Syntheses and Crystal Structures of Hydrated Ternary Cerium Sulfates: Mixed-valence $K_5Ce_2(SO_4)_6$ ·H₂O and $K_2Ce(SO_4)_3$ ·H₂O

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Abstract. A new chemical and structural interpretation of $K_5Ce_2(SO_4)_6$ ·H₂O (I) and a redetermination of the structure of $K_2Ce(SO_4)_3$ ·H₂O (II) is presented. The mixed-valent compound I crystallizes in the space group C2/c with a = 17.7321(3), b = 7.0599(1), c = 19.4628(4) Å, β = 112.373(1)° and Z = 4. Compound I has been discussed earlier with space group Cc. In the structure of I, there are pairs of edge sharing cerium polyhedra connected by sulfate oxygen atoms in the μ_3 bonding mode. These cerium dimers are linked through edge and corner sharing sulfate bridges, forming layers. The layers are joined by potassium ions which together with the water molecules are placed between the layers. No irregularity in the distribution of the Ce^{III} and Ce^{IV} to cause the lost of a crystallographic center of symmetry was detected. We suggest that the charge exerted by the extra f^{T} electron for every cerium dimer is delocalized over the Ce1–O₂–Ce2 moi-

ety in a non-bonding mode. As a result, the oxidations state of each cerium ion is a mean value between III and IV at each atomic position. Compound **II** crystallizes in the space group C2 with a = 20.6149(2), b = 7.0742(1), c = 17.8570(1) Å, β = 122.720(1)° and Z = 8. The hydrogen atoms have been located and the absolute structure has been established. Neither hydrogen atom positions nor anisotropic displacement parameters were given in the previous reports. In compound **II**, the cerium polyhedra are connected by edge and corner sharing sulfate groups forming a three-dimensional network. This network contains Z-shaped channels hosting the charge compensating potassium ions.

Keywords: Cerium; Mixed-valent compounds; Lanthanides; Ternary lanthanide sulfates; Ternary cerium sulfates; Crystal structures

Introduction

Among the rare-earth materials, cerium compounds attract research attention owing to their applications as ion conductors, catalysts, magnetic and fluorescence materials. Recently, during investigations of rare-earth frameworks, advances in the syntheses of new inorganic materials [1] with interesting applications [2] have been achieved. In the chemistry of the rare-earth elements, the sulfate ion, together with other complex inorganic anions, plays an important role. A comprehensive review of the lanthanide compounds with complex anions was presented in 2002 by *Wickleder* [3] covering the structurally characterized compounds to that date. These materials are intriguing due to the complexity of their structural arrangements with high coordination numbers and a variety of coordination geometries.

* Barbara M. Casari Inorganic Chemistry, Department of Chemistry Göteborg University SE-412 96 Göteborg Sweden Phone: +46(0)317722877 Fax: +46(0)317722853 E-mail: casari@chem.gu.se The existence of alterable oxidation states for the cerium ion will result in compounds with new structural designs and interesting properties [4].

There is structural information on anhydrous ternary rare-earth sulfates, $AM(SO_4)_2$, with all alkaline ions (A^+) nearly for the whole lanthanide series [3]. Anhydrous as well as hydrous ternary sulfates with other composition $A^+:M^{3+}$ than 1:1 are not well characterized, although a number of phases are supposed to exist [3]. Nearly all the structurally characterized sulfates with an A:M ratio $\neq 1$ are described as non-centrosymmetric [3]. The most common ternary rare-earth hydrates are mono and tetrahydrates, for the smaller A^+ ions the monohydrates dominate while for the bigger monovalent ions the tetrahydrates prevail. Five hydrated alkali cerium sulfates have been structurally characterized up to date, one Ce^{IV} compound, K₂Ce(SO₄)₃·H₂O [5] and four Ce^{III} compounds, ACe(SO₄)₃·H₂O (A = Li [6a], Na [6b], K [6c], Rb [6d]).

