Preparation and Characterization of Some Sodium-, Rubidium-, Cesium- and Ammonium-Oxodiperoxooxalato-Molybdates (VI) and Tungstates (VI)

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INTRODUCTION

Potassium derivatives of oxodiperoxooxalato- molybdates and tungstates were prepared before 1, 2 studied by infrared, Raman and X-ray methods. The crystal structure of corresponding molybdate with literature survey was published recently. As a part of our interest on transition metal peroxo compounds, some sodium-, rubidium-, cesium- and ammonium- oxodiperoxooxalato- molybdates and corresponding rubidium- and cesium- tungstates were prepared and characterized by chemical analysis, i.r. spectra, X-ray and conductivity measurements. Rubidium, cesium and ammonium compounds are anhydrous, the sodium compound is trihydrate. Our attempts to prepare the anhydrous sodium compound failed so far. Compounds are sensitive on light.

EXPERIMENTAL

The crystals were obtained by similar methods as described before. Their composition was proved by the determination of carbon, metals and peroxides. In the sodium compound hydrogen, and in the ammonium compound nitrogen was also determined.

Conductances were determined in water solutions using a 1000 cps conductivity bridge at 25.00 ± 0.05°C and bright platinum electrodes. The specific conductance of the water used was not greater than 3.0 × 10⁻⁶ ohm⁻¹ cm².

I.r. spectra were obtained over the range 4000–400 cm⁻¹ on a Perkin-Elmer model 337 using Nujol or hexachlorobutadiene mulls.

The morphology of the crystals was determined with an optical goniometer. The lattice constants were obtained from oscillation and Weissenberg X-ray diffraction photographs with CuKα radiation; densities (Dm) by picnometer with decalin as liquid. No piezoelectric effect was detected. Systematic absences of reflections are as follows: a) for rubidium and ammonium compounds h0l : h + l = 2n + 1 and 0k0: k = 2n + 1, these determine the space group as P2₁/n; b) for the cesium compounds 0kl: k + l = 2n + 1 and h0l: h = 2n + 1, these determine the space group as Pna2₁; c) for the sodium compound 0kl: k = 2n + 1, h0l: l = 2n + 1 and hk0: h = 2n + 1, these determine the space group as Pbca.

RESULTS AND DISCUSSION

The conductivity of sodium, rubidium, cesium and ammonium compounds was measured in water solutions over a range of concentrations from 10⁻² to

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According to the graphical treatment of the data\(^6\) the complexes behave in aqueous solutions as though they are 2:1 electrolytes, because their molar conductivities for concentrations of \(10^{-4}\) M are from 296 to 312 ohm\(^{-1}\) cm\(^2\). In dilute solutions (less than \(10^{-3}\) M) the conductivity increases rapidly, probably because of partial hydrolysis or decomposition of the complex anion.

### TABLE I

**Infrared Spectra**

<table>
<thead>
<tr>
<th>Compound</th>
<th>M=O bands*</th>
<th>((\text{O-O}))</th>
<th>M(O(_2)) asym.</th>
<th>M(O(_2)) sym.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Rb}_2[\text{MoO(O}_2\text{)}_2\text{C}_2\text{O}_4])</td>
<td>973</td>
<td>874, 885</td>
<td>594</td>
<td>542</td>
</tr>
<tr>
<td>(\text{Cs}_2[\text{MoO(O}_2\text{)}_2\text{C}_2\text{O}_4])</td>
<td>950</td>
<td>868, 875</td>
<td>588</td>
<td>540</td>
</tr>
<tr>
<td>((\text{NH}_4)_2[\text{MoO(O}_2\text{)}_2\text{C}_2\text{O}_4])</td>
<td>965</td>
<td>862, 876</td>
<td>640</td>
<td>570</td>
</tr>
<tr>
<td>(\text{Na}_2[\text{MoO(O}_2\text{)}_2\text{C}_2\text{O}_4] \cdot 3\text{H}_2\text{O})</td>
<td>965</td>
<td>860, 880</td>
<td>593</td>
<td>540</td>
</tr>
<tr>
<td>(\text{Rb}_2[\text{WO(O}_2\text{)}_2\text{C}_2\text{O}_4])</td>
<td>975</td>
<td>845, 860</td>
<td>587</td>
<td>544</td>
</tr>
<tr>
<td>(\text{Cs}_2[\text{WO(O}_2\text{)}_2\text{C}_2\text{O}_4])</td>
<td>954</td>
<td>842, 860</td>
<td>587</td>
<td>544</td>
</tr>
</tbody>
</table>

(* values in cm\(^{-1}\))

I.r. spectra (Table I) are similar to those of the analogous potassium compounds\(^3\), but there are some differences in number and positions of bands, e.g. frequencies which belong to peroxo bands are splitted. The listed frequencies are assigned according to the values obtained for some other complexes of molybdenum and tungsten\(^7,8\). Oxalato bands are not listed in Table I. By comparison with i.r. studies of other oxalato complexes\(^9\), oxalato ligands are bidentate. That was confirmed by crystal structure analysis of \(\text{K}_2[\text{MoO(O}_2\text{)}_2\text{C}_2\text{O}_4]\), where oxalato and peroxo groups are bidentate and the molybdenum atom is seven coordinated\(^4\).

