The Crystal Structure of Lithium fac-Triaquatrisulfitorhodate(III)hydroxide, Li₄[Rh(SO₃)₃(OH₂)₃](OH)

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Sulfitorhodates(III), trans-Influence, Network, Layer Structure

fac-Li₄[Rh(SO₃)₃(OH₂)₃](OH) crystallizes in the rhombohedral space group R₃-C₃₄, Z = 1, in trigonal setting a = 807.7(2), c = 1339.0(3) pm, V = 756.6(2)·10⁶ pm³, Z = 3. Rh is octahedrally coordinated by three facial S-bonded sulfite groups with Rh–S = 222.6(1) pm and three aqua ligands with Rh–O bonds Rh–O = 217.5(3) pm, elongated by a trans-influence. The average S–O bond length is 148.0(3) pm. All hydrogen atoms have been located. The OH⁻ ion is coordinated exclusively to Li⁺. The anions are held together by Li⁺ cations in octahedral environment and by hydrogen bonds of medium strength. Alternatively, the structure can be considered to be built of packages of two oxygen nets and a metal layer, stacked in a sequence similar to that in the CdCl₂-structure.

1. Introduction

Our studies of sulfito complexes of platinum-group metals have provided evidence for the strong trans-influence of the S-bonded SO₃⁻ ligand. This influence has been proved for square-planar Pd(II) and Pt(II) centers [1] and also for a few octahedral Rh(III) [2] and Ru(II) [3] complexes. In the latter case the trans-influence is diminished on peripheral O-protonation [4–6].

On the whole there is only little structural data available for sulfitorhodates, because they tend to form amorphous S–O– bridged polymers, as e.g. in K₃[Rh(SO₃)₃]·2H₂O. Up to now studies of the bonding situation around the rhodium center were mainly based on vibrational spectroscopy [7].

However, it was possible to synthesize fac-Li₄[Rh(SO₃)₃(OH₂)₃](OH) (1), to grow single crystals and to solve the crystal structure of 1. The geometrical data were used in the normal coordinate treatment of the anion [8].

2. Experimental

Preparation of Li₄[Rh(SO₃)₃(OH₂)₃](OH) (1)

SO₂ was slowly bubbled into a stirred solution of 0.273 g (1.00 mmol) RhCl₃·3.5H₂O and 0.443 g (6.00 mmol) Li₂CO₃ in 100 ml H₂O at room temperature. On neutralization to pH 7 the dark violet solution turned orange to yellow. Light yellow micro-crystals of Li₄[Rh(SO₃)₃(OH₂)₃](OH) were obtained by slow evaporation of water. Yield: 0.410 g (92.8%).

Analysis of metals with photometrical methods:

- Li by flame photometry and Rh by UV/VIS-spectrometry as [RhCl₆]³⁻ (λₐx = 273.5(5) nm) [9].

H₂O₁₃Li₄RhS₃ (441.92)
Calcd H 1.60 Li 6.28 S 21.76 Rh 23.29%
Found H 1.63 Li 6.3 S 21.47 Rh 23.5%.

Single crystals for X-ray structure analysis were obtained by diffusion of acetone into an aqueous solution via the gas phase.

The dried crystals are stable to air. Magnetic measurement confirms the oxidation state Rh(III). The density was determined in dibromomethane with a pyknometer (Table I).

<table>
<thead>
<tr>
<th>Molecular weight M</th>
<th>441.92 g mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>R₃-C₃₄</td>
</tr>
<tr>
<td>a</td>
<td>807.7(2) pm</td>
</tr>
<tr>
<td>c</td>
<td>1339.0(3) pm</td>
</tr>
<tr>
<td>γ</td>
<td>120</td>
</tr>
<tr>
<td>Cell volume V</td>
<td>756.6(2)·10⁶ pm³</td>
</tr>
<tr>
<td>Density calcd.</td>
<td>2.910(1) g cm⁻³</td>
</tr>
<tr>
<td>Density obs.</td>
<td>2.896(6) g cm⁻³</td>
</tr>
</tbody>
</table>

