RARE EARTH SULFATES AND SELENATES

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ABSTRACT

Tetrahedral oxoanions are among the most typical inorganic ligands for the rare earths. Especially the sulfates and selenates have been studied extensively but only recently the X-ray structural investigations have revealed that these compounds should be regarded as complexes and not as simple or double salts. Besides the structural features in the solid state, thermal stabilities and conversions of the representative compounds are discussed.

1. INTRODUCTION

Many of the early investigators in the field of rare earth chemistry were concentrating their efforts to find better ways for the separation and purification of these closely related elements. In this connection, the sulfates and selenates were also studied and found that especially the alkali and ammonium double compounds were quite useful in the fractional precipitation and crystallization processes [1]. Even today, the alkali sulfate precipitation is used in the processing of monazite to separate the more soluble yttrium-group sulfates from the cerium-group [2].
In the course of separational studies some other properties, such as thermal and magnetic, were also investigated but the structures of the rare earth sulfates and selenates remained unknown until a number of X-ray crystallographic studies were recently performed.

2. COMPOSITION AND STRUCTURE OF THE SULFATES

On the basis of composition, the sulfates may be conveniently divided into two groups: (i) 'simple' sulfates $\text{Ln}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ and (ii) 'double' sulfates $M_2\text{Ln}_y(\text{SO}_4)_{(x+3y)/2} \cdot z\text{H}_2\text{O}$, where M is ammonium ion or an alkali metal. The words 'simple' and 'double' are used for historical reasons and it may be noted that in the older literature the formulae of 'double' sulfates are usually given as $xM_2\text{SO}_4 \cdot y\text{Ln}_2(\text{SO}_4)_3 \cdot z\text{H}_2\text{O}$ and the ratio $x:y:z$ is used to characterize the stoichiometry. In addition to the alkali metals, some other low valent metals may form double sulfates [3,4].

'Simple' sulfates. Table 1 lists the stoichiometries and main structural features of the 'simple' sulfates. The first attempt to solve one of these structures was made already in 1950's but it was only partially successful [13]. The first X-ray diffraction study which unambiguously established the coordination around the lanthanoid ion was not made until the late 60's [5] and it showed several surprising features. The coordination number for cerium was found to be unusually high; in this case 9 and 12 for the two crystallographically independent cerium atoms. Secondly, the coordination of water molecules was interesting: there were no water molecules around the first cerium atom with a CN of 12 but in the case of second cerium with CN = 9 the majority of ligands were water oxygens.

Other sulfates listed in Table 1 have not revealed upon X-ray study so striking structural features but, nevertheless, they form an interesting series of compounds.
where the degree of hydration and also the ionic radius changes. As an example of a structure in this series, the coordination in the structure \( \text{Nd}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O} \) is depicted in Fig. 1.

**Table 1. Structure types and coordination numbers in the series \( \text{Ln}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O} \)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Isostructural with</th>
<th>CN</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ce}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} )</td>
<td>P6\text{}_3/m</td>
<td>La</td>
<td>9,12</td>
<td>5</td>
</tr>
<tr>
<td>( \text{La}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O} )</td>
<td>Pc</td>
<td>Ce</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>( \text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O} )</td>
<td>C2/c</td>
<td>Pr,Sm-Lu,Y</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>( \text{Nd}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O} )</td>
<td>C2/c</td>
<td>La-Pr</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>( \text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O} )</td>
<td>P1</td>
<td>-</td>
<td>6</td>
<td>9,10</td>
</tr>
<tr>
<td>( \text{Ce}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O} )</td>
<td>P2\text{}_1/c</td>
<td>-</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>( \text{Nd}_2(\text{SO}_4)_3 )</td>
<td>C2/c</td>
<td>Ce-Gd</td>
<td>9</td>
<td>12</td>
</tr>
</tbody>
</table>

Double' sulfates. Due to the almost unlimited number of stoichiometric possibilities, these compounds have not been systematically studied and X-ray diffraction studies were initiated somewhat later than for the 'simple' sulfates.