There are seven mixed-valence cerium compounds in the ICSD Database (2006-1): $Ce_4O_4S_3$ [7], $Ce_3O_3S_2$ [8], $Ce_{10}(GeO_4)_3(Ge_2O_7)_2(Ge_3O_{10})$ [9], $(H_3O)(Ce_2(SeO_4)_4)$ [10], $KCe_2(SO_4)_4$ [11], $Ce_6Ta_6O_{25}$ [12] and $Ce_{0.968}H_{10.432}O_{12.924}S_2$ [13]. All of the mixed-valence cerium compounds described earlier [7–13] have the f^{i} electron localized at one single cerium nucleus. Here we present the first structural interpretation of a cerium compound where the f^{i} electron is delocalized over two cerium atoms, resulting in a valence of 3.5 for each cerium ion.



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Results and Discussion

Synthesis of K₅Ce₂(SO₄)₆·H₂O (I)

Crystals of I were formed from Ce^{IV} species, $[Cr_2O_7]^{2-}$ and sulfuric acid as starting materials. Cerium(IV) in acidic aqueous solutions is metastable with respect to the oxidation of water to produce gaseous oxygen. The attainment of equilibrium is kinetically controlled and the reaction is observed only in the presence of a catalyst [14]. In the absence of added ions, the glass vessel might act as the catalytic agent [14], thus in an acidic aqueous media cerium(III) will be formed. On the other hand, 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 [15] encountered also in our previous work [16]. The chromium system is able to produce a variety of transient and intermediate species and several competing redox reactions can take place [16] but the redox equilibriums involved in this case can be written as following total reactions:

$$2Ce^{4+} + H_2O \rightarrow 2Ce^{3+} + 2H^+ + \frac{1}{2}O_2$$
$$[CrO_4]^{2-} + 3Ce^{3+} + 8H^+ \rightarrow Cr^{3+} + 3Ce^{4+} + 4H_2O$$

Purbaix diagrams on cerium and chromium species have been revised recently [17] showing that the first reaction prevails in acidic solutions while the second reaction is dominant in neutral and basic solutions. Accordingly, in acidic aqueous solutions small quantities of mixed valent cerium species may form despite the presence of chromium(VI) compounds.

Structural description of K₅Ce₂(SO₄)₆·H₂O (I)

The mixed-valence cerium compound I crystallizes in the space group C2/c with a = 17.7321(3), b = 7.0599(1), c = 19.4628(4) Å, $\beta = 112.373(1)^{\circ}$ and Z = 4. Compound (I) has been discussed by Tursina and Iskhakova [18] who reported space group to be Cc. There is one cerium atom, three potassium ions (one is on the two fold axis), three sulfate groups and a water molecule in the asymmetric unit. The water molecule is disordered with respect to the twofold axis, with 50 % occupancy. The cerium atom is in contact with nine oxygen atoms belonging to five corner sharing and two edge sharing sulfate groups (Fig. 1). The coordination polyhedron is a slightly distorted tri-capped trigonal prism, not a singly-capped tetragonal antiprism as described by Tursina and Iskhakova [18]. Coordination numbers such as nine are expected for the large Ce^{III} ion but is rarely encountered for the smaller Ce^{IV} ion. The Ce-O distances average to 2.47(7) Å (Table 1) and the bond-valence sum is 3.49 or 3.20 v.u. for the cerium atom regarded as Ce^{III} and Ce^{IV}, respectively (using parameter from Trzesowska et al. [19]). The three sulfate groups show a small departure from the ideal tetrahedral symmetry and the S-O distances average to 1.48(2) Å (Table 1). The



Fig. 1 Coordination geometry for cerium in compound I. The displacement ellipsoids are drawn at 50 % probability level.

Table 1 Bond lengths /Å and angles /° for I.