Collection and reduction of data

The space group was determined on the basis of Weissenberg (CuKα radiation, λ = 154.06 pm) and precession photographs (MoKα, λ = 70.93 pm). Refined lattice parameters (Table I) were calculated by least-squares refinement (program GIVER [10]).
Single crystal diffractometer: Philips PW 1100
Crystal size: 0.13 x 0.14 x 0.17 mm³
\( \lambda (\text{AgK} \alpha) = 56.014 \text{ pm} \)
Linear absorption coefficient \( \mu \): 11.21 cm⁻¹
Range of diffraction angle \( \theta \): 2.5 - 30°
\( \sin \theta / \lambda \): 9.32 x 10⁻³ pm⁻¹
\( hkl \) range: \( \pm 14, \pm 14, 23 \)
Standard reflections: 110, 101, 012, 024
Standard instability: < 0.015
Scan mode: \( \omega \)-scan
Scan width: 0.15° s⁻¹
Scan speed: 0.2 tanθ
Temperature: 293 K
Number of measured reflections: 3085
Observed independent reflections: 1002
with \( I > 3 \sigma I \): 973
Internal R-value: 0.0314
F(000): 648
Ratio reflexes/parameters: 973/67 = 14.5
R-values on \( F \), \( w = 0.5851/\sigma^2(Fo) \):
\( R = 0.0286 \), \( R_w = 0.0232 \)
Maximum shift/e.s.d. in the last cycle: 0.002
Maximum residual electron density: 0.14 e⁻³ Å⁻³
Minimum residual electron density: -0.14 e⁻³ Å⁻³

Table II. Data collection and reduction, structure solution and refinement.

### Structure solution and refinement

The structure was solved by Direct Methods and Patterson syntheses with SHELXS-86 [12]. Rh, S, O atoms were refined (SHELX-76 [13]) anisotropically; Li and H atoms (the latter positions found from weighted difference Fourier syntheses) were treated isotropically. A refinement with anisotropic Li² yielded the same atomic coordinates, with the thermal ellipsoid compressed normal to the short Li²-O5 bond; nevertheless the equivalent isotropic displacement factor did not decrease with respect to the isotropic one. The final atomic coordinates and equivalent displacement factors are given in Table III. Table IV summarizes bond distances and angles.

During the refinement an empirical isotropic extinction correction (SHELX 76) was applied, but it was abandoned later on, because the parameters did not change significantly.*

* Further details may be obtained from: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry-No. CSD 57642, the names of the authors and the journal citation.

Table III. Atomic coordinates and equivalent isotropic displacement factors (trigonal setting).

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{eq} ) pm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>87(1)</td>
</tr>
<tr>
<td>S</td>
<td>0.2588(2)</td>
<td>0.0681(2)</td>
<td>0.9103(1)</td>
<td>145(3)</td>
</tr>
<tr>
<td>O1</td>
<td>0.2384(4)</td>
<td>0.0943(4)</td>
<td>0.8020(2)</td>
<td>227(7)</td>
</tr>
<tr>
<td>O2</td>
<td>0.2969(4)</td>
<td>-0.0923(4)</td>
<td>0.9229(2)</td>
<td>299(8)</td>
</tr>
<tr>
<td>O3</td>
<td>0.4177(4)</td>
<td>0.2462(4)</td>
<td>0.9516(2)</td>
<td>227(7)</td>
</tr>
<tr>
<td>O4</td>
<td>0.0583(5)</td>
<td>-0.1749(5)</td>
<td>0.1016(2)</td>
<td>203(7)</td>
</tr>
<tr>
<td>H1</td>
<td>0.1308(21)</td>
<td>-0.1033(21)</td>
<td>0.1477(19)</td>
<td>418(22)*</td>
</tr>
<tr>
<td>H2</td>
<td>-0.0577(21)</td>
<td>-0.2649(21)</td>
<td>0.1166(21)</td>
<td>865(22)*</td>
</tr>
<tr>
<td>O5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>416(4)</td>
</tr>
<tr>
<td>H3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>461(20)</td>
</tr>
<tr>
<td>Li1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>243(16)*</td>
</tr>
<tr>
<td>Li2</td>
<td>0.4189(14)</td>
<td>0.2802(14)</td>
<td>0.6892(9)</td>
<td>746(18)*</td>
</tr>
</tbody>
</table>

