
Abstract

Ti$_2$TiOH(SO$_4$)$_2$ est monoclinique, espace group $Cc$ or $C2/c$. Les paramètres de la cellule sont $a = 7.758$ (3), $b = 17.587$ (9), $c = 7.356$ (3) Å, $\beta = 119.91$ (3)°, $Z = 4$. Les composés de la série $M^2_TiOH(XO_4)_2$ (avec $M^2 = K$, Rb, Ti, NH$_4$; $M^m = Ti$, In; $X = S$, Se) sont isotypiques. Les paramètres cristallins et les données de diffraction de la poudre sont données.

Tableau 1. Diagramme de poudre de Ti$_2$TiOH(SO$_4$)$_2$

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>$d_0$</th>
<th>hkl</th>
<th>l/I_0</th>
</tr>
</thead>
<tbody>
<tr>
<td>6,104</td>
<td>6,122</td>
<td>11T</td>
<td>10</td>
</tr>
<tr>
<td>5,151</td>
<td>5,162</td>
<td>021</td>
<td>20</td>
</tr>
<tr>
<td>4,414</td>
<td>4,419</td>
<td>130</td>
<td>45</td>
</tr>
<tr>
<td>4,354</td>
<td>4,362</td>
<td>13T</td>
<td>45</td>
</tr>
<tr>
<td>3,693</td>
<td>3,696</td>
<td>111</td>
<td>55</td>
</tr>
<tr>
<td>3,619</td>
<td>3,619</td>
<td>041</td>
<td>15</td>
</tr>
<tr>
<td>3,599</td>
<td>3,599</td>
<td>112</td>
<td>15</td>
</tr>
<tr>
<td>3,543</td>
<td>3,547</td>
<td>22T</td>
<td>10</td>
</tr>
<tr>
<td>3,363</td>
<td>3,362</td>
<td>200</td>
<td>20</td>
</tr>
<tr>
<td>3,262</td>
<td>3,265</td>
<td>202</td>
<td>100</td>
</tr>
<tr>
<td>3,185</td>
<td>3,188</td>
<td>002</td>
<td>25</td>
</tr>
<tr>
<td>3,177</td>
<td>3,177</td>
<td>131</td>
<td>35</td>
</tr>
<tr>
<td>3,140</td>
<td>3,141</td>
<td>220</td>
<td>40</td>
</tr>
<tr>
<td>3,117</td>
<td>(3,117)</td>
<td>150</td>
<td>65</td>
</tr>
<tr>
<td>3,093</td>
<td>(3,097)</td>
<td>151</td>
<td>20</td>
</tr>
<tr>
<td>2,997</td>
<td>2,997</td>
<td>022</td>
<td>40</td>
</tr>
<tr>
<td>2,932</td>
<td>2,931</td>
<td>060</td>
<td>10</td>
</tr>
<tr>
<td>2,909</td>
<td>2,908</td>
<td>24T</td>
<td>5</td>
</tr>
<tr>
<td>2,672</td>
<td>2,671</td>
<td>240</td>
<td>5</td>
</tr>
<tr>
<td>2,622</td>
<td>2,621</td>
<td>242</td>
<td>10</td>
</tr>
<tr>
<td>2,582</td>
<td>2,581</td>
<td>042</td>
<td>10</td>
</tr>
<tr>
<td>2,542</td>
<td>2,542</td>
<td>152</td>
<td>35</td>
</tr>
<tr>
<td>2,524</td>
<td>2,523</td>
<td>31T</td>
<td>15</td>
</tr>
<tr>
<td>2,409</td>
<td>2,408</td>
<td>221</td>
<td>15</td>
</tr>
<tr>
<td>2,378</td>
<td>2,377</td>
<td>112</td>
<td>15</td>
</tr>
<tr>
<td>2,338</td>
<td>(2,338)</td>
<td>261</td>
<td></td>
</tr>
<tr>
<td>2,338</td>
<td>(2,338)</td>
<td>331</td>
<td>10</td>
</tr>
<tr>
<td>2,315</td>
<td>2,313</td>
<td>332</td>
<td>5</td>
</tr>
</tbody>
</table>

Préparation et caractérisation

Nos travaux sur les sulfates et sélénates doubles de thallium (III) et d'éléments monovalents (Jolibois, 1978) nous ont amenés à examiner les conditions d'existence des hydroxydes doubles $M^2_TiOH(XO_4)_2$ dont le seul représentant signalé jusqu'ici était K$_2$TiOH(SO$_4$)$_2$ (Marshall, 1902).

Ces composés sont préparés par mélange d'une solution de thallium(III) dans l'acide sulfurique (ou sélénique) 1 mol dm$^{-3}$ et d'une solution de sulfate (ou sélénate) $M^2XO_4$ dans le rapport $M^2/TTi$ égal à deux. L'analyse chimique des poudres obtenues leur attribue la formule $M^2_TiOH(XO_4)_2$ avec $M^2 = K$, Rb, Ti, NH$_4$ quand $X = S$, et $M^2 = K$, Rb quand $X = Se$.