Ce1-013	2 604(2)	K2-031	2,780(3)
Ce1-O13 ⁱⁱ	2.435(2)	K2-034	2.939(2)
Ce1-014	2.415(2)	K3-011	2.702(2)
Ce1-O22	2.460(2)	K3-O22 ^{ix}	2.988(3)
Ce1-O23iv	2.488(2)	K3–O23 ^{ix}	2.758(3)
Ce1-O24 ^{iv}	2.531(2)	K3-O24 ⁱ	2.928(3)
Ce1-O32	2.491(3)	K3–O24 ^{vii}	2.784(3)
Ce1-O33 ⁱⁱⁱ	2.439(2)	K3-O32 ⁱ	3.008(3)
Ce1-O34 ⁱ	2.382(2)	K3-O33vii	2.894(2)
K1-O14	2.760(2)	K3-O50vii	3.081(12)
K1-O14 ^{vi}	2.760(2)	S1-O11	1.454(2)
K1-O21	2.776(3)	S1-O12	1.447(2)
K1-O21vi	2.776(3)	S1-O13	1.517(2)
K1-O22	3.056(2)	S1-O14	1.495(2)
K1-O22 ^{vi}	3.056(2)	S2-O21	1.442(3)
K1-O31	2.892(2)	S2-O22	1.480(2)
K1-O31 ^{vi}	2.892(2)	S2-O23	1.497(2)
K1-O50 ⁱⁱⁱ	2.939(9)	S2-O24	1.492(2)
K2-O11	2.690(2)	S3-O31	1.455(2)
K2-O11 ^v	2.863(2)	S3-O32	1.476(2)
K2-O12 ^v	2.891(2)	S3-O33	1.491(2)
K2-O12viii	2.679(2)	S3-O34	1.488(2)
K2-O21 ^{vi}	2.725(3)	O50-H51	0.95(2)
K2–O23 ^{ix}	2.779(2)	O50-H52	0.95(2)

Symmetry transformations for equivalent atoms:

 $\begin{array}{c} (i) & -x+1/2, -y+5/2, -z \\ (iv) & -x+1, -y+2, -z \\ (vi) & x+1/2, -y+1/2, -z+1/2 \\ (vii) & x-1/2, -z+1/2, -z+1/2, -z+1/2, -z+1/2 \\ (vii) & x-1/2, -z+1/2, -z+1/2, -z+1/2 \\ (vii) & x-1/2, -z+1/2, -z+1/2, -z+1/2 \\ (vii) & x-1/2, -z+1/2, -z+1/2, -z+1/2, -z+1/2 \\ (vii) & x-1/2, -z+1/2, -z+1/2, -z+1/2 \\ (vii) & x-1/2, -z+1/2, -z+1/2, -z+1/2, -z+1/2 \\ (vii) & x-1/2, -z+1/2, -z+1/$

S1-group is edge sharing with the Ce-polyhedron, with one of the edge sharing oxygen atoms in the μ_2 bonding mode and the other (O13) in the μ_3 bonding mode, connecting two cerium polyhedra. The S2-group is both edge sharing and corner sharing with Ce-polyhedra. The S3-group is corner sharing with three Ce-polyhedra. There are no real terminal sulfate oxygen atoms since these all are in contact with potassium ions but as expected, these S-O distances (average: 1.449(6) Å) are slightly shorter than the remaining S-O distances (average: 1.49(1) Å) with the S1-O13 in S-O μ_3 -Ce₂ bonding mode being the longest



Fig. 2 Coordination geometry for pairs of edge sharing cerium polyhedra in compound **I**. The oxygen atoms are marked by dark ellipsoid and the sulfur atoms by light ellipsoids. The displacement ellipsoids are drawn at 50 % probability level.

(1.517(2) Å). The potassium ions are in contact with nine (K1) or eight (K2 and K3) oxygen atoms at distances ranging between 2.679(2) and 3.081(12) Å, see Table 1. The water molecule (O50) is in contact with the K1 and K3 ions.

Within the structure of I there are pairs of edge sharing cerium polyhedra connected by sulfate oxygen atoms in the μ_3 bonding mode (Fig. 2). In addition each cerium atom is also connected to four other cerium atoms, through edge and corner sharing sulfate bridges, forming layers in the ab plane with the composition [Ce₂(SO₄)₆]_n⁵ⁿ⁻. Perpendicular to these layers, in the c direction, there are channels hosting the K3 ions (Fig. 3a). The layers are joined by the K1 and K2 ions which together with the water molecules are placed between the layers (Fig. 3b). The structure of I has the main structural features common with the structure of $K_5NaCe_2(SO_4)_6$ [20]. That compound also forms layers, but with a different charge $[Ce_2(SO_4)_6]_n^{6n-}$, with channels hosting potassium ions, and the layers are connected by sodium and potassium ions. The general architectural features of the structure of I is the one adopted by some Ce^{III} compounds, but not by Ce^{IV} compounds.

