Table 1. The solubility at 25°C of calcium oxalate monohydrate in ammonium oxalate solutions and in water.

<table>
<thead>
<tr>
<th>Ammonium Ionic Strength of Mean</th>
<th>Solubility of Calcium Oxalate Molarity (\times 10^4)</th>
<th>Activity Coefficient Calculated Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalate, Molarity</td>
<td>CaC_2O_4·H_2O</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.96·10^{-4}</td>
<td>0.88</td>
</tr>
<tr>
<td>0.001</td>
<td>0.003</td>
<td>0.62</td>
</tr>
<tr>
<td>0.003</td>
<td>0.009</td>
<td>0.46</td>
</tr>
<tr>
<td>0.01</td>
<td>0.03</td>
<td>0.28</td>
</tr>
<tr>
<td>0.03</td>
<td>0.09</td>
<td>0.16</td>
</tr>
<tr>
<td>0.1</td>
<td>0.3</td>
<td>0.060</td>
</tr>
<tr>
<td>0.5</td>
<td>0.9</td>
<td>0.027</td>
</tr>
</tbody>
</table>

The product was calculated to be \(2.12 \cdot 10^{-9}\), using the mean activity coefficient calculated from the formula

\[-\log \gamma = 0.5 z^2 \sqrt{\frac{\mu}{\mu + 1}}\]

The activity coefficients used for calculating the solubility in the oxalate solutions having an ionic strength of 0.003—0.09 were interpolated from tables published by Kielland; for an ionic strength of 0.3—0.9, they have been calculated from Mc Comas and Riemann's values on the solubility of calcium oxalate monohydrate in sodium chloride solutions.

The considerable differences between observed and calculated values indicate complex formation. Minimum solubility occurs at an oxalate concentration of about 0.01 M but the solubility differences in the concentration range 0.001—0.1 M ammonium oxalate are not large; 5 micromoles per litre, i.e. 0.2 mg Ca per litre, may be accepted as an approximate mean.

The author wishes to thank Miss Ulla Friberg for valuable help with the experimental work.


Received April 25, 1951.

Tetragonal Tungsten Bronzes of Degenerated Perovskite Type

Arne Magnéli

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The existence of isomorphous tetragonal sodium and lithium tungsten bronzes, \(\text{Me}_4\text{WO}_6\), of previously unknown structural type was reported in a recent paper from this Institute. This note will present an account of the determination of the crystal structure of these compounds.

The investigation was based on powder and single crystal photographs of the sodium compound, the preparation examined having the composition \(\text{Na}_{0.16}\text{WO}_6\). The radiation used was Cu-K. The lattice constants of the tetragonal unit cell, as obtained from the powder photographs are referred to the wave-length of Cu-Ka radiation equal to 1.5418 Å:

\[a = 5.248 \text{ Å}, c = 3.895 \text{ Å}, V = 107.3 \text{ Å}^3\]

The observed density of 7.25 corresponds to a cell content of 2 formula units of \(\text{Na}_{0.16}\text{WO}_6\).

The Laue symmetry was found from Weissenberg photographs to be 4\(\overline{mmn}\). The only systematic absences are \(hk0\) reflections with \(h + k\) odd, which unequivocally suggests \(P4\overline{mmn}\) as the most probable space-group.

A striking feature of the diffraction pattern is the decisive significance of the \(l\) index for the intensities of the reflections. In rough outline the following regularities could be observed:

- for reflections \(hkl\ (h + k\ even): hf0\ (strong), hk1\ (strong), hk2\ (medium), hk3\ (weak), hk4\ (not visible), hk5\ (weak, only \(\beta\) reflections observed);
- for reflections \(hkl\ (h + k\ odd): hf0\ (absent), hk1\ (medium), hk2\ (medium), hk3\ (medium), hk4\ (medium).
Table 1. Observed and calculated intensities in Weisenberg photographs of Na_{0.15}WO_{3}. Rotation axis [110]. Cu-K radiation.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>(110^0 \text{st} 79)</td>
</tr>
<tr>
<td></td>
<td>(001^0 \text{st} 35)</td>
</tr>
<tr>
<td></td>
<td>(002^0 \text{st} 10)</td>
</tr>
<tr>
<td></td>
<td>(003^0 \text{w} 12)</td>
</tr>
<tr>
<td></td>
<td>(004^0 \text{w} 02)</td>
</tr>
<tr>
<td></td>
<td>(005(\beta)_2^w 115(\beta)_2^w 225(\beta)_4^w)</td>
</tr>
<tr>
<td>First</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(010^0 \text{w} 0)</td>
</tr>
<tr>
<td></td>
<td>(011^0 \text{st} 11)</td>
</tr>
<tr>
<td></td>
<td>(012^0 \text{st} 12)</td>
</tr>
<tr>
<td></td>
<td>(013^0 \text{m} 5)</td>
</tr>
<tr>
<td></td>
<td>(014^0 \text{m} 7)</td>
</tr>
<tr>
<td>Second</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(020^0 \text{st} 60)</td>
</tr>
<tr>
<td></td>
<td>(021^0 \text{st} 33)</td>
</tr>
<tr>
<td></td>
<td>(022^0 \text{m} 5)</td>
</tr>
<tr>
<td></td>
<td>(023^0 \text{m} 1)</td>
</tr>
<tr>
<td></td>
<td>(024^0 \text{m} 2)</td>
</tr>
</tbody>
</table>

