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THE THERMAL DECOMPOSITION OF $K_2Pt(CN)_4Br_2$ AND $K_2Pt(CN)_4$

P. K. GALLAGHER AND J. P. LUONGO
Bell Laboratories, Murray Hill, N. J. 07974 (U.S.A.)

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ABSTRACT

The thermal decomposition of $K_2Pt(CN)_4Br_2$ was studied by thermogravimetry, evolved gas analysis, X-ray diffraction and infrared spectroscopy. The reduction of the platinum occurs in several steps, each evolving cyanogen. The first step corresponded to the formation of a complex of apparently Pt(III) with bridging cyanide ions. The second and third steps which form Pt(II) with primarily terminal cyanide ions and finally the metal, are not well resolved. $K_2Pt(CN)_4 \cdot 8H_2O$ first lost water of hydration and then a single molecule of cyanogen corresponding to the formation of platinum metal and KCN.

INTRODUCTION

There is considerable current interest in a series of non-stoichiometric mixed valence compounds best represented by $K_2Pt(CN)_4Br_{0.3} \cdot XH_2O$ because of their unidimensional electrical conductivity[1,2]. It has been shown that part of the ambiguity in published results[3] concerning these materials may arise from variability in the number of waters of hydration, X, or possibly in the number of halide ions as well. Thermogravimetry (TG) is a potentially useful and rapid technique to determine the value of X in a series of preparations. Prior to investigating a series of single crystals of this compound, it was decided to first study the thermal decomposition of the fully oxidized, $K_2Pt(CN)_4Br_2$, and unoxidized $K_2Pt(CN)_4$ end members.

EXPERIMENTAL AND RESULTS

Sample preparation

The compounds $K_2Pt(CN)_4$ and $K_2Pt(CN)_4Br_2$ were prepared from high purity C.P. platinum metal[4] by chemical reaction followed by crystallization. The bromide content or more correctly the oxidizing power of the $K_2Pt(CN)_4Br_2$ was checked by an iodimetric titration. Weighed quantities of the crystals were dissolved in an aqueous solution of excess KI. The iodine formed was titrated with a standard $Na_2S_2O_3$ solution using a starch indicator. The results indicated a bromide content of 2.00 ± 0.01.

Thermal analysis

Thermogravimetric (TG) experiments were performed using a Perkin-Elmer thermobalance and controller which had been modified to produce a digital output on punched paper tape[5]. Approximately 10 mg samples were heated in air (50 ml min^{-1}) at a rate of 10°C min^{-1}. Figure 1 shows the resulting computer generated plots.

Evolved gas analysis (EGA) was performed by heating about 0.1 g of $K_2Pt(CN)_4Br_2$ in a platinum crucible suspended in an evacuated platinum tube. The surrounding furnace was programmed to heat at a rate of about 2°C min^{-1}. The tube was evacuated by a turbomolecular pump and an AEI, MS-10 mass spectrometer was inserted between the sample and the pump. The mass range from 36–200 was constantly cycled and the output of the mass spectrometer was fed to an Infotronics Model CS-204 integrator. The timing was reset for each cycle (~13 min) by a microswitch closure on the mass spectrometer. The experiment was repeated using the mass range from 12–45. A calibration plot was made of peak time versus mass number using CO_2. Figure 2 is a plot of the relative area of the mass 52 peak as a function of temperature. The actual sample temperature lags significantly due to the poor thermal conductivity of the vacuum. The background pressure in the absence of decomposition is about 2×10^{-7} Torr.

X-ray diffraction analysis was performed on the residues from the TG and EGA experiments. The results indicated KBr and Pt for the residue from $K_2Pt(CN)_4Br_2$ and KCN and Pt from $K_2Pt(CN)_4 \cdot 8H_2O$.

Infrared spectroscopy

The residues from the two EGA experiments were measured. Both samples were derived from $K_2Pt(CN)_4Br_2$. The first one was stopped just at the beginning of the positive slope on the second or larger peak in Fig. 2 while the second sample was the residue from experiment shown in Fig. 2 and hence was well over the maximum in the second evolution. These two samples along with the parent compound $K_2Pt(CN)_4Br_2$ were prepared as KBr pellets and their spectra recorded using a Perkin-Elmer Model 421 spectrometer. The resulting spectra are shown in Fig. 3.