* \( U_{eq} = 1/3(\sum_{i<j}^3 u_{ij} + 1/\sin^2(\gamma)(u_{11} + u_{22} + 2u_{12} \cos\gamma)) \) [14]: isotropic.
Table IV. Bond lengths (pm) and angles (°) with e.s.d.'s.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh–S</td>
<td>222.6(1)</td>
<td></td>
<td></td>
<td>217.5(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh–O4</td>
<td>217.5(3)</td>
<td>222.6(1)</td>
<td>217.5(3)</td>
<td>148.5(3)</td>
<td>148.2(3)</td>
<td>147.4(3)</td>
</tr>
<tr>
<td>S–O1</td>
<td>148.2(3)</td>
<td>148.5(3)</td>
<td>113.8(1)</td>
<td>107.6(1)</td>
<td>106.9(1)</td>
<td>108.8(2)</td>
</tr>
<tr>
<td>S–O2</td>
<td>147.4(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Aqua ligand and hydrogen bonding:

| O4–Li2a                  | 211.2(11)     | Rh–O4–Li2a | 110.8(8)   |
| O4–H1⋯O2ad               | 270.2(4)      |            |            |
| O4–H2⋯O1bc               | 283.9(4)      |            |            |
| O4–H2⋯O2ad               | 296.7(4)      |            |            |
| O4–H2⋯O3                 | 277.1(4)      |            |            |

Li1O6 octahedron:

| Li1–O1d                  | 207.7(7)      | O1–Li1–O1c | 88.8(4)    |
| Li1–O3bd                 | 215.5(8)      | O3bd–Li–O3be | 90.4(4) |

Li2O6 octahedron:

| Li2–O5a                  | 199.6(11)     | O5a–Li2–O4b | 96.9(4)    |
| Li2–O4b                  | 211.2(11)     | O5a–Li2–O1f | 97.0(5)    |
| Li2–O1c                  | 211.4(11)     | O5a–Li2–O3bd | 175.7(5)  |
| Li2–O3bd                 | 217.9(13)     | O5a–Li2–O2b | 89.4(6)    |
| Li2–O2bg                 | 227.1(12)     | O5a–Li2–O2bg | 83.1(6)   |

Coordinaton of OH⁻:

| Li2–O5                   | 199.6(11)     | H3–O5–Li2b  | 114.0(4)   |
| H3–O5                   | 59.7(26)      | Li2b–O5–Li2bc | 104.6(4) |

Symmetry operations:

| a x+2/3, y+1/3, z+1/3    | b x+1/3, y+2/3, z+2/3 |
| c −y, x, −z             | d y, −x, z           |
| e x+1, y+1, z           | f x, y, z+1          |
| g x, y−1, z           |        |

3. Results and Discussion

The structure consists of complex anions fac-[Rh(SO₃)₃(OH₂)₃]³⁻ (Rh in position 0,0,z with z set to zero) linked by Li⁺ cations (z ~ 0) to form layers perpendicular to the c-axis which in turn are connected by covalent S–O bonds and O–H⋯O hydrogen bonds of medium strength.

The structure can also been considered to consist of two different quasi-parallel nets of oxygen atoms between which the metal atoms are intercalated.

Coordination of the OH⁻ anion

The hydroxide anion (special site) is very strongly coordinated to three Li²⁺ (general site) spanning the trigonal basis of a OHLi₂₅ tetrahedron. Considering the over-all coordination of Li²⁺ this special O5 atom forms the common corner of three edge-sharing distorted Li₂O₆ octahedra. The Li–O5 distance of 199.6(11) pm (octahedral LiO₆) is almost comparable to Li–O = 196.3 pm in LiOH [15] (tetrahedral LiO₄ coordination!).

The proton is not involved in hydrogen bonding since the distance to the nearest O atoms is too far away...
for formation of a (trifurcated) hydrogen bond (O5⋯O3 = 322.5(5) pm; H3⋯O3 = 275(2) pm). Independently, the high frequency ν(OH) 3543 cm⁻¹ precludes a hydrogen bond.

The connection pattern around the OH⁻ ion thus reminds of that in brucite Mg(OH)₂.

The complex anion

Figure 1 shows an ORTEP plot [16] of the complex anion down [0001]. For bond lengths and angles see Table IV.

The Rh–O bond Rh–O = 217.5(3) pm is significantly longer than the Rh–O bond length in the [Rh(OH₂)₆]³⁺ ion, which is not affected by the trans-influence. For the latter Rh–O distances of 200–204 pm are usually found, e.g. in CsRh(SO₄)₂·12H₂O 201.6(3) pm [17], in CsRh(SeO₄)₂·12H₂O 200.4(3) pm [18] and for [Rh(OH₂)₆]³⁺ in rhodium(III) perchlorate solution 204(1) pm [19–21].