To better understand the mixed valence features in compound I we also refined the structure of I in space group Cc, so that the two cerium atoms within the edge sharing dimer were allowed to refine independently. Structure solution of I in space group Cc resulted in full occupancy of the water molecule, larger su's values, but no significant differences between the coordination spheres of the two nonequivalent cerium atoms, Ce1 and Ce2. The Flack parameter [21] was refined to 0.43(2) on 3743 Friedels pairs. No irregularity in the distribution of the Ce^{III} and Ce^{IV}, stated by Tursina and Iskhakova [18] to cause the lost of a crystallographic center of symmetry, was detected. The bond-valence sums are 3.51 and 3.49 v.u. for Ce1 and Ce2, respectively (using parameter for Ce^{III} from Trzesowska et al. [19]). For I we suggest that the charge exerted by the extra f^{\prime} electron for every cerium dimer is delocalized over the dimer, through $Ce1-O_2-Ce2$, in a non-bonding mode. The ability of the f^{I} electron to delocalize over the dimer is enabled by the planar geometry of the $Ce1-O_2-Ce2$ moiety, with maximal departure from mean least-square plane



Fig. 3 Packing diagram of compound I. 3a: Layers in the *ab* plane with the composition $[K_2Ce_2(H_2O)(SO_4)_6]_n^{3n-}$. 3b: Stacking of the layers in the **c** direction.

 Table 2
 Bond-valence sum, mean values [v.u.]

	Ce ^{IV}	Ce ^{III}
$Ce_4O_4S_3^{[7]}$	4.01	3.08
$Ce_{3}O_{3}S_{2}^{[8]}$	4.00	3.04
$Ce_{10}(GeO_4)_3(Ge_2O_7)_2(Ge_3O_{10})^{[9]}$	3.71	2.78
$(H_3O)(Ce_2(SeO_4)_4)^{[10]}$	4.09	3.05
$KCe_2(SO4)_4^{[11]}$	4.03	3.05
$Ce_6Ta_6O_{25}^{[12]}$	4.39	2.76
$Ce_{0.968}H_{10.432}O_{12.924}S_2^{[13]}$	4.21	2.76

0.002(8) Å and 0.000(2) Å when the structure is refined in Cc and C2/c, respectively.

Confronting the values for the bond-valence sums for cerium atoms for compound I with the values of the bond-valence sums from reported mixed-valence cerium compounds [7-13] one can see (Table 2) that I is the only compound that has almost the same values for the bond valence sums of the cerium atoms (parameters from *Trzesowska* et al. [19] were used for calculations). In the case of compound I we believe that the oxidations state of each cerium ions

position, presumably a class III-A compound according to the *Robin* and *Day* classification [22]. Possibly this special case of mixed valence might contribute to novel properties among cerium compounds.

Structural description of K₂Ce(SO₄)₃·H₂O (II)

Here we present a redetermination of the structure of **II**. In this study the hydrogen atoms have been located and the absolute structure has been established. This structure determination is more precise than the previous ones, based on three times as many independent reflections, making the structure features well defined. Neither hydrogen atom positions nor anisotropic displacement parameters were given in the previous reports [5].

The hydrated ternary cerium sulfate II, crystallizes in the space group C2 with a = 20.6149(2), b = 7.0742(1), c = 17.8570(1) Å, β = 122.720(1)° and Z = 8. There are two cerium atoms, five potassium ions (two on 2-fold axis), six sulfate groups and two water molecules in the asymmetric unit. Each cerium atom is in contact with nine oxygen atoms, belonging to four corner sharing, two edge sharing sulfate groups and one water molecule (Fig. 4). The coordination polyhedra are slightly distorted tricapped trigonal prisms. Nine-fold coordination is not so frequent as eightfold coordination for the Ce(IV) ion. The Ce1–O and Ce2–O distances average to 2.39(6) and 2.40(6) Å, respectively (Table 2). The bond-valence sums are 3.93 and 3.82 v.u. for Ce1 and Ce2, respectively (using parameter from *Trzesowska* et al. [19]).



Fig. 4 Coordination of the two cerium atoms in compound II. The displacement ellipsoids are drawn at 50 % probability level.

