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Electronic structure of the linear chain $K_2Pt(CN)_4\cdot xH_2O$ studied by means of electron-energy-loss spectroscopy

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The electronic structure of the linear-chain $[Pt(CN)_4]^{2-}$ has been studied by means of x-ray photoelectron and electron-energy-loss spectroscopies. The peaks present in the spectra are attributed to valence levels and interband transitions and compared with the theoretically calculated energy-level diagram.

INTRODUCTION

Much attention has been paid to metallic pseudo-one-dimensional compounds. The most extensive research has been developed on systems containing square planar tetracyanoplatinate ion $[Pt(CN)_4]^{2-}$ which builds along the *c* axis of the crystal to form a columnar stack (Fig. 1). This columnar stack involves a infinite platinum atom chain with an overlap between the $5d_{z^2}$ platinum orbitals. Their electrical properties are, to a large extent, determined by the Pt-Pt distance in the chain, by the staggered configuration, and by the electron-energy-level distribution.

The precursor of these materials, the *tris*-hydrated $K_2[Pt(CN)_4]\cdot 3H_2O$, is an insulator. In the presence of oxidizing agents, such as halogen, this compound may be transformed from an insulator to very interesting conductor materials with highly one-dimensional metallic properties.[1] Doping with oxidants gives rise to a drastic change in the level's energy distribution on each monomer, particularly near the Fermi level. Structurally, the more evident consequence is the decrease of the distance between the stacks, e.g., in $K_2[Pt(CN_4)_4]\cdot 3H_2O$, the Pt-Pt distance is 3.48 Å and goes down to 2.89 Å in $K_2[Pt_2(CN)]Br_{0.3}\cdot 3H_2O$. Other causes of shortening in the Pt-Pt distance may be, as we will see in the following, the water content in the crystal (dehydration is a very important factor) or temperature and pressure variations. Because of their unusual physical properties, such compounds have been the subject of many experimental and theoretical investigations. The aim of this paper is to provide further experimental information, as regards interband transitions on the dehydrated precursor $K_2[Pt(CN)_4]\cdot xH_2O$ crystal by means of electron-energy-loss (EELS) and x-ray photoelectron (XPS) spectroscopies. The usefulness of the EELS measurements in providing information concerning the higher-energy-level structure in solids is well known.[2]

EXPERIMENTAL

The measurements were carried out in a high-vacuum (HV) apparatus (VG ESCA-MK2) from Vacuum Generators Ltd.) with a chamber equipped with an electron gun useful for Auger and energy-loss experiments. The x-ray spectra were recorded using Al $K\alpha_{1,2}$ radiation as a source ($h\nu = 1486$ eV).

In electron-energy-loss spectroscopy the incident energy adopted was $E_p = 200$ eV with a peak-to-peak modulation of 1.0 ev. At this energy, the recorded surface phenomena are weak and the net peaks present in the spectra can be predominantly considered as bulk transitions.

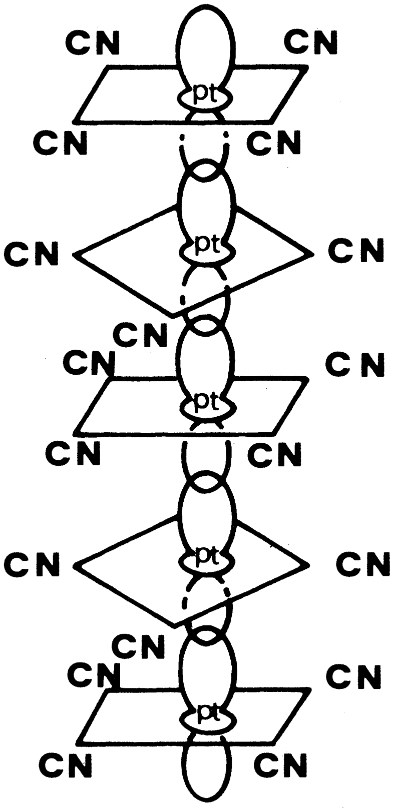

FIG. 1. Chain of square-planar $[Pt(CN)_4]^{2-}$ groups showing the overlapping Pt d_{z^2}.