DISCUSSION

Examination of the weight loss in Fig. 1a indicated that the cyanogen evolved during the decomposition and concomitant reduction in the valence of platinum occurred in at least two distinct steps. The first stage, around 360°C, evolved about one quarter of the total and that around 500°C the remainder. This suggested that an intermediate occurred around 400°C which contained platinum(III) or possibly platinum(II, IV). Such an intermediate would result from the reaction:

$$2K_2Pt(CN)_4Br_2 \rightarrow K_4Pt_2(CN)_6Br_4 + (CN)_2\uparrow \tag{1}$$

The resulting intermediate, $K_4Pt_2(CN)_6Br_4$, does not imply any particular structure

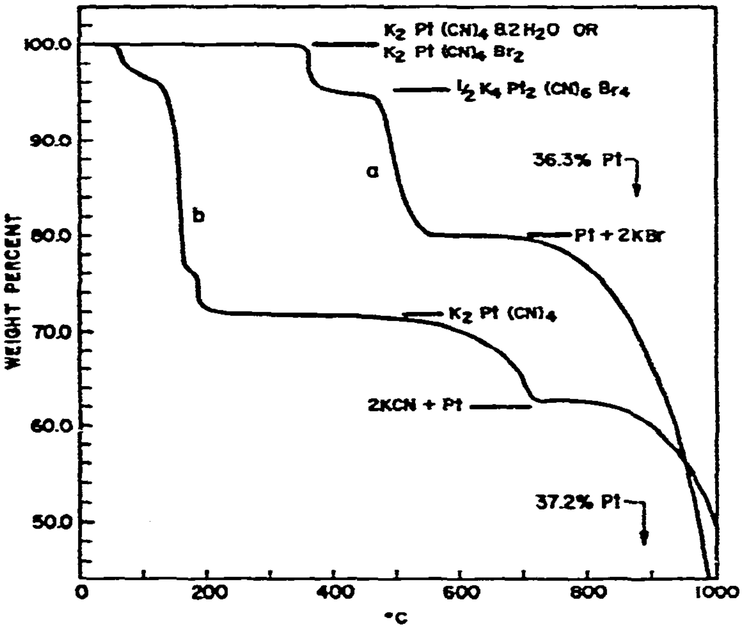

Fig. 1. Thermograms in air at 10°C min^{-1}. (a) $K_2Pt(CN)_4Br_2$, 12.02 mg. (b) $K_2Pt(CN)_4 \cdot 8H_2O$, 8.76 mg.

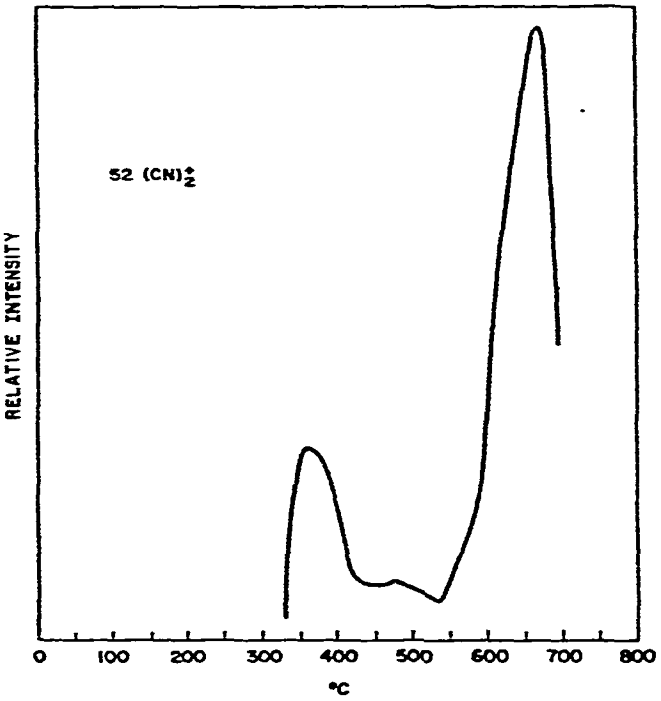

Fig. 2. Evolved gas analysis of $K_2Pt(CN)_4Br_2$, mass 52 peak.