The S–O distances within the six sulfate groups average to 1.48(2) Å (Table 3) and the edge sharing ones (S1, S2, S4 and S5) show a departure from the ideal tetrahedral symmetry, angles ranging from $100.51(16)^{\circ}$ to $113.06(19)^{\circ}$. The sulfate groups S1, S4 and S5 are both edge and corner sharing, S3 and S6 are corner sharing, while S2 is edge sharing, but not linking. The potassium ions are in contact with eight (K4 and K5), nine (K1) or ten (K2 and K3) oxygen atoms at distances ranging between 2.625(3) and 3.366(4) Å, see Table 3.

Table 3	Bond	lengths	/A	for	II.
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Ce1-O1	2,466(3)	K3-O51 ⁱⁱ	3,198(3)
Ce1-O11 ⁱⁱ	2.423(3)	K3-Q54	2.942(3)
Ce1-012	2.405(3)	K3-Q54 ⁱⁱ	2.942(3)
Ce1-014	2.441(3)	K4-O23 ^{xi}	2.733(3)
Ce1-042	2.417(3)	K4-O23 ^{ix}	2.733(3)
Ce1-043	2.436(3)	K4-032 ^x	2.668(3)
Ce1-051	2.354(3)	K4-032 ^{iv}	2.668(3)
Ce1-O61 ⁱ	2.283(3)	K4-O41 ^{xi}	3.280(3)
Ce1-O62	2.302(3)	K4-O41 ^{ix}	3.280(3)
Ce2-O2	2.438(3)	K4-O44 ^{xi}	2.776(3)
Ce2-O21	2.351(3)	K4-O44 ^{ix}	2.776(3)
Ce2-O23	2.406(3)	K5-O13	2.710(3)
Ce2-O31 ^{iv}	2.469(3)	K5-O22 ^{vii}	2.994(3)
Ce2-O33iii	2.363(3)	K5-O24 ^{xii}	2.677(3)
Ce2-O34	2.278(3)	K5-O32 ⁱⁱ	2.710(3)
Ce2-O41	2.401(3)	K5-O44 ^{xiii}	3.100(3)
Ce2-O52	2.446(3)	K5-O54 ⁱⁱ	3.033(3)
Ce2-O53	2.468(3)	K5-O63	3.366(4)
K1-012	2.879(3)	K5-O64	2.802(3)
K1-013	2.810(3)	S1-011	1.482(3)
K1-O22vii	2.942(3)	S1-O12	1.505(3)
K1-O24vii	2.937(3)	S1-O13	1.446(3)
K1-O43 ⁱ	2.625(3)	S1-O14	1.494(3)
K1-O61 ⁱ	2.885(3)	S2-O21	1.516(3)
K1-O62 ⁱ	2.938(3)	S2-O22	1.454(3)
K1-O63vi	2.699(3)	S2-O23	1.506(3)
K1-O64	2.695(3)	S2-O24	1.452(3)
K2-O11	2.954(3)	S3-O31	1.493(3)
K2-O13	2.691(3)	S3-O32	1.442(3)
K2-O21vii	2.797(3)	S3-O33	1.491(3)
K2-O24vii	2.995(3)	S3-O34	1.490(3)
K2-O31 ^{vii}	2.691(3)	S4-O41	1.476(3)
K2-O33vii	2.949(3)	S4-O42	1.496(3)
K2-O42 ⁱⁱ	2.688(3)	S4-O43	1.495(3)
K2-O52 ⁱⁱ	2.859(3)	S4-O44	1.456(3)
K2-O53viii	2.946(3)	S5-O51	1.481(3)
K2-O54viii	2.940(3)	S5-O52	1.488(3)
K3-O1 ^v	3.181(4)	S5-O53	1.499(3)
K3-O1 ^{ix}	3.181(4)	S5-O54	1.449(3)
K3-O12 ^v	3.076(3)	S6-O61	1.505(3)
K3-O12 ^{ix}	3.076(3)	S6-O62	1.516(3)
K3-O14	2.890(3)	S6-O63	1.456(3)
K3-O14 ⁱⁱ	2.890(3)	S6-O64	1.446(3)
K3-O51	3.198(3)		

Symmetry transformations for equivalent atoms:

 $\begin{array}{ll} (i) & -x+1/2, y-1/2, -z+1 & (ii) & -x+1, y, -z+1 & (iii) & -x+3/2, y-1/2, -z+2 \\ (iv) & -x+3/2, y+1/2, -z+2 & (v) & -x+1, y+1, -z+1 & (vi) & x, y-1, z & (vii) & x-1/2, \\ y-1/2, z-1 & (viii) & -x+1, y-1, -z+1 & (ix) & x, y+1, z & (x) & x-1/2, y+1/2, z \\ (xi) & -x+1, y+1, -z+2 & (xii) & x-1/2, y+1/2, z-1 & (xiii) & -x+1/2, y+1/2, -z+1 \end{array}$

In compound II, the Ce1 and Ce2 polyhedra are connected by the S4 and S5 sulfate groups and the Ce1 and Ce2 ions are connected to themselves by bridging S6 and S3 groups, respectively, forming infinite layers (Fig. 5). These layers are held together by edge and corner sharing S1 groups forming a three-dimensional network with the composition $[Ce(SO_4)_3]_n^{2n-}$. In the network, there are Z-shaped channels (in **b** direction) hosting the charge compensating potassium ions, see Figure 6. The four hydrogen bonding contacts (Table 4) are intra layer connecting, three of them acting towards terminal sulfate oxygen atoms, see Figure 7.

Experimental Section

Sample preparations

Several unsuccessful attempts to synthesize mixed valence cerium sulfates were performed, also by hydrothermal hydrolysis, starting



Fig. 5 Single layer of II, with the composition $[Ce_2(SO_4)_5]_n^{2n-}$, parallel with the ($\overline{1}01$) plane. From the top; non linking S2 sulfate groups, S3 groups connecting Ce2 polyhedra, S4 and S5 groups linking Ce1 and Ce2 polyhedra and S6 groups linking Ce2 polyhedra.



Fig. 6 Layers in **II**, with the composition $[Ce_2(SO_4)_5]_n^{2n-}$, held together by S1 sulfate groups forming a three-dimensional network with Z-formed channels hosting the intercalating potassium ions.

Table 4 H	ydrogen	bonds	for	Π	/Å	and	۰.
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D–H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O1-H1A···O63 ⁱ	0.86(3)	2.25(4)	3.048(5)	156(6)
O1-H1B···O53 ⁱ	0.82(3)	2.39(5)	3.020(4)	134(6)
O2-H2A···O22 ⁱⁱⁱ	0.89(3)	1.89(3)	2.744(4)	160(6)
O2-H2B···O44 ⁱⁱ	0.85(3)	2.06(5)	2.773(4)	140(6)

Symmetry transformations to generate equivalent atoms: (i) x,y-1,z (ii) x,y+1,z (iii) -x+1,y,-z+2



Fig. 7 Compound II: hydrogen bonding contacts.

from different molar ratios of various Ce^{III} and Ce^{IV} materials, with and without alkali or ammonium ions. Finally, crystals of $K_5Ce_2(SO_4)_6$ ·H₂O (I) and $K_2Ce(SO_4)_3$ ·H₂O (II) were formed, during the studies on the Ce^{IV}/Ce^{III} – Cr^{VI}/Cr^{III} redox system [16] at different stages of the following reaction conditions:

1) Equal volumes of a slightly acidic (with H_2SO_4) saturated water solution of $Ce(SO_4)_2$ ·4 H_2O and a saturated concentrated sulfuric acid solution of $K_2Cr_2O_7$ was brought together during slow heating and stirring. A small fraction of solid residue was removed and the supernatant was left uncovered, after four months small yelloworange colored crystals of I were formed.

2) Ce(SO₄)₂·4H₂O (3.0 g, 7.5 mmol) was dissolved in water (20 mL) and Ce(OH)₄ was precipitated with 15 M ammonia. Ce(OH)₄ (0.25 g, 1.6 mmol) was added to a concentrated sulfuric acid solution (5.5 mL) of K₂Cr₂O₇. The solid residue was removed and the supernatant was divided in three parts. Water (3.0^a, 2.0 and 1.0^b mL) was added to each part. After 24 h a small fraction of solid residue was removed from each solution and the supernatants were left covered. 2a). After two months small both yellow and orange colored crystals of I were formed. 2b) After seven months small yellow-orange colored crystals of I were formed together with small good quality orange colored crystals of II suitable for single crystal diffraction analysis.