Commercial $K_2[Pt(CN)_4]\cdot 3H_2O$ powders of high purity were used to prepare samples as pellets under a pressure of 4 kbars. To stabilize the material in the apparatus, the more volatile water was previously removed by dehydration in an oven at about 60 °C. Upon dehydration, single crystals break up into small crystallites without changes in the crystal structure[3] but with evident consequences on their electrical conductivity.[4] Since the surface of the sample may be damaged under radiation, the measurements were performed at liquid-nitrogen temperature and recorded many times very quickly (35–40 sec). On lowering the temperature, a thermal contraction in the Pt-Pt distance may occur.[5] Also, the pressure used to press the pellets (4 kbars) may slightly reduce the Pt-Pt distance, with a red shift in the electronic transitions[6,7] and a further improvement in their electrical conductivity. The vacuum in the apparatus was about 1×9^{-9} Torr. The EELS spectra were recorded in a second derivative because of their greater accuracy in determining the energy position of the peaks. In XPS, the zero in the binding energies (Fig. 2) was estimated to lie at the beginning of the valence bands. For the present data, we evaluate an error limit of ±0.3–0.4 eV.

DISCUSSION

In this report we are concerned with a low-conductivity, strongly dehydrated $K_2[Pt(CN)_4]\cdot xH_2O$ compound (x is of the order of 0.3). As reported in Ref. 3, dehydration breaks the crystal into powdered polycrystals without any apparent deterioration of the sample, but with substantial improvement in the conductivity of the sample.[4,7] This increase in the conductivity, together with the shortening of the Pt-Pt distance along the c axis due to the low temperature and to the pressure used to build the pellets,[5,6] contributes to a sensible lowering of the band gap. Given the experimental conditions used in our measurements, we consider the reported EELS data suitable for comparison with the theoretical calculations on dimer or trimer $[Pt(CN)_4]^{2-}$ units as proposed by Neto *et al.*[8] and Lopez *et al.*[9] These recent theoretical analyses lead, for several conclusions to the conduction mechanisms of these materials. For example, the staggered configuration of the square-planar $[Pt(CN)_4]^{2-}$ groups in the unity cell is important as regards the conductivity properties of the material.[8] Indeed, it has been observed that, while in the nonoxidized *tris*-hydrated $K_2(Pt(CN)_4)\cdot 3H_3O$, each square-planar group is rotated by only a small angle (16°);[10] in the oxidized conducting compounds this rotation around the Pt chain axis can go up to 45°.[11] Since in these structures the important interaction between monomers involves the Pt d_{z^2}-like orbitals along the c-axis direction, the columnar stacking becomes essential in describing the "d-orbital ordering" in the energy diagram. Controversies are present in the literature about this ordering as regards the position of the Pt d_{z^2} level both in the monomer or in dimer or trimer cluster models.[8,9,12–14] While Piepho *et al.*[13] and Viswanath *et al.*[14] set the d_{z^2} orbital at the highest occupied level in the valence band, a different level distribution is proposed by Interrante and Messmer[12] as well by the more recent theoretical reports of Neto *et al.*[8] and Lopez *et al.*[9]

Employing a more or less modified self-consistent x_α scattered-wave method, all these authors agree in concluding that, in the $(Pt(CN)_4)_n^{2-}$ chain (Pt-Pt distance about 3.5 Å), the d_{z^2}-like orbital lies 1.0–1.5 eV below the top of the valence band, while the higher position in the energy diagram is occupied by an extensive mixture of metal $d_{yz,xz}$ orbitals with the ligand p_σ, p_π orbitals.

The presence of a partial oxidation in this columnar stacking yields drastic changes both in the crystal and in the electronic structure: (a) a shortening in the interstack distance, (b) a rotation of the $[Pt(CN)_4]^{2-}$ units by about 45° around the Pt chain, and (c) an inversion in the energy-level ordering that shifts the d_{z^2} orbital to the top position in the valence band.