Les essais de préparation des hydroxydes de cesium n'ont pas abouti. En revanche, un composé homologue K$_2$InOH(SO$_4$)$_2$ est préparé dans des conditions similaires.

Il faut noter que tous les hydroxydesulfates peuvent également être préparés par chauffage à 353 K de mélanges de TiOH(SO$_4$)$_2$·2H$_2$O et de $M^2SO_4$.

Seul le composé Ti$_2$TiOH(SO$_4$)$_2$ a pu être préparé à l'état monocristallin par évaporation lente à 298 K de solutions plus diluées.

Étude cristallographique

Le monocristal de Ti$_2$TiOH(SO$_4$)$_2$ se présente sous forme d'un prisme droit à base parallélogramme. Les analyses en rayonnement polychromatique montrent qu'il possède la symétrie monoclinique. L'examen des clichés de cristal tournant et de Weissenberg conduit aux paramètres de la maille à base $C$ centrée.

L'affinement, par la méthode des moindres carrés, à partir des données angulaires déduites du diagramme de poudre (Tableau 1) réalisé avec la radiation Cu K$\alpha$ donne: $a = 7.758$ (3), $b = 17.587$ (9), $c = 7.356$ (3) Å; $\beta = 119.91$ (3)°; $\rho_{\text{exc}} = 6.16$, $\rho_0 = 6.28$ Mgm$^{-3}$; $Z = 4$.

Les conditions d'existence ($hkl$: $h + k = 2n$ et $h0l$: $l = 2n$) ne sont compatibles qu'avec les groupes $Cc$ et $C2/c$: le choix

<table>
<thead>
<tr>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
<th>$V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$TiOH(SO$_4$)$_2$</td>
<td>7,784 (6)</td>
<td>17,063 (6)</td>
<td>7,344 (3)</td>
<td>120,75 (4)</td>
</tr>
<tr>
<td>(NH$_4$)$_2$TiOH(SO$_4$)$_2$</td>
<td>7,733 (3)</td>
<td>17,571 (7)</td>
<td>7,345 (3)</td>
<td>119,85 (3)</td>
</tr>
<tr>
<td>Rb$_2$TiOH(SO$_4$)$_2$</td>
<td>7,821 (3)</td>
<td>17,502 (6)</td>
<td>7,339 (3)</td>
<td>120,34 (3)</td>
</tr>
<tr>
<td>Ti$_2$TiOH(SO$_4$)$_2$</td>
<td>7,758 (3)</td>
<td>17,587 (9)</td>
<td>7,356 (3)</td>
<td>119,91 (3)</td>
</tr>
<tr>
<td>K$_2$TiOH(SeO$_4$)$_2$</td>
<td>8,019 (5)</td>
<td>17,713 (7)</td>
<td>7,408 (4)</td>
<td>120,95 (3)</td>
</tr>
<tr>
<td>Rb$_2$TiOH(SeO$_4$)$_2$</td>
<td>8,087 (2)</td>
<td>18,123 (4)</td>
<td>7,519 (2)</td>
<td>120,44 (1)</td>
</tr>
<tr>
<td>K$_2$InOH(SO$_4$)$_2$</td>
<td>7,642 (3)</td>
<td>16,812 (5)</td>
<td>7,165 (2)</td>
<td>119,98 (3)</td>
</tr>
</tbody>
</table>
entre ces deux groupes sera déterminé par la résolution de la structure (étude en cours).

L'isotypie marquée entre le cliché de poudre de Tl₂TOH(SO₄)₂ et ceux des hydroxysels doubles a permis de leur attribuer des caractéristiques cristallographiques voisines (Tableau 2). Il est à noter que la réflexion 020 apparaît forte pour tous les composés sauf Tl₂TOH(SO₄)₂.

**Références**


Crystal data for the decavanadates of 2,4-,3,4- and 3,5-dimethylpyridine and 2,4,6-trimethylpyridine. By J. M. ARRIETA, Departamento de Química and J. M. AMIGO, Departamento de Cristalografía y Mineralogía, Universidad del País Vasco, PO Box 644, Bilbao, Spain and P. GIL, Departamento de Química Inorgánica, Universidad de la Laguna, Tenerife, Spain

(Received 16 February 1981; accepted 26 February 1981)

**Abstract**

Indexed powder patterns of four monoclinic compounds of general formula (BH)₃H₃VₓO₁₈ .xH₂O, where x=1–2.5 and B=2,4-dimethylpyridine (J8), (C₉H₁₉N)₃H₃V₁₈O₁₈ .10H₂O, 3,4-dimethylpyridine (J10), (C₉H₁₉N)₃H₃V₁₈O₁₈ .14H₂O, 3,5-dimethylpyridine (J11), (C₉H₁₉N)₃H₃V₁₈O₁₈ .25H₂O, and 2,4,6-trimethylpyridine (J12), (C₁₈H₂₁N)₃H₃V₁₈O₁₈ .10H₂O, are given. The cell dimensions of the unit cells with two molecules are: J8 a=18.360 (2), b=10.438 (2), c=13.503 (2) Å, β=95.99 (1)°; J10 a=12.538 (3), b=13.634 (5), c=16.662 (5) Å, β=111.82 (2)°; J11 a=19.483 (5), b=10.711 (2), c=13.020 (4) Å, β=101.52 (2)°; J12 a=12.776 (3), b=22.470 (4), c=11.790 (3) Å, β=91.54 (1)°.

