In Table 1, the observed and calculated d values, $\sin^2 \theta$ and $\Delta \sin^2 \theta = \sin^2 \theta_{\text{calc}} - \sin^2 \theta_{\text{obs}}$ are listed for the monoclinic indexing as given in the JCPDS file. Three fitting parameters are defined as the average of $\Sigma \pm \Delta \sin^2 \theta$, $\Sigma + \Delta \sin^2 \theta$ and $\Sigma - \Delta \sin^2 \theta$.

The agreement between the observed and calculated X-ray diffraction patterns is not satisfactory. The monoclinic crystal system was chosen by Chang & Margrave by analogy with the LiBO$_2$ and HBO$_2$ systems, for which some crystal data are given in Table 2 (Chang & Margrave, 1968; JCPDS, 1977).

In view of these results, an attempt was made to index the X-ray diffraction pattern of $\beta$-LiAlO$_2$ by analogy with the indexing used for some alkali aluminates and ferrates (Lejus & Collongues, 1962). Some data for these systems are also given in Table 2 (Wyckoff, 1964).

Assuming parallel behavior between the NaFeO$_2$ and LiAlO$_2$ systems, an orthorhombic cell was chosen and a least-squares refinement was carried out based on orthorhombic indexing. This treatment yielded the cell dimensions: $a = 5.283 (3)$, $b = 6.306 (4)$ and $c = 4.908 (2)$ Å. The observed and calculated d values, $\sin^2 \theta$ and $\Delta \sin^2 \theta = \sin^2 \theta_{\text{calc}} - \sin^2 \theta_{\text{obs}}$ are listed in Table 3.

Clearly, the calculated X-ray diffraction pattern of the orthorhombic indexing fits the observed data better than the monoclinic indexing. As can be seen in Table 2, there is a very clear correspondence between the NaFeO$_2$ and LiAlO$_2$ systems.

References

Crystal Data


Crystal data for isotypic Cs$_2[M$(CN)$_4$]·H$_2$O compounds, $M = $ Pt, Pd and Ni. By W. HOLZAPFEL, H. H. OTTO, H. YERSIN and G. GLEIMANN, Institut für Chemie und Fachbereich Physik der Universität Regensburg, Postfach 397, D-8400 Regensburg, Federal Republic of Germany

(Received 20 November 1978; accepted 21 December 1978)

**Abstract**

Cs$_2$[Pt(CN)$_4$]·H$_2$O and Cs$_2$[Ni(CN)$_4$]·H$_2$O were found to be isotypic with the known hexagonal Pt compound which shows an unusual helical chain of six [Pt(CN)$_4$]$^{2-}$ groups in the unit cell, space group P6$_3$ or P6$_5$. The crystal data are $a = 9.559 (2)$ and $c = 19.308 (4)$ Å, $D_m = 2.87 (4)$, $D_x = 2.912$ Mg m$^{-3}$ for the Ni compound, and $a = 9.704 (2)$, $c = 19.388 (4)$ Å, $D_m = 3.12 (4)$, $D_x = 3.115$ Mg m$^{-3}$ for the Pd compound. X-ray powder data are given.

**Introduction**

For several years we have studied systematically the crystal chemistry and the physical properties of non partially oxidized tetracyanoplatinates(II) crystallizing in linear chain structures. The main emphasis was given to spectroscopic properties in the optical energy range (Yersin & Gliemann, 1978).

Cs$_2$[Pt(CN)$_4$]·H$_2$O was the first hexagonal compound of the tetracyanoplatinate family to be found (Otto, Holzapfel, Yersin & Gliemann, 1976). The crystal structure has been determined by X-ray (Otto et al., 1977) and neutron diffraction methods (Johnson, Koch & Williams, 1977). It shows an unusual helical arrangement of six [Pt(CN)$_4$]$^{2-}$ groups along the z axis. The 1.471 (1) Å distance of the Pt atoms from this axis represents a remarkable deviation from a linear chain structure which is of considerable crystallographic and spectroscopic interest (Holzapfel, Yersin, Gliemann & Otto, 1979). Recently we synthesized the isotypic Pd and Ni compounds.

**Origin of specimens**

Cesium tetracyanopalladate and niccolate were synthesized by the reaction of cesium sulfate with barium tetracyanopalladate and niccolate, respectively, in aqueous solution. The precipitated barium sulfate was removed by filtration. The solvent was slowly evaporated at room temperature, until small single crystals grew. These were recrystallized from aqueous solution.

**Chemical characterization**

The stoichiometric composition of both compounds was determined by elemental analysis, which verified the analogy to Cs$_2$[Pt(CN)$_4$]·H$_2$O:

<table>
<thead>
<tr>
<th>M</th>
<th>Ni (FW)</th>
<th>Pd (FW)</th>
<th>Pt* (FW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>446.61</td>
<td>494.3</td>
<td>582.99</td>
</tr>
</tbody>
</table>

Table 1. Crystal data for isotypic Cs$_2[M$(CN)$_4$]·H$_2$O compounds

The 3σ errors associated with the final digit of the lattice constants are given in parentheses.

<table>
<thead>
<tr>
<th>M</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>$b$ (Å)</td>
<td>$c$ (Å)</td>
</tr>
<tr>
<td></td>
<td>9.559 (2)</td>
<td>9.704 (2)</td>
<td>19.308 (4)</td>
</tr>
<tr>
<td></td>
<td>19.388 (4)</td>
<td>19.336 (6)</td>
<td>2.912</td>
</tr>
</tbody>
</table>

* Otto et al. (1976).
**CRYSTAL DATA**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Found</th>
<th>Calcd</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Calcd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(_2)[Pd(CN)(_4)].H(_2)O</td>
<td>9.79</td>
<td>9.72</td>
<td>0.41</td>
<td>0.41</td>
<td>11.31</td>
<td>11.33</td>
</tr>
<tr>
<td>Cs(_2)[Ni(CN)(_4)].H(_2)O</td>
<td>10.71</td>
<td>10.76</td>
<td>0.49</td>
<td>0.45</td>
<td>12.29</td>
<td>12.55</td>
</tr>
</tbody>
</table>

**X-ray powder data**

The powder data were collected with a Guinier counter diffractometer using Cu K\(_{\alpha}\) radiation (\(\lambda = 1.54051\) Å) and are given in Tables 2 and 3. The mean angle errors for the lines listed in the tables are \((2 \theta) = 0.007°\) and 0.006°, respectively. Intensities represent relative peak heights.

**Unit-cell data**

Precession photographs taken with Cu K\(_{\alpha}\) radiation showed that the unit cell of both compounds is hexagonal, space group P\(_{6}\)(or P\(_{6\bar{5}}\)), with the lattice constants given in Table 1. These constants were refined from the indexed powder data with the program PULVER (Weber, unpublished). The densities measured by toluene displacement in a pycnometer are also given in Table 1. The calculated densities agree with six formula units in the unit-cell in analogy with Cs\(_2\)[Pt(CN)\(_4\)].H\(_2\)O.

The crystal data summarized in Table 1 verify that the three Cs\(_2\)[M(CN)\(_4\)].H\(_2\)O compounds are isotypic and so have a helical arrangement of the [M(CN)\(_4\)]\(^2-\) groups along the z axis.

**References**