Since these structural changes influence the conducting

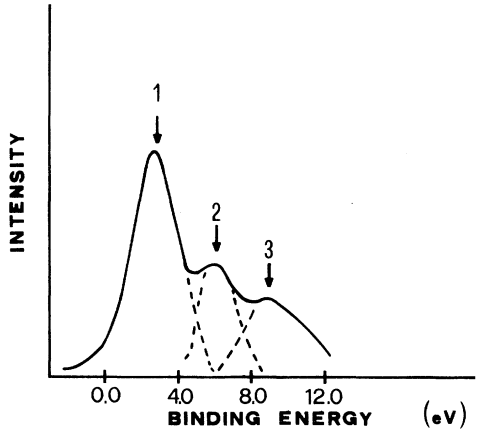

FIG. 2. XPS spectrum of $K_2[Pt(CN)_4]\cdot xH_2O$ in the valence region.

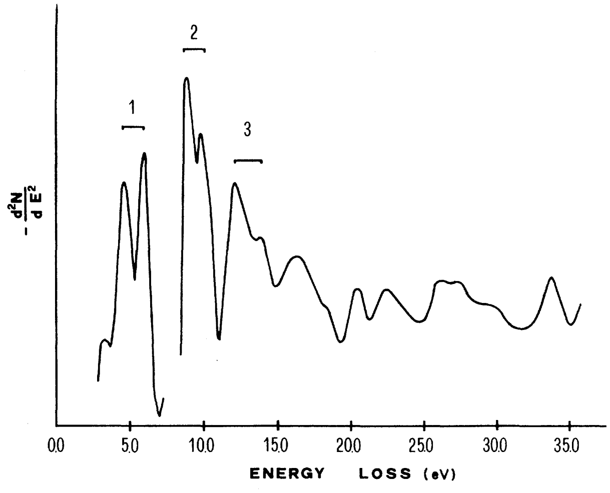

FIG. 3. EELS spectrum of $K_2[Pt(CN)_4]\cdot xH_2O$ at $E_p = 200$ eV and low temperature.

TABLE I. EELS peak positions below the elastic peak ($\Delta\varepsilon$ in eV, $E_p = 200$ eV); error limit ± 0.3 eV.

3.2	18.3
4.7	20.5
6.0	22.4
9.0	26.1
9.8	27.4
12.2	30.0
14.0	33.7
16.5	

properties of the oxidized compounds, they are a main point in understanding the relevant mechanism that shifts the metal d_{z^2} orbital to the higher occupied level. Neto *et al.*[8] and Lopez *et al.*[9] have taken an interest in this problem, but reached different conclusions. For Lopez, the removal of a fraction of an electron from the metal ($d\sigma + d\pi$) orbitals produces a shortening in the interstack distance and it is this circumstance which pushes up the antibonding d_{z^2}-like state as far as the highest occupied level, when the maximum of the partial oxidation is reached.

A different interpretation is proposed by Neto *et al.* who calculate the energy-level diagram for a dimer unit at two different Pt-Pt distances. They find that the positions of the energy levels are not a sensitive function of the Pt-Pt bond length, and conclude that, in the oxidized samples, the d_{z^2} level shift (and change in conducting properties) must, instead, be ascribed to the rotation of the $(\mathrm{Pt(CN)_4})^{2-}$ unit around the Pt chain by 45°.

TABLE II. Table II. XPS peak positions ($\Delta\varepsilon$ in eV).

Peak	eV
1	2.7
2	6.0
3	8.9

With the help of XPS and EELS spectra (Figs. 2 and 3 and Tables I and II) we attempt to quantify some of the theoretically predicted interband transitions in the nonoxidized, low-conducting $\mathrm{K_2(Pt(CN)_4) \cdot x H_2O}$ sample. The XPS spectrum (Fig. 2) describes the energy distribution of the occupied valence-band levels. First observed by Bastasz *et al.*,[15] this spectrum was assigned by Interrante and Messmer[12] on the basis of their calculated electronic structure and represents a useful landmark in attributing the interband transitions present in the EELS spectrum.

