

NOTIZEN

Some New One-dimensional Compounds: Preparation and Optical Properties

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New mixed-valence compounds of the type $K_2[Pt(NH_3)X_3][Pt(NH_3)X_5]$ (where X = Cl or Br) were prepared by partial oxidation-addition of $K[Pt(NH_3)X_3]$ 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 $\cdots Pt(II)\cdots X-Pt(IV)-X$ chain.

In the course of the synthesis of platinum compounds having the molecular formula $K_2[Pt(NH_3)Cl_3][Pt(NH_3)Cl_5] \cdot 2 H_2O$ [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 needleshaped crystals are obtained.

For our present synthesis Cossa's salts $K[Pt(NH_3)Cl_3]$ and $K[Pt(NH_3)Br_3]$ 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 on a water bath it was left at room temperature for slow evaporation and crystal growth. Some green shining metallic crystals result along with the orange red crystals.

b) Cossa's salt was oxidised with bromine-water and excess bromine was removed by evaporation on a steam bath which leaves a deep red residue. The 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.

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 KBr instead of KCl give golden shining metallic well-defined needle-like crystals.

d) $K[Pt(NH_3)Br_3]$ was oxidized with bromine water; after evaporation the red residue was treated with a little excess of $K[Pt(NH_3)Br_3]$ and KBr. After concentrating, the mixture was left for crystal growth, which resulted in bronze coloured shining metallic crystals.

Chemical analysis, resonance Raman spectra (RRS) and preliminary crystal structure showed that these new compounds are of the type $K_2[Pt(NH_3)X_3][Pt(NH_3)X_5]$, where X = Cl or Br with varied proportions. The results of chemical

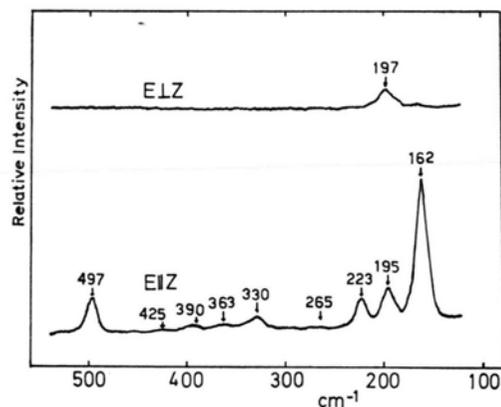


Fig. 1. Resonance Raman spectra of $K_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ single crystal with $E||Z$ and $E\perp Z$.

analysis are given in Table I. Figure 1 shows the resonance Raman spectra of a single crystal of $K_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ for two different polarizations (Electric vector of light parallel or perpendicular to the needle axis).

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 $K_2[Pt(NH_3)Cl_3][Pt(NH_3)Cl_5]$ in a pellet has bands at 205 (0.13), 295 (1.00), 328 (0.40), 595–635 (0.19),

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Table I. Chemical analysis of $K_2[Pt(NH_3)X_3][Pt(NH_3)X_5]$.

Compound	X (Cl + Br)		H		N	
	Found	Calcd	Found	Calcd	Found	Calcd
a $K_2[Pt(NH_3)Cl_3][Pt(NH_3)Cl_5]$	36.30	36.11	0.72	0.77	3.58	3.56
b $K_2[Pt(NH_3)Cl_3][Pt(NH_3)ClBr_4]$	47.20	47.87	0.59	0.63	2.79	2.90
c $K_2[Pt(NH_3)ClBr_2][Pt(NH_3)ClBr_4]$	53.01	52.27	0.55	0.57	2.64	2.66
d $K_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$	55.97	55.99	0.49	0.52	2.44	2.45

900 (0.08) and 1200 (0.03) cm^{-1} , while RRS of $K_2[Pt(NH_3)Cl_3][Pt(NH_3)Cl_5] \cdot 2 H_2O$ 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 $\cdots Pt(II) \cdots X-Pt(IV) \cdots$ exists (See ref. 4 and 5). The crystal structure of

$K_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ is under way [6] and at present indicates an alternative stacking of $Pt(NH_3)Br_3^-$ and $Pt(NH_3)Br_5^-$ with a Pt-Pt distance of 5.61 Å, the same as in the case of other compounds with same chain [7].

The position, the intensity and the shape of the optical absorption spectra of suspension in CCl_4 or deposits on quartz depend on the size and the shape of the particles. These effects are analogous to those of compounds $[M(en)_2][M(en)_2X_2] (ClO_4)_4$ (see [8]). The polarized reflectance spectra of the single crystals show semiconductor behaviour as in the case of $[Pd(en)_2][Pd(en)_2Cl_2] (ClO_4)_4$ (see [8]).

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.

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