First structural reports became available for \( \text{NH}_4\text{Sm}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \) [14,15] and for \( \text{K}_6\text{Pr}_4(\text{SO}_4)_9 \cdot 8\text{H}_2\text{O} \) [16]. They indicated that, in spite of the presence of the extra cations, the structures were not very much different from those of the 'simple' sulfates but contained a central lanthanoid ion where the sulfato ligands and part or all of the water molecules were bound. Subsequent structural studies on a number of 'double' sulfates have confirmed this conclusion [17].
Fig. 1. The unit cell packing in the structure of Nd$_2$(SO$_4$)$_3$·5H$_2$O [7].
One of the water molecules is not coordinated to neodymium but held in the structure by hydrogen bonds.

Fig. 2. The unit cell packing of NH$_4$Sm(SO$_4$)$_2$·4H$_2$O. Ammonium ions and other water molecules are held in the structure by hydrogen bonds [15].
As an example the case of ammonium samarium sulfate tetrahydrate NH$_4$Sm(SO$_4$)$_2$·4H$_2$O may be discussed in more detail. The samarium ion is nine-coordinated by six sulfate oxygens and three water molecules; one of the water molecules and the ammonium ions lie outside the inner coordination sphere and are held in the structure by hydrogen bonds. The coordination polyhedron is an intermediate between a mono-capped square antiprism and a tricapped trigonal prism, cf. Figs. 2 and 3. The polyhedra are joined into infinite chains due to the bridging function of the sulfate ligands.

3. COMPOSITION AND STRUCTURE OF THE SELENATES

The selenate ion has the same symmetry as the sulfate but is slightly larger; if the S-O bond length in the free sulfate ion is 1.49 Å the corresponding Se-O bond may be taken as 1.64 Å [18,19]. The similarity being so close one, it is not surprising to find the same stoichiometries and structural features in the rare earth selenates as discussed above in the case of sulfate structures.

Like the sulfates, the rare earth selenates crystallize normally with eight molecules of water; the sulfate and selenate octahydrates (Pr-Lu) are isostructural [20,21]. There are, however, some examples of structural differences between the corresponding sulfates and selenates. For instance, the cerium selenate pentahydrate crystallizes in the space group P2$_1$/c [22] while the sulfates from La to Nd form monoclinic crystals belonging to the space group C2/c [8]. On the other hand, the scandium sulfate and selenate pentahydrates are isostructural [9]; in these compounds as well as in all other sulfates and selenates studied so far scandium has an octahedral coordination.
Fig. 3. The two possibilities for the description of the coordination polyhedra in the structure of $\text{NH}_4\text{Sm(SO}_4\text{)}_2\cdot4\text{H}_2\text{O}$: (a) monocapped square antiprism (b) tricapped trigonal prism.
4. THERMAL DECOMPOSITION

The rare earth sulfate and selenate hydrates form an interesting case for comparative thermoanalytical studies where the effects of crystal structure, radius of the lanthanoid ion, and the effect of anion size and character may be studied. Since the early work of Wendlandt et al. [23] the sulfates and selenates, especially the octahydrate series, have been studied extensively using TG and/or DTA/DSC methods [24]. The most recent study employs high resolution luminescence spectroscopy to monitor the decomposition products of Eu₂(SO₄)₃·8H₂O during the TG experiments [25].

In addition to studies dealing with 'simple' sulfates and selenates, the 'double' compounds have been investigated frequently; especially the studies by Nabar et al. [26] and Giolito et al. [27] should be mentioned in this connection. Due to the multitude of double compounds available, it is, however, not yet possible to obtain a comprehensive picture of the structure - thermal stability relationships although some cases have been studied in detail.

Decomposition schemes and trends. There are three main steps in the thermal degradation of rare earth sulfate octahydrates in air (cf. Fig. 4):

\[
\begin{align*}
\text{Ln}_2\text{(SO}_4\text{)}_3 \cdot 8 \text{H}_2\text{O}(s) & \rightarrow \text{Ln}_2\text{(SO}_4\text{)}_3(s) + 8 \text{H}_2\text{O}(g) \quad /1/ \\
\text{Ln}_2\text{(SO}_4\text{)}_3(s) & \rightarrow \text{Ln}_2\text{O}_2\text{SO}_4(s) + 2 \text{SO}_3(g) \\ \\
\text{Ln}_2\text{O}_2\text{SO}_4(s) & \rightarrow \text{Ln}_2\text{O}_3(s) + \text{SO}_3(g) \quad /3/ 
\end{align*}
\]

The temperatures involved for each step vary along the rare earth series but are generally in the range 100 - 250°C for the dehydration reactions, 800 - 1100°C for the oxysulfate formation and 1000 - 1350°C for the oxide formation. As an example, the typical U-shape curve of the oxysulfate formation temperatures is depicted in Fig. 5.
Fig. 4. Thermal decomposition of Dy$_2$(SO$_4$)$_3$$\cdot$8H$_2$O in air using a heating rate of 10$^\circ$/min and a sample of 200 mg.
Fig. 5. The starting ($T_2$) and end ($T_1$) temperatures for the decomposition $\text{Ln}_2(\text{SO}_4)_3 \rightarrow \text{Ln}_2\text{O}_2\text{SO}_4 + 2 \text{SO}_3$. The experimental conditions are as follows: I 200 mg sample, $10^\circ$/min; II 20 mg sample, $2^\circ$/min.
The trends and mechanism of dehydration reactions are more difficult to investigate as the stability of the intermediate hydrates is generally low. By the use of so-called quasi-isothermal heating technique [28] or kinetic analysis [24] it is, however, possible to separate the partially overlapping dehydration steps. There seems to be a connection between the structure and the dehydration mechanism; the cases of Nd(SO₄)₃·5H₂O [24] and CsPr(SO₄)₃·4H₂O [30] have been discussed in the literature and recently it has been shown that the decomposition of La₂(SeO₄)₃·12H₂O proceeds via the stable octahydrate intermediate [29].

The decomposition of selenate hydrates upon heating is generally a complicated problem. The ultimate product is the oxide and also the first step is the same as in the case of the sulfates. However, the second step, viz., selenate decomposition, may involve the formation of various oxy-selenite compounds [31-33] or the oxyselenate [34]. As quantitative analytical data are lacking, it is not possible to present a simple and generally valid reaction equation for the decomposition but it seems plausible to assume that both Se(IV) and Se(VI) oxocompounds may be involved and present simultaneously. Recent thermogravimetric studies on the selenate hydrates under various experimental conditions are in agreement with this assumption [29].

5. CONCLUDING REMARKS

The sulfates and selenates form a representative group of rare earth oxoanion compounds which have interesting structural and thermal properties. As the presentation above has only been able to give a few examples of these compounds and their properties in the solid state, concluding remarks will be given below summarizing the discussion.
Structures. The sulfate and selenate ligands tend to behave in a similar way forming inner-sphere complexes with the trivalent rare earth ions. In the solid state these complexes have coordination numbers ranging from 6 to 12; the average being around 8 - 9. The smallest CN seems to be limited to scandium only while the high coordination numbers (ten or higher) are encountered in some lanthanum and cerium compounds.

The coordination geometries are distorted or intermediate as expected when two types of ligands, oxoanion and aqua, are present and when the oxoanion has several bonding possibilities. The sulfates and selenates are often isostructural but exceptions are found.

Thermal stability. Apart from the dehydration, the rare earth sulfates and selenates are highly stable compounds which decompose to oxides only at elevated temperatures. Oxysulfate can be identified as an intermediate phase during decomposition of sulfates in air or nitrogen.

In the case of the selenate decomposition, the mechanism is more complicated and may involve simultaneously the presence of Se(IV) and Se(VI) oxoanion compounds.
REFERENCES