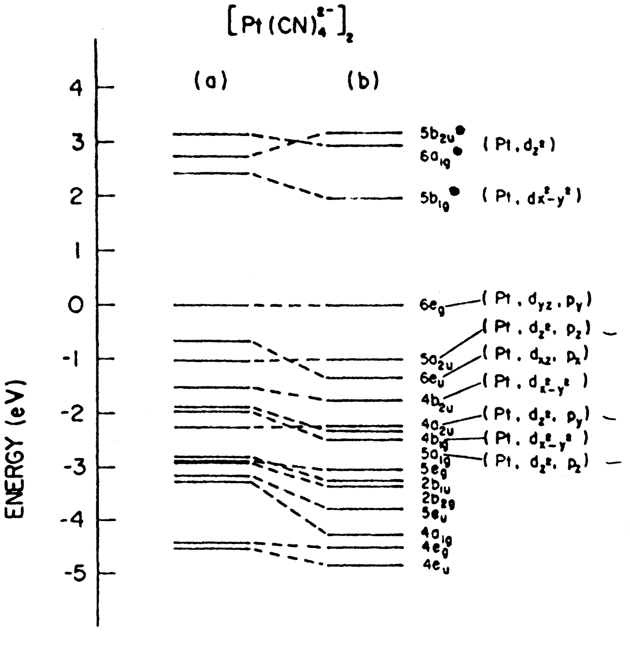

FIG. 4. Energy spectra of the $[\mathrm{Pt(CN)_4^{2-}}]$ dimer: (a) bond length $d_{\text{Pt-Pt}} = 6.578$ bohr; and (b) $d_{\text{Pt-Pt}} = 5.462$ bohr [from Neto *et al* (Ref. 8)].

In our Figs. 2 and 3 we remark the valence XPS (occupied states) and the EELS (interband transitions) peaks by the numbers 1, 2, 3, to identify the electron-level positions in the valence occupied states and their transitions to the first empty states. The first step is to understand which energy levels and which interactions are convoluted into the three broad valence XPS bands (see Fig. 2 and Table II). An attempt has been previously made by Interrante and Messmer.[12] In a very schemetic form, their valence-level distribution, in agreement with those reported in Refs. 8 and 9, may be summarized as the following.

(1) Between the highest occupied states there is an admixture of metal Pt $d_{xz,yz}$ orbitals with the ligand p-like orbitals. The covalent character of this metal-ligand bonding interaction builds up a bonding-antibonding state in which the antibonding partner is located at the top of the valence band (1 in Fig. 2) and the bonding partner in the lower position marked as 3 in the same figure.

(2) The position of the d_{z^2} orbitals, in the nonoxidized samples, lies midway between these two states (2 in Fig. 2).

It is accepted that the first transition from the top of the valence band to the first empty orbital lies at about 4.5 eV.[12,13] This value agrees with our experimental finding. The maximum of the first occupied state (see Table II) lies at 2.7 eV: if we add the calculated gap[8] of about 2.0 eV, our first interband transition results (as in EELS) at 4.7 eV. The second peak of the EELS doublet (6.0 eV) is clearly a transition to the second empty level (see Fig. 4). For the next two splittings[2,3] in EELS, two interpretations are possible: (i) They represent transitions from two levels of each of the 2 and 3 broad valence band (see Ref. 12) to the first empty level, and (ii) they are transitions from the maximum of these valence bands to the two lowest empty levels in the conduction band. The second hypothesis presumes an identical splitting in all three doublets. Since this is not the case, hypothesis (i) appears more reasonable and we assign the EELS doublet at 9.0 and 9.8 eV as a transition from the d_{z^2} valence levels (2) to the first empty level and the doublet at 12.2–14.0 eV as transitions from the hybrid bonding state (3) to the first empty level. In EELS, the peak positions may be lightly shifted toward a higher energy with respect to the optical data according to the dielectric theory. The next EELS transitions observed in the range between 15.0 and 28.0 eV may be viewed as a series of three doublets arising from the three valence bands to higher conduction levels. Also, the 30.0- and the 33.7-eV peaks are ascribable to interband transitions. The presence in our EELS spectrum of a peak at 3.2 eV is not clear: it may be a surface transition or a *d-d* transition between Pt *d* levels.

In conclusion, this note offers an experimental view of possible interband transitions and, consequently, the possibility to experimentally set the lower empty levels in the energy-level diagram of the $[Pt(CN)_4]^2$ chain in accordance with the proposed theoretical schemes.

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