Some New One-dimensional Compounds: Preparation and Optical Properties

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Raman Spectra, Preparation, Platinum-mixed Valence

New mixed-valence compounds of the type K$_2$[Pt(NH$_3$)$_3$X$_3$]·[Pt(NH$_3$)$_3$X$_3$] (where X = Cl or Br) were prepared by partial oxidation-addition of K[Pt(NH$_3$)$_3$X] with Cl$_2$ and Br$_2$. The absorption and polarized reflectance spectra of these compounds show a semiconductor behaviour in one dimension and the resonance Raman spectra indicate the ...-Pt(II)···X-Pt(IV)-X chain.

In the course of the synthesis of platinum compounds having the molecular formula K$_2$[Pt(NH$_3$)$_3$Cl$_3$][Pt(NH$_3$)$_3$Cl$_5$] · 2 H$_2$O [1] in addition to lustrous orange crystals we observed some green lustrous metallic crystals, which raised our interest for the present investigation. Again when these green crystals are recrystallized in the presence of excess KBr golden-lustrous metallic needle-shaped crystals are obtained.

For our present synthesis Cossa’s salts K[Pt(NH$_3$)$_3$Cl$_3$] and K[Pt(NH$_3$)$_3$Br$_3$] were prepared according to [2, 3]. The new compounds were prepared as follows.

a) A part of Cossa’s salt was oxidised by bubbling chlorine gas in its aqueous solution. The excess chlorine was removed by evaporation on a steam bath resulting in a bright yellow residue. This residue was dissolved in water and treated with a little excess of Cossa’s salt and excess KCl. After concentrating the mixture was left at room temperature for crystal growth, which resulted in shining greenish-golden metallic, needle-shaped crystals.

b) Cossa’s salt was oxidised with bromine-water; after evaporation the red residue was treated with a little excess of K[Pt(NH$_3$)$_3$Br$_3$] and KBr. After concentrating, the mixture was left for crystal growth, which resulted in bronze coloured shining metallic crystals.

c) The similar mixture of bromine oxidised product of Cossa’s salt and a little excess of Cossa’s salt crystallized in the presence of excess KCl instead of KBr give golden shining metallic well-defined needle-like crystals.

d) K[Pt(NH$_3$)$_3$Br$_3$] was oxidised with bromine water; after evaporation the red residue was treated with a little excess of K[Pt(NH$_3$)$_3$Br$_3$] and KBr. After concentrating, the mixture was left for crystal growth, which resulted in bronze coloured shining metallic crystals.

For the preparation of the new compounds a slight excess of Cossa’s salt was used. The results of chemical analysis are given in Table I. Figure 1 shows the resonance Raman spectra of K$_2$[Pt(NH$_3$)$_3$Br$_3$][Pt(NH$_3$)$_3$Cl$_3$] single crystal with E||Z and E⊥Z.

For parallel polarization the bands occur at 162 (rel. intensity 1.00), 195 (0.25), 223 (0.18), 265 (0.03), 330 (0.08), 363 (0.03), 390 (0.04), 425 (0.02) and 497 (0.25) cm$^{-1}$, and for perpendicular direction they occur at 167 (0.03), and 197 (0.12) cm$^{-1}$. The RRS of K$_2$[Pt(NH$_3$)$_3$Cl$_3$][Pt(NH$_3$)$_3$Cl$_3$] in a pellet has bands at 205 (0.13), 295 (1.00), 328 (0.40), 595-635 (0.19), 695 (0.03), 745 (0.12) cm$^{-1}$.

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Table I. Chemical analysis of \( \text{K}_2[\text{Pt(NH}_3\text{)}\text{X}_3][\text{Pt(NH}_3\text{)}\text{X}_5]\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\text{X(Cl + Br)})</th>
<th>(\text{H})</th>
<th>(\text{N})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>\text{Found}</td>
<td>\text{Calcd}</td>
<td>\text{Found}</td>
</tr>
<tr>
<td>a (\text{K}_2[\text{Pt(NH}_3\text{)}\text{Cl}_3][\text{Pt(NH}_3\text{)}\text{Cl}_3])</td>
<td>36.30</td>
<td>36.11</td>
<td>0.72</td>
</tr>
<tr>
<td>b (\text{K}_2[\text{Pt(NH}_3\text{)}\text{Cl}_3][\text{Pt(NH}_3\text{)}\text{Cl}_3])</td>
<td>47.20</td>
<td>47.87</td>
<td>0.59</td>
</tr>
<tr>
<td>c (\text{K}_2[\text{Pt(NH}_3\text{)}\text{ClBr}_2][\text{Pt(NH}_3\text{)}\text{Cl}_3])</td>
<td>53.01</td>
<td>52.27</td>
<td>0.55</td>
</tr>
<tr>
<td>d (\text{K}_2[\text{Pt(NH}_3\text{)}\text{Br}_3][\text{Pt(NH}_3\text{)}\text{Br}_5])</td>
<td>55.97</td>
<td>55.99</td>
<td>0.49</td>
</tr>
</tbody>
</table>

900 (0.08) and 1200 (0.03) cm\(^{-1}\), while RRS of \(\text{K}_2[\text{Pt(NH}_3\text{)}\text{Cl}_3][\text{Pt(NH}_3\text{)}\text{Cl}_3]\) \(\cdot\) 2 \(\text{H}_2\text{O}\) has bands at 220 (0.14), 320 (1.00), 505 (0.13), 635 (0.14), 750 (0.07), 915 (0.04), 1300 (0.02), 3210 (0.13) and 3470 (0.27) cm\(^{-1}\). Resonance Raman spectra show that the chain \(\cdots\text{Pt(II)}\cdots\text{X-Pt(IV)}\cdots\) exists (See ref. 4 and 5). The crystal structure of \(\text{K}_2[\text{Pt(NH}_3\text{)}\text{Br}_3][\text{Pt(NH}_3\text{)}\text{Br}_3]\) is under way [6] and at present indicates an alternative stacking of \(\text{Pt(NH}_3\text{)}\text{Br}_3^-\) and \(\text{Pt(NH}_3\text{)}\text{Br}_3^-\) with a Pt–Pt distance of 5.61 Å, the same as in the case of other compounds with same chain [7].

We are now going to prepare the Pd–Pt and Pd–Pd analogues of these compounds because, according to previous results (see [9]), Pd-compounds are more conducting than Pt-compounds.


