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Polarized Electronic Absorption Spectra of $(n\text{-Bu}_4\text{N})_2[\text{Pt(CN)}_4]$ at 5 K

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The polarized absorption spectra of thin single crystals of $(n\text{-Bu}_4\text{N})_2[\text{Pt(CN)}_4]$ have been studied in the region 282–218 nm at 5 K. The observed spectral bands in D_{4h} Pt(CN)_4^{2-} may be assigned satisfactorily to transitions of the metal-to-ligand charge transfer (MLCT) type. Band polarizations and intensities establish that the excited states, which are derived from $d \rightarrow a_{2u}$ transitions, are strongly mixed by spin–orbit coupling. The lowest absorption system (35 520 cm^{-1}; σ polarized) is attributed to $^1A_{1g} \rightarrow E_u(^3A_{2u})$. Two intense, π-polarized bands are observed, at 38 020 and 45 290 cm^{-1}. These bands are assigned to the two π-allowed $d \rightarrow a_{2u}$ transitions $^1A_{1g} \rightarrow A_{2u}(^3E_u)$ and $^1A_{1g} \rightarrow A_{2u}(^1A_{2u})$, respectively. Intense, σ-polarized features at 38 880 and 45 700 cm^{-1} are attributed to $^1A_{1g} \rightarrow E_u(^3E_u)$ and $^1A_{1g} \rightarrow E_u(^1E_u)$. A weaker system ($\sigma > \pi$) at 41 070 cm^{-1} cannot be assigned unambiguously. It is suggested that the σ component be interpreted as either $^1A_{1g} \rightarrow E_u(^3B_{1u})$ or $^1A_{1g} \rightarrow E_u(^3E_u) + \bar{\nu}(\text{C}{\equiv}\text{N})a_{1g}$.

Introduction

Interest in the electronic structure of Pt(CN)_4^{2-} has been intense in recent years.[1-9] Although an interpretation of the lowest electronic absorption bands of the planar anion in terms of metal-to-ligand charge transfer (MLCT) transitions of the type $d \rightarrow a_{2u}$ was suggested as early as 1963,[1] the complexities in the spectrum were not understood at all until Piepho, Schatz, and McCaffery showed[4] the importance of including spin-orbit coupling in the d^7 a_{2u} excited states. Most recently, Isci and Mason have refined[8] the basic "spin–orbit $d \rightarrow a_{2u}$" interpretation, and Marsh and Miller have reviewed[9] the merits of various assignment schemes.

It became apparent to us some time ago that the polarizations of the lowest electronic absorption bands in suitable crystals containing relatively isolated Pt(CN)_4^{2-} units would be required to provide a sound experimental basis for a detailed set of transition assignments. Thus we have measured and analyzed the polarized electronic spectra of thin crystals of $(n\text{-Bu}_4\text{N})_2[\text{Pt(CN)}_4]$ at 5 K.

Experimental Section

Crystals of $(n\text{-Bu}_4\text{N})_2[\text{Pt(CN)}_4]$ were prepared as described previously.[3] Thin crystals for spectroscopic measurements were grown from 1,2-dichloroethane solution.

Electronic spectral data were obtained using a Cary Model 17 spectrophotometer equipped with an extended cell compartment. An Andonian Associates liquid helium optical Dewar was placed in the sample beam. Temperature (5.0 ± 0.1 K) was monitored with a calibrated carbon resistor. A double Glan-Taylor air-spaced calcite polarizing prism (uv cutoff 2150 Å) was positioned in front of the sample, and a matching polarizer in the reference beam was rotated in tandem. All spectra were measured along the extinction directions of the crystal faces as determined with a polarizing microscope. Baselines for the polarizers and Dewar assembly were obtained for the same polarizer orientations and later subtracted from the spectra.

Results and Discussion

Absorbances measured parallel ($A_\parallel$) and perpendicular ($A_\perp$) to a crystal extinction direction were transformed into out-of-plane ($A_\pi \equiv A_z$) and in-plane ($A_\sigma \equiv A_{x,y}$) profiles under the assumption that