3) Ce(OH)₄ (0.25 g, 1.6 mmol) was added to a saturated water solution (6.0 mL) of $K_2Cr_2O_7$. Concentrated sulfuric acid was added to the solution until the solid residue was dissolved. After one year, good quality orange colored crystals of I suitable for single crystal diffraction analysis were formed.

Crystals of I and II are difficult to distinguish optically, their shape may be both parallelepipeds with square faces or with hexagonal faces and the crystal color might vary from yellow to dark orange for both compounds.

Single crystal X-ray analysis

Data were collected using a Siemens SMART CCD diffractometer equipped with a Siemens LT-2A low temperature device, at 22 °C

Table 5 Crystal data and structure refinement for I and II.

Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions	K ₅ Ce ₂ (SO ₄) ₆ ·H ₂ O (I) 1070.12 295(2) K 0.71073 Å monoclinic C2/c a = 17.7321(3) Å b = 7.0599(1) Å c = 19.4628(4) Å $\beta = 112.373(1)^{\circ}$	K ₂ Ce(SO ₄) ₃ ·H ₂ O (II) 524.52 173(2) K 0.71073 Å monoclinic C2 a = 20.6149(2) Å b = 7.0742(1) Å c = 17.8570(1) Å $\beta = 122.720(1)^{\circ}$
Volume Z Density (calculated) Absorption coefficient F(000) Crystal size θ range for data collection Index ranges Reflections collected Independent reflections Completeness to $\theta = 30.50^{\circ}$ Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F2 Final R indices [I>20(I)] B indices (all data)	2253.08(7) A ² 4 3.155 Mg/m ³ 5.584 mm ⁻¹ 2036 $0.06 \times 0.03 \times 0.02 \text{ mm}^3$ 2.26 to 32.88°. $-26 \le \le 26, -10 \le k \le 10, -29 \le 1 \le 29$ 17812 4022 [R(int) = 0.0270] 99.9 % multi-scan 0.8965 and 0.7305 Full-matrix least-squares on F ² 4022 / 2 / 184 1.003 R1 = 0.0253, wR2 = 0.0663 R1 = 0.0201, wR2 = 0.0661	$ \begin{array}{l} 2190.93(4) \text{ A}^{2} \\ 8 \\ 3.180 \text{ Mg/m}^{3} \\ 5.557 \text{ mm}^{-1} \\ 2000 \\ 0.20 \times 0.12 \times 0.05 \text{ mm}^{3} \\ 1.36 \text{ to } 32.81^{\circ} \\ -31 \leq 4 \leq 30, -10 \leq k \leq 10, -26 \leq l \leq 27 \\ 17878 \\ 7616 [\text{R(int)} = 0.0303] \\ 100.0 \% \\ \text{multi-scan} \\ 0.7686 \text{ and } 0.4028 \\ \text{Full-matrix least-squares on F}^{2} \\ 7616 / 5 / 357 \\ 1.002 \\ \text{R1} = 0.0254, \text{ wR2} = 0.0576 \\ \text{P1-} = 0.0283 \text{wR2} = 0.0590 \end{array} $

for I and at -100 °C for II. Full spheres of the reciprocal space were scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm and exposure time per frame, being 15 s for I and 20 s for II. Preliminary orientation matrices were obtained using SMART (Siemens, 1995) [23]. The collected frames were integrated with the orientation matrices updated every 100 frames. Final cell parameters were obtained by refinement on the position of 8192 reflections with $I > 10\sigma(I)$ after integration of all the data using SAINT (Siemens, 1995) [23]. The data were corrected empirically for absorption and other effects using SADABS (Sheldrick, 2002) [24]. The structures were solved by direct methods and refined by full-matrix least squares on all F² data using SHELXTL (Bruker, 2001) [25]. The non hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps and refined isotropically with common O-H distances and a common temperature factor. The Flack parameter [21] was refined to 0.011(8) on 3422 Friedel pairs for II.

Details on data collections and refinements are given in Table 5. Further details of the crystal structures may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-417496 for I and CSD-417497 for II. Molecular graphics: DIAMOND (Brandenburg, 2001) [26].

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