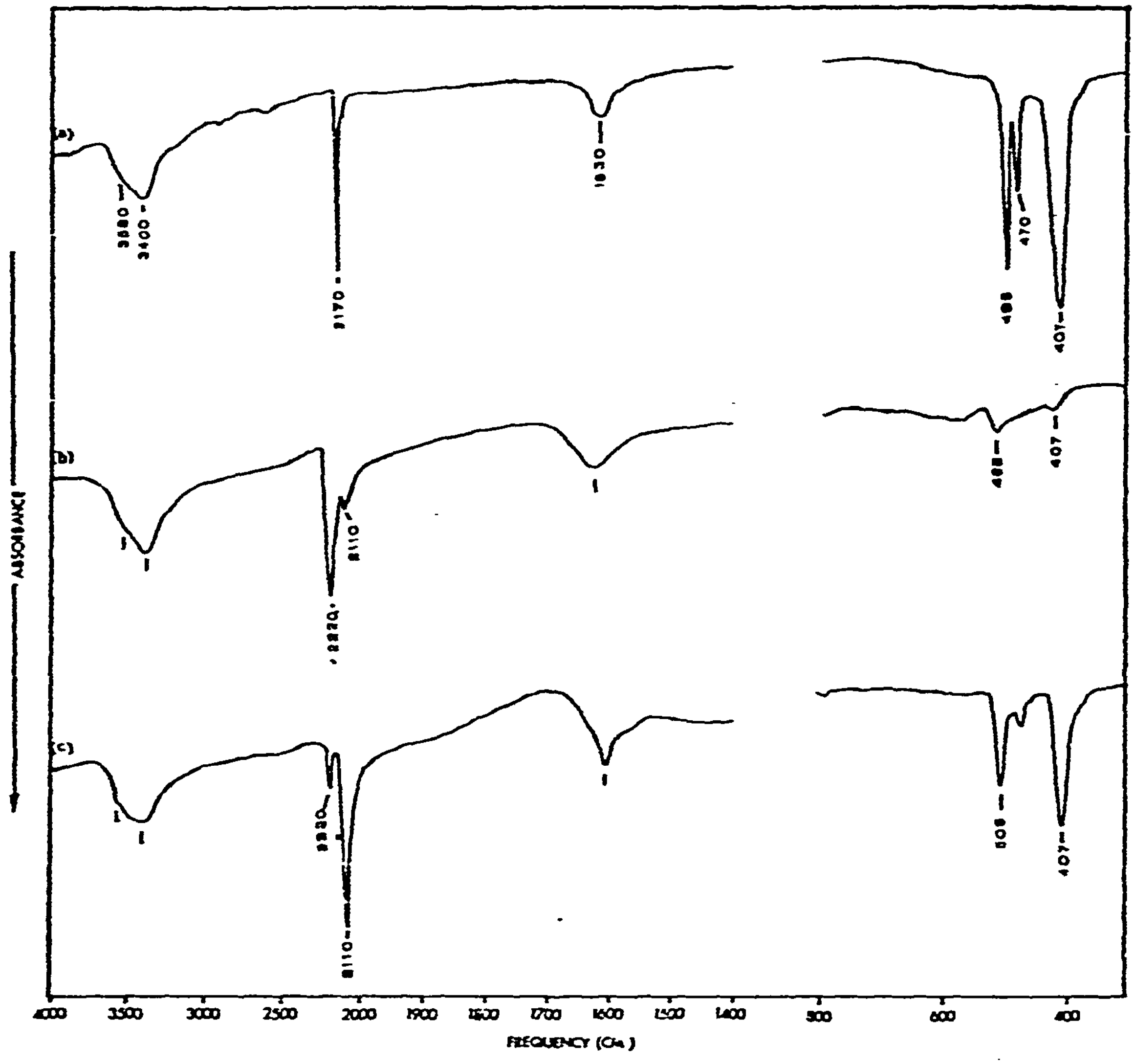

Fig. 3. Infrared spectra at room temperature of $K_2Pt(CN)_4Br_2$ at various stages of decomposition. (a) Unheated. (b) Preheated in vacuum-furnace at 600 °C. (c) Preheated in vacuum-furnace at 700 °C.

but merely a stoichiometric assemblage. This assemblage then decomposes in the second stage around 500 °C as follows:

$$K_4Pt_2(CN)_6Br_4 \rightarrow 4KBr + 2Pt + 3(CN)_2\uparrow \qquad (2)$$

Finally, the KBr vaporizes at temperatures beyond 700 °C.

Figure 1b is a similar TG plot for $K_2Pt(CN)_4 \cdot 8H_2O$. The compound was deliberately kept moist to preserve the finely formed crystals and hence there is slightly more weight loss corresponding to about 8.2 molecules of water. This water of hydration is readily lost by 200 °C. The anhydrous compound begins to decompose at about 450 °C to evolve cyanogen and form platinum metal and KCN around 800 °C. At higher temperatures the KCN vaporizes or decomposes leaving platinum.

