound, the Ce^{III} polyhedra are shown in light shades and the Ce^{IV} polyhedra are shown in dark shades. The solvent water molecules are not shown. (a) One single layer extending through sulfate bridges forming channels. (b) There are two layers per unit cell. Adjacent layers are held together by hydrogen-bonding contacts from $[Cr(H_2O)_6]^{3+}$ and from water molecules coordinated to Ce^{III} towards terminal sulfate oxygen atoms.

as a hydrogen-bond donor towards O91 and O103 (oxygen atoms belonging to the S9 and S10 sulfate groups, respectively), in addition, it acts as a hydrogen-bond acceptor from O24 and O53 (water molecules attached to Ce2 and Ce5, respectively). The water molecules coordinated to the Cr^{III} and Ce^{III} ions all participate in the hydrogen-bonding network connecting adjacent layers. Furthermore, there are approximately five additional water molecules that are disordered (see Experimental Section) within the open channel and the two voids, corresponding to 18 water molecules per unit cell in the channel (volume: 861 $Å^3$) plus 12 water molecules per unit cell in the two voids (volume: 2×257 $Å^3$).

According to the Robin and Day classification,[20] this compound could belong to Class II since the oxidized and reduced cerium ions occupy sites of similar geometry. The structure of the title compound can be regarded as consisting of six $[Ce^{III}(H_2O)_6(SO_4)_{3/2}]$, six $[Ce^{IV}(HSO_4)_{2/2}(SO_4)_{1/3}(SO_4)_{3/2}]^{2/3-}$, $[Ce^{III}(H_2O)_6(SO_4)_{3/3}]^{+}$, $[Cr(H_2O)_6]^{3+}$, and solvent water molecules as the main structural units.

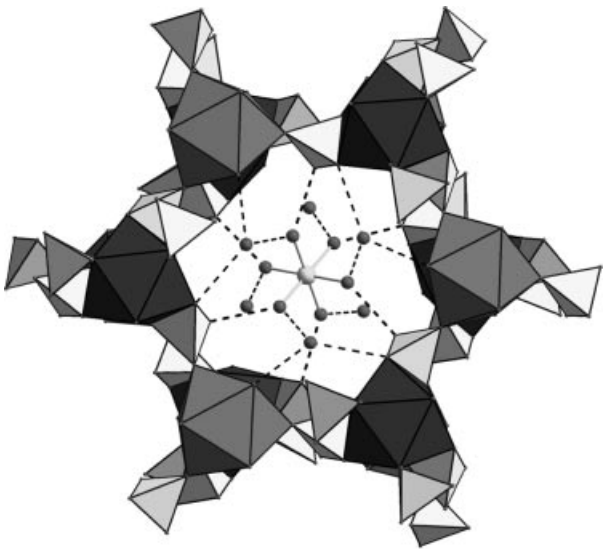

Figure 2. View through one of the channels showing one $[Cr(H_2O)_6]^{3+}$ ion, solvent water molecules, and part of the hydrogen-bonding network. The Ce^{III} polyhedra are shown in light shades and the Ce^{IV} polyhedra are shown in dark shades.

Hence, a possible donor–acceptor couple could be $[Ce^{III}(H_2O)_6(SO_4)_{3/2}]$ and $[Ce^{IV}(HSO_4)_{2/2}(SO_4)_{1/3}(SO_4)_{3/2}]^{2/3-}$ which are linked by one sulfate bridge, Ce^{III}–O–S–O_2–Ce^{IV}. The geometrical distance between the metal sites (>6.5 Å) is sufficiently large to decline direct overlap of the electronic wave functions. Prior to an electron transfer, the nuclear configurations of the reactants and the surrounding medium must adjust to an intermediate configuration with no energy change when the electron moves from the donor to the acceptor.[21] For metal complexes in a polar solvent, the nuclear configuration changes involve adjustments in the metal–ligand bond lengths and angles, and changes in the orientations of the surrounding solvent molecules.[21] Similar adjustments are also required in the stiffer inorganic solid state. Therefore, due to the difference in bond lengths at the donor and acceptor sites, a substantial energy barrier to their interconversion exists, and since electronic coupling with orbitals of appropriate symmetry in the sulfate bridge probably is negligible, this mixed-valence cerium compound presumably is a Class I compound. If there is no electronic interaction between the acceptor and donor sites then the properties of this compound are essentially those of the separate acceptor and donor sites. However, a small portion of Class II character cannot be completely dismissed since the geometry of the donor site, $[Ce^{III}(H_2O)_6(SO_4)_{3/2}]$, is quite flexible due to the coordinated water molecules and further, the oxidizing ability of the acceptor site, $[Ce^{IV}(HSO_4)_{2/2}(SO_4)_{1/3}(SO_4)_{3/2}]^{2/3-}$, may increase if it becomes protonated by the adjacent slightly acidic $[Cr(H_2O)_6]^{3+}$ species. Class II compounds generally possess new optical and electronic properties in addition to those of the separate sites and might be semiconductors or ionic conductors.

