CRYSTAL STRUCTURE OF CERIUM(III) SULFATE-2-UREA-5-WATER
Ce₂(SO₄)₃·2O(CNH₂)₂·5H₂O AND THE STRUCTURAL CHARACTERISTICS
OF THE SULFATES OF THE RARE EARTH ELEMENTS

V. I. Ponomarenko, M. A. Porai-Koshits, E. N. Kurkutova, and K. Sulaimankulov

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The structure of the triclinic crystal Ce₂(SO₄)₃·2O(CNH₂)₂·5H₂O has been determined by an analysis of the function of interatomic vectors and difference syntheses. A detailed description of the structure has been given, and the regular crystal-chemical features in the series of rare earth metal sulfates and selenates have been discussed.

The structural study of the product of the addition of urea to cerium sulfate represents a continuation of the systematic study of the crystal chemistry of the sulfates of the rare earth elements (REE), begun earlier [1-5]. The direct aim of the present study was to investigate the structural role of urea and to analyze the changes in the general motif of the structure and the form of the coordination polyhedra of the REE when additional polar molecules are introduced into the sulfate.

The synthesis of cerium sulfate-2-urea-5-water Ce₂(SO₄)₃·2O(CNH₂)₂·5H₂O (I) was described in [6]. The preliminary results of a structural analysis of the crystal were given in [7]. The present paper gives more detailed characteristics of the crystal structure and discusses the general regular features of the structures of REE sulfates with different compositions.

EXPERIMENTAL AND STRUCTURAL ANALYSIS

The studies were carried out using nonfaceted fragments of colorless transparent single crystals with dimensions 0.2 × 0.2 × 0.2 mm. The crystals are triclinic, a = 11.097(5), b = 13.409(6), c = 6.830(3) Å, α = 85.50(4), β = 92.23(4), γ = 104.98(4), Z = 2, Ce₂(SO₄)₃·2O(CNH₂)₂·5H₂O

The unit cell parameters and the intensities of the reflections were measured on a "Hilger-Watts" automatic diffractometer (λMoKα, planar graphite monochromator, 2θ/θ scanning, (sin θ/λ)max = 0.67 Å⁻¹; 4680 independent nonzero reflections). Statistical analysis of the intensities using the program "Rentgen-70" indicated the space group P₁⁻, which was confirmed by the P(uvw) synthesis.

Mamedov-Belov "peak triplets" [8] were distinguished on the Patterson distribution, and this made it possible to determine the coordinates of the two Ce atoms. Minimization by Buerger's method [9], carried out from the observed single peaks of the Ce-Ce coupling, was completed with the additional localization of three S atoms. The coordinates of the five atoms (2Ce, 3S) were used as a basis for calculating the first synthesis of the electron density (R = 0.327), in which the oxygen atoms of the SO₄ tetrahedra were localized. A series of successive difference syntheses was completed with the determination of the positions of the remaining atoms other than hydrogen. The model of the structure was refined by the method of least squares in the isotropic approximation with respect to all nonzero reflections (Rhk ≤ 0.078, Btotal = 0.40 Å²).

The final coordinates of the atoms, bond lengths, and valence angles are given in Tables 1-3. The characteristic features of the structure can be seen from Fig. 1.
DESCRIPTION OF THE STRUCTURE

The sulfate is based on sulfate–cerium columns of complex structure, elongated along the c axis. In transverse section, each column has three rigidity ribs, arranged in zigzag fashion. The central rigidity rib (vertical, oriented in the ac plane) is made up of Ce₁ atoms and (SO₄)₁ groups in the form of a ribbon

\[ \text{Ce}(1) - S(1) - \text{Ce}(1) - S(1) - \]
\[ \text{S}(1) - \text{Ce}(1) - \text{S}(1) - \text{Ce}(1), \]

Scheme I

where each SO₄ group is joined to three Ce atoms through oxygen atoms, and each Ce atom is attached to three SO₄ groups. The adjoining ribs (horizontal, parallel to the bc plane) are constructed similarly of alternating Ce(1) and Ce(2) atoms and (SO₄)(₁) and (SO₄)(₂) groups, except that the (SO₄)(₂) groups are joined to one of the Ce(2) atoms through not one but two oxygen atoms (the oxygen polyhedra of Ce(2) and S(2) have a common edge)

\[ \text{Ce}(1) - S(1) - \text{Ce}(1) - S(1) - \]
\[ \text{S}(2) - \text{Ce}(2) \]

Scheme II

The (SO₄)(₂) groups are not bridging, but are "attached" to the Ce(2) atoms as bidentate cyclic ligands and screen the central rigidity rib on both sides, giving the column the form of a pillar with approximately rectangular cross section.

Thus all three independent sulfato groups play different roles in the structure: The (SO₄)(₁) group is bridging on four sides, the (SO₄)(₂) group is bridging on three sides, but forms two bonds in the direction of one of the three cerium atoms (tetradentate triply-bridging cyclic group); and the (SO₄)(₃) group is bidentate and cyclic. Only two of the 12 oxygen atoms of the SO₄ groups are not joined to cerium atoms.

The two independent cerium atoms are coordinates not only to the oxygen atoms of the sulfate groups but also to one urea group each. Moreover, the coordination environments of Ce(1) and Ce(2) contain respectively three and one water molecules. The fifth water molecule is water of crystallization.

The urea molecules attached to Ce(1) and Ce(2) act as "side-arms" on the columns, extending along the α axis on both sides of each column. These side-arms and the molecules of water of crystallization w(₃) are chiefly responsible for the interaction between neighboring columns, with the formation of a branched system of hydrogen bonds (see below).

The coordination numbers of both cerium atoms are the same and equal to eight. The apices of the Ce(₁) polyhedron (Fig. 2a) are occupied by three oxygen atoms of (SO₄)(₁) groups, one from a (SO₄)(₂) group, one from a urea molecule, and three from water molecules. The analogous polyhedron of Ce(₂) (Fig. 2b) contains one oxygen atom of a (SO₄)(₁) group, three from a (SO₄)(₂) group, two from a (SO₄)(₃) group, one from a urea molecule, and one from a water molecule.

The Ce(₁) polyhedron has a form close to that of a doubly-capped trigonal prism. One of the triangular bases of the prism is occupied by O₁₁, O₁₂, and O₂₂, and the other (correspondingly along approximately parallel edges) by O₁ (urea), w₂, and O₁₂. Two lateral faces of the prism are centered by water molecules w₁ and w₃. The "square" face O₁₃O₂₃O₁₂w₂ is bent along the line O₁₃...O₁₂ to give the polyhedron features which bring it close to a Hoard tetragonal dodecahedron [10] (with a 4 axis through the middle of the O₁₁-O₁₂(K) and O₁₃-O₁₂ edges). The role of the four-edge apices of type A is played by water molecules and the O₂₃