A close examination furthermore revealed that the structure amplitudes \(|F(hkl)|\) of the reflections of each of these two series are, within the error of estimation, independent of the values of \(h\) and \(k\), but varying with \(l\) only. These regularities can only be accounted for if the two tungsten atoms of the unit cell occupy a twofold point position \(2(c) : 0 \frac{1}{2} \frac{1}{2} \frac{1}{2}\), with \(z\) equal to 0.065 ± 0.01 or 0.435 ± 0.01. The latter value of the parameter will be arbitrarily adopted for the following discussion. Table 1 gives a comparison between the observed intensities and those calculated on the basis of this arrangement of the tungsten atoms.

It is not possible to find the positions of the oxygen and sodium atoms from
the X-ray data as the scattering power
of these atoms is too low in comparison
with that of the tungsten atoms. The
arrangement of the latter, however, is very
similar to that derived by Hägg 2 for the
cubic sodium tungsten bronze of perov-
skite type. This fact suggests that the
two structures are closely related, and
leads to the following atomic configuration
of the tetragonal bronze, which corresponds
throughout to plausible interatomic dis-
tances:

\[
\text{Cell content: } 2 \text{Na}_2\text{WO}_4 \\
\text{Space-group: } D_{4h}^{7} - P4/nmm \\
2 \text{W in } 2(c): \frac{1}{2}, \frac{1}{2}, 0 \\
2 \text{Na in } 2(a): 0, 0, \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \\
2 \text{O in } 2(c): \frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{3}{4} \\
4 \text{O in } 4(c): \frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{3}{4}, \frac{1}{4}, \frac{3}{4}, \frac{1}{4}, \frac{3}{4}
\]

The structure may be described as built
up of deformed WO₄ octahedra, joined
by sharing corners. The alkali metal atoms
are statistically distributed and occupy
approximately 10 per cent of the major
interstices of the lattice. (It must be
emphasized that this scheme presupposes
the unit cell dimensions and symmetry of
the actual structure to be identical with
those of the tungsten lattice.)

The tungsten atoms form puckered net-
works extending parallel to the ab plane, by
being a little displaced alternately + 0.25 A
and - 0.25 A in the direction of the c
axis. In this respect which constitutes the
difference from a lattice of perovskite type,
the structure is reminiscent of the tungsten
trioxide structure of deformed ReO₃-type,
the metal atoms of which show similar
displacements parallel to two of the axes
of the cubic substructure cell (± 0.23 A
and ± 0.24 A respectively). It is note-
worthy that another tetragonal sodium
tungsten bronze, NaₓWO₄(x ≈ 0.3), of
complicated structure also contains puck-
ered networks of tungsten atoms 4.

These structural relationships evidently
demonstrate the character of the bronzes
of degenerated perovskite type to be a
distinct intermediate state in the transitions
with decreasing alkali metal content
from the cubic sodium 2 and lithium 5
bronzes of perovskite type to tungsten
trioxide.

The author is indebted to Miss Birgitta
Blomberg for her valuable assistance. The
work has been supported by a grant from the
Swedish Natural Science Research Council,
whose assistance is gratefully acknowledged.

1. Magnéli, A., and Blomberg, Birgitta Acta
Scand. 4 (1950) 398.

Received May 5, 1951.

Estimation of Xylocaine * by
Nitration

BERTIL ORTENBLAD

Central Laboratories, Astra,
Södertälje, Sweden

Comprehensive experiments have shown
that Xylocaine (α-diethylenamino-2,6-
acetoxylidide) can be nitrated in a simple
manner with analytical reproducibility.
However the nitrination conditions must be
rigidly controlled since the course of the
reaction is easily affected by variations in
the reagent and the temperature employed.
Nitrination at 80° C with one part of conc.
nitric acid and five parts of acetic acid
seems to be most suitable. Hydrogenation
of the nitrination product is subject to simi-
lar limitations. The method would appear
to be specially suitable for estimation of
Xylocaine in small amounts, in dilute solu-
tions and possibly also in biological mate-
rial. The procedure and applicability of
the method are being further investigated at
present.

* Regd. trade mark.