The EGA results in Fig. 2 also clearly show the stepwise release of the cyanogen from $K_2Pt(CN)_4Br_2$. Besides the regular cracking pattern associated with cyanogen there were other minor constituents resulting from the reactivity of cyanogen. Traces of moisture react according to:

$$(CN)_2+2H_2O \rightleftarrows HCN+NH_3+CO_2 \qquad (3)$$

Nitrogen was present at higher temperatures indicating some dissociation which was probably catalytically instigated by the extensive platinum surface.

Although the TG and EGA suggest a stoichiometry for the intermediates, they do not provide any structural information other than by inference or speculation.

Figure 3 shows the spectra of $K_2Pt(CN)_4Br_2$ before and after heating to about 600 and 700 °C in vacuum. The top trace, Fig. 3a, is the spectrum of $K_2Pt(CN)_4Br_2$ before heating. The spectrum is in good agreement with that of Jones and Smith[6]. The band at 3400 cm^{-1} is due to the OH of water in the KBr matrix, but the shoulder at 3580 cm^{-1} is due to a small amount ($<1\%$) of molecular water molecules in the material. The strong sharp band at 2170 cm^{-1} is the C≡N stretching vibration and the band at 1630 cm^{-1} is also due to the trace of water in the material. The bands at 495 cm^{-1} and 470 cm^{-1} correspond to Pt–C≡N deformation vibrations[6]. The assignment of the band at 412 cm^{-1} is associated with the Pt–C stretch[6].

Spectrum 3b is of the residue from a sample heated to 600 °C at about 2×10^{-7} Torr. It is the residue from an abbreviated EGA experiment. The strong C≡N band has shifted to a higher frequency at 2220 cm^{-1}. A weaker C≡N band also appears at 2110 cm^{-1} showing the presence of some terminal C≡N groups. At this stage the Pt should be very predominantly trivalent or as relatively equal amounts of Pt(II) and Pt(IV). Mössbauer spectroscopy[10] and infrared and Raman spectroscopy[11] of $K_2Pt(CN)_4Br_{0.30}\cdot3H_2O$ have both concluded that there is apparently a single oxidation state of Pt rather than a mixed valency situation in this related compound. Consequently the band at 2220 cm^{-1} in Fig. 3b is assigned to the C≡N stretching of groups bonded to Pt(III). The high frequency further indicates that they are bridging cyanide groups[7–9].

A possible structure might be octahedra of $Pt(CN)_6$ sharing edges or corners within the plane or layer and apexes between layers so that each cyanide ion is shared. The minor peak at lower energy, 2110 cm^{-1}, then is attributed to a small amount of the next decomposition product which is predominant in Fig. 3c.

The weakening of the 495 and 407 cm^{-1} bands is believed to be due to the effect of bridging on the Pt–C and Pt–C≡N groups.

Spectrum 3c is the spectrum of the sample after heating to 700 °C at about 2×10^{-7} Torr. It is the residue from the EGA experiment in Fig. 2. Two bands are also observed in the 2100–2200 cm^{-1} region of this spectrum. The weaker band at 2220 cm^{-1} represents residual bridged –C≡N groups and the stronger band at 2110 cm^{-1} is assignable to terminal C≡N groups associated with Pt(II)[7]. This shows that, in this case, the bridged C≡N groups no longer form the predominant structure. The bands at 505 and 407 cm^{-1} are characteristic of the Pt–C and Pt–C≡N vibrations in $Pt(CN)_4^{2-}$ and therefore are also indicative of terminal C≡N groups associated with Pt(II)[7]. Although there was no plateau in the TG curve corresponding to Pt(II), the infrared data indicate its presence as an intermediate in the final decomposition of $K_4Pt_2(CN)_6Br_4$.

CONCLUSIONS

The compound $K_2Pt(CN)_4Br_2$ loses a half molecule of cyanogen around 360°C. The intermediate compound formed contains bridging cyanide groups and is a compound of platinum(III). At about 500°C it loses the remaining cyanogen to form platinum metal and KBr. Infrared spectra of incompletely decomposed material suggest that a Pt(II) entity with terminal cyanide groups exists as a very transient intermediate.

The compound $K_2Pt(CN)_6 \cdot 8H_2O$ loses its water of hydration by 200°C and then evolves cyanogen around 500°C to form platinum metal and KCN.

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