There are two structurally related compounds $H_9Nd_7Ce_6(SO_4)_{27}\cdot 72.33H_2O$[22] and $H_9Tb_7Ce_6(SO_4)_{27}\cdot$

$72.2H_2O$.[23] These compounds contain channels and voids of comparable dimensions but they are not mixed-valence compounds and do not contain any hydrated transition-metal ions participating in the hydrogen-bonding network. One compound containing chromium(III) combined with a rare-earth element is samarium chromium silicon oxynitride[24] (space group $P6_3$), but its crystal structure differs from the title compound as it is apatite-like and extends through silicate bridges forming a compact three-dimensional network.

Experimental Section

Sample Preparation: $Ce(SO_4)_2{\cdot}4H_2O$ (0.50 g, 1.27 mmol), CrO_3 (0.38 g, 3.8 mmol), and water (5.0 mL) were mixed in a round-bottomed microflask connected to a reflux water condenser. The reaction mixture was refluxed for 24 h until orange crystals of $Ce(CrO_4)_2(H_2O)_2$ were formed. These crystals were dissolved in sulfuric acid (4 M). Concentration at room temperature gave light yellow crystals shaped as hexagonal needles. The title compound may also be produced from $Ce(OH)_4$ and CrO_3 in diluted sulfuric acid solution but the best single crystals were achieved with the former description.

Single Crystal X-ray Analysis: Data were collected with a Siemens SMART CCD diffractometer equipped with a Siemens LT-2A low-temperature device at –100 °C. A full sphere of the reciprocal space was scanned by 0.3° steps with a crystal-to-detector distance of 3.97 cm and an exposure time per frame of 2 s. A preliminary orientation matrix was obtained using the SMART software.[25] The collected frames were integrated with the orientation matrix which was updated every 100 frames. Final cell parameters were obtained by refinement from 8192 reflections with $I > 10\sigma(I)$ after integration of all the data using the SAINT software.[25] The data were corrected empirically for absorption and other effects using the SADABS software.[26] The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL software package.[27] Disordered solvent water molecules (five water molecules in the asymmetric unit) were removed using the PLATON[28] (version 1.10) squeeze instruction. All non-hydrogen atoms were refined anisotropically. Details on data collection and refinement are given in Table 2. Further details of the crystal structures may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-417583. Molecular graphics were drawn with the DIAMOND software package.[29]

Table 2. Crystal data and structure refinement.

Empirical formula	$H_{156}Ce_{13}CrO_{183}S_{27}$
Formula mass	5824.48
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	hexagonal
Space group	$P6_3$
Unit cell dimensions	a = 19.3015(2) Å, c = 25.2684(4) Å
Volume	8152.49(18) Å^3
Z	2
Density (calcd.)	2.395 Mg/m^3
Absorption coefficient	4.106 mm^{-1}
F(000)	5720
Crystal size	0.40 × 0.10 × 0.08 mm
θ range for data collection	2.11–33.02°
Index ranges	$-29 \le h \le 28$, $-26 \le k \le 29$, $-38 \le l \le 38$
Reflections collected	102247
Independent reflections	19680 [R(int) = 0.0406]
Completeness to θ = 31.00°	99.9%
Absorption correction	Multi-scan
Max./min. transmission	0.7347/0.2904
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	19680/1/657
Goodness-of-fit on F^2	1.006
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0362, wR_2 = 0.0930
R indices (all data)	R_1 = 0.0460, wR_2 = 0.0997
Twin volume ratio	0.692(10):0.308(10) on 9462 Friedel pairs
Largest diff. peak/hole	2.603/–2.104 eÅ^{-3}

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