In [Rh(OH₂)₆](ClO₄)·3H₂O [22] an unusually long Rh–O bond of 213.2(6) pm (averaged) is thought to be caused by a rigid H₂O/ClO₄⁻ framework (see discussion in [22]).

The determined distance equals or exceeds Rh–O bond lengths trans to phosphine ligands [23,24], which suggests a similar or even stronger trans-influence of the S-bonded SO₃ group.

A relatively strong bond to Li²⁺ completes the tetrahedral surrounding of the aqua oxygen O₄. This additional coordination to Li²⁺ could also assist in lengthening of the Rh–O bond, cf. the bond-valence method of Brown [25]. The medium-strong hydrogen bond O–H1⋯O2 with O⋯O = 270.2 pm aligns the aqua ligand, as given in the perspective view of the trigonal cell (Fig. 2). The H2 atom resides in a local potential-minimum, within a trifurcated hydrogen bond to O1 and O2 of different SO₃-groups in an adjacent anion and to O3 of the same anion (intramolecular H-bond). One of them is shown in Fig. 2. All intermolecular hydrogen bonds link [Rh(SO₃)₃(OH₂)₃]⁻ anions coarsely along the rhombohedral axes and thus provide a connection between the layers.

As to the Rh–S bond length of 222.6(1) pm, there is little comparable data. In trans-Na[Rh(SO₄)₂(en)₂]·3H₂O [2] the Rh–S distance is increased to 232.3(1) pm by the mutual trans-influence. This 10 pm difference between cis- and trans-disulfitorhodates(III) exceeds the 6–8 pm found for cobaltates(III) [27]. The present strong Rh–S bond is shorter than bonds in Rh(III) DMSO complexes [28,29]. Along with the short Rh–S bond there are remarkably strong S–O bonds of 147.4(3)–148.5(3) pm, taking into account that they are acceptors of hydrogen bonds and also donors in coordination to Li⁺ cations. The S–O
bond lengths are of course influenced by being further involved in dative bonding; thus the shorter S–O3 bonds are tied up with longer O3–Li+ distances (Table IV).

At the octahedral RhS₃O₃ center the S–Rh–S angles are increased by electrostatic repulsion of the SO₃-groups, with consistently reduced O–Rh–O angles. (The small difference in the O–Rh–S angles shows the very small torsional angle between the RhS₃- and the RhO₃-fragments.) Also for electrostatic reasons, the SO₃ ligands are tilted off the threefold axis, such that the angle Rh–S–O1 is the biggest among the Rh–S–O angles. As a consequence the S–O1 bond is directed almost parallel to the c-axis. This S–O1 bond supplies a covalent link between the oxygen nets of adjacent layers, besides the mentioned hydrogen-bond links.

**Formation of networks**

Figure 3 shows the trigonal layer around the a,b-plane with Rh at z = 0, Li¹⁺ and Li²⁺ slightly higher (z = 0.0439 and z = 0.0225, respectively), the latter being bonded to O5 (z = 0.0833 ~ 1/12) above the a,b-plane.

The set of oxygen atoms with z = 1/12 (O5, O4 and O1 of the next anion layer) may be considered as a slightly puckered 6-connected net (3⁶ net) of partly distorted triangles (cf. Wells [30]). 4 out of the 14 triangles of this net in the section limited by the unit cell (unit area) form one face each of an octahedron around the Li⁺ cations.

A regular triangle defined by the three *fac* aqua oxygens is one face of the coordination polyhedron around rhodium, which is part of the metal layer at z ≈ 0 (see above).

Opposite to this layer another set of the oxygen atoms O2, O3 forms a 5-connected net of 8 triangles and one hexagon per unit area. Inside the hexagon resides the RhS₃-pyramid. If this fragments were replaced by a single oxygen atom a complete 6-connected net would result.

The described sequence of a 6-connected O-net, a layer of metals and a 5-connected O-net, and the stacking of these packages along the trigonal c-axis resembles the arrangement of the layers in the CdCl₂-structure.

There is also a group theoretical relationship of the space group of the CdCl₂-structure (R 3m) and the space group of the present structure R 3 (descent in symmetry in two steps: R 3m $\rightarrow$ R 3 $\rightarrow$ R 3).

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