**Origin of specimens**

These compounds were synthesized in a way similar to the method described by Arrieta, Gill & Amigó (1981). Chemical analysis gave the results shown in Table 1.

**Powder data**

Cu Kα₂ radiation (λ=1.54051 Å) was used in a standard diffractometer. Indexing on the basis of de Wolff's (1957) method gave very similar monoclinic cells for all three decavanadates of the dimethylpyridines and a different monoclinic cell for the decavanadate of trimethylpyridine. The unit cells so determined were refined by a least-squares method. The reliability indices (M) (de Wolff, 1968; Kennard, Hannawalt, Wilson, de Wolff & Frank-Kamenetsky, 1971) were never less than 40. By the pycnometric method the following experimental densities were found: J8 Dₐ=1.64 (3); J10 Dₐ=1.65 (6); J11 Dₐ=1.63 (2); J12 Dₐ=1.30 (4) Mg m⁻³, to be compared with the calculated: J8 Dₓ=1.68; J10 Dₓ=1.64; J11 Dₓ=1.66; J12 Dₓ=1.32 Mg m⁻³. Powder pattern data for the compounds J8, J10, J11 and J12 are shown in Tables 2, 3, 4 and 5, respectively.

**Crystal physics**

TG curves in N₂ atmosphere show that these compounds decompose in three steps, VO₂ being the final product of the heating. The water is evolved in the first step of the decomposition with some of the organic base at 434–519 K for

**Table 2. Powder data for the decavanadate of 2,4-dimethylpyridine (J8)**

<table>
<thead>
<tr>
<th>d₀</th>
<th>d₁</th>
<th>hkl</th>
<th>l/1₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.412</td>
<td>11-401</td>
<td>101</td>
<td>67</td>
</tr>
<tr>
<td>10.439</td>
<td>10-438</td>
<td>010</td>
<td>67</td>
</tr>
<tr>
<td>9.063</td>
<td>9-062</td>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>7.946</td>
<td>7-946</td>
<td>201</td>
<td>43</td>
</tr>
<tr>
<td>7.601</td>
<td>7-699</td>
<td>111</td>
<td>33</td>
</tr>
<tr>
<td>7.208</td>
<td>7-208</td>
<td>201</td>
<td>39</td>
</tr>
<tr>
<td>5.776</td>
<td>5-775</td>
<td>301</td>
<td>19</td>
</tr>
<tr>
<td>5.533</td>
<td>5-534</td>
<td>112</td>
<td>19</td>
</tr>
<tr>
<td>5.257</td>
<td>5-258</td>
<td>310</td>
<td>13</td>
</tr>
<tr>
<td>3.973</td>
<td>3-973</td>
<td>402</td>
<td>15</td>
</tr>
<tr>
<td>3.863</td>
<td>3-863</td>
<td>203</td>
<td>19</td>
</tr>
<tr>
<td>3.652</td>
<td>3-652</td>
<td>500</td>
<td>16</td>
</tr>
<tr>
<td>3.315</td>
<td>3-315</td>
<td>322</td>
<td>23</td>
</tr>
<tr>
<td>3.270</td>
<td>3-270</td>
<td>223</td>
<td>19</td>
</tr>
<tr>
<td>3.213</td>
<td>3-213</td>
<td>413</td>
<td>19</td>
</tr>
</tbody>
</table>

**Table 1. Chemical analysis for the decavanadates of 2,4-,3,4-, and 3,5-dimethylpyridine and 2,4,6-trimethylpyridine**

<table>
<thead>
<tr>
<th></th>
<th>%V₂O₅</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>Found</td>
<td>Theoretical</td>
<td>Found</td>
<td>Theoretical</td>
</tr>
<tr>
<td>J8</td>
<td>69.80</td>
<td>70.04</td>
<td>19.36</td>
<td>20.00</td>
</tr>
<tr>
<td>J10</td>
<td>69.80</td>
<td>69.71</td>
<td>19.36</td>
<td>19.39</td>
</tr>
<tr>
<td>J11</td>
<td>68.38</td>
<td>68.26</td>
<td>18.97</td>
<td>19.70</td>
</tr>
<tr>
<td>J12</td>
<td>67.61</td>
<td>67.66</td>
<td>21.43</td>
<td>21.66</td>
</tr>
</tbody>
</table>

* Present address: Fac. de Químicas, Universidad de Valencia, Burjasot, Valencia, Spain.