Crystal data are listed in Table II along with the data for potassium derivatives\(^4,5\) for comparison. Crystals of molybdenum derivatives are yellow, prismatic, those of tungsten derivatives colourless, transparent and prismatic. All are elongated along the c axis. Figures 1—4 represent their crystal habits. Compounds, listed in Table II, except sodium, which is hydrate, have similar values of lattice constants. Volumes of their unit cells increase from smaller to larger cations. Rubidium and ammonium compounds are monoclinic with the same systematic absences of reflections as potassium compounds; cesium compounds are orthorhombic. Similar values of lattice constants and the same space group extinctions suggest isomorphism between molybdenum and tungsten derivatives of the same type and either isomorphism or close structural relationship between potassium, ammonium and rubidium compounds. The differences in space groups between cesium and rubidium, ammonium or potassium compounds can be attributed to the packing rearrangement of the cations and anions without change of anion configuration. The crystal structure determinations on \(\text{Na}_2[\text{MoO(O}_2\text{)}_2\text{C}_2\text{O}_4] \cdot 3\text{H}_2\text{O}\), \((\text{NH}_4)_2[\text{MoO(O}_2\text{)}_2\text{C}_2\text{O}_4]\) and \(\text{Cs}_2[\text{WO(O}_2\text{)}_2\text{C}_2\text{O}_4]\) are in course.
<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β</th>
<th>V (Å³)</th>
<th>Z</th>
<th>Space group</th>
<th>Dm (g. cm⁻³)</th>
<th>Dx (g. cm⁻³)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂[MoO₃C₂O₄]</td>
<td>13.721</td>
<td>8.335</td>
<td>6.885</td>
<td>92°26 (6)'</td>
<td>833.9</td>
<td>4</td>
<td>P₂₁/n</td>
<td>2.68</td>
<td>2.725</td>
<td>(4)</td>
</tr>
<tr>
<td>(NH₄)₂[MoO₃C₂O₄]</td>
<td>14.07</td>
<td>9.14</td>
<td>7.06</td>
<td>90°25 (5)'</td>
<td>907.9</td>
<td>4</td>
<td>P₂₁/n</td>
<td>2.19</td>
<td>2.20</td>
<td>This work</td>
</tr>
<tr>
<td>Rb₂[MoO₃C₂O₄]</td>
<td>14.33</td>
<td>9.13</td>
<td>6.97</td>
<td>90°25 (2)'</td>
<td>911.9</td>
<td>4</td>
<td>P₂₁/n</td>
<td>3.16</td>
<td>3.17</td>
<td>&quot;</td>
</tr>
<tr>
<td>Rb₂[WO₃C₂O₄]</td>
<td>14.13</td>
<td>9.18</td>
<td>7.02</td>
<td>91°42 (5)'</td>
<td>910.2</td>
<td>4</td>
<td>P₂₁/n</td>
<td>3.78</td>
<td>3.82</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cs₂[MoO₃C₂O₄]</td>
<td>7.43</td>
<td>13.16</td>
<td>9.62</td>
<td>Orthorhombic</td>
<td>940.6</td>
<td>4</td>
<td>Pna₂₁</td>
<td>3.74</td>
<td>3.74</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cs₂[WO₃C₂O₄]</td>
<td>7.41</td>
<td>13.15</td>
<td>9.60</td>
<td>&quot;</td>
<td>935.4</td>
<td>4</td>
<td>Pna₂₁</td>
<td>4.38</td>
<td>4.39</td>
<td>&quot;</td>
</tr>
<tr>
<td>Na₂[MoO₃C₂O₄] · 3 H₂O</td>
<td>18.62</td>
<td>16.38</td>
<td>6.85</td>
<td>&quot;</td>
<td>2089.2</td>
<td>8</td>
<td>Pbcма</td>
<td>2.29</td>
<td>2.32</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

(Errors are in parentheses)
Fig. 1. Crystal habit of Na₂[MoO₃(OH)₂C₂O₄] · 3 H₂O. The combination of crystal forms is: a{100}, b{010}, m{110}, d{101}.

Fig. 2. Crystal habit of Cs₂[MoO₃(OH)₂C₂O₄]. The combination of crystal forms is: b{010}, m{110}, w{011}. Crystals of Cs₂[WO₃(OH)₂C₂O₄] have a similar habit.

Fig. 3. Crystal habit of Rb₂[MoO₃(OH)₂C₂O₄]. The combination of crystal forms is: c{001}, a{100}, m{110}, k{310}, p{111}, e{111}, d{301}. Crystals of (NH₄)₂[MoO₃(OH)₂C₂O₄] have a similar habit.

Fig. 4. Crystal habit of Rb₂[WO₃(OH)₂C₂O₄]. The combination of crystal forms is: c{001}, a{100}, m{110}, p{111}, e{111}, d{301}. 
REFERENCES


IZVOD

Preparacija i karakterizacija nekih natrium-, rubidium-, cezium- i amonium-oksodiperoksooksalato-molibdata (VI) i volframata (VI)

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Pristrojeni su: \( M^I \) [MoO(O\(_2\))\(_2\)C\(_2\)O\(_4\)], \( M^I = \) Rb, Cs, NH\(_4\); \( M^I_2 \) [WO(O\(_2\))\(_2\)C\(_2\)O\(_4\)], \( M^I = \) Rb, Cs i Na\(_2\) [MoO(O\(_2\))\(_2\)C\(_2\)O\(_4\)] \( \cdot 3\) H\(_2\)O. Formule tih spojeva određene su na temelju kemijskih analiza. Iz rezultata dobivenih mjerjenj vodljivosti ustanovljeno je da se navedeni spojevi ponašaju u vodenim otopinama u koncentracijama većim od \( 10^{-3} \) M kao 2 : 1 elektroliti. Izmjereni su infracrveni spektri i uspoređeni sa spektrom analognih kalijevih spojeva. Metodama rendgenske difrakcije određeni su kristalografski podaci (tabela II). Na temelju sličnih dimenzija elementarnih čelija i istih prostornih grupa ustanovljeno je izomorfizam između molibdenovih i volframovih derivata iste vrste. Rubidijevi i amonijevi spojevi su izostrukturni s odgovarajućim kalijevim spojevima koji su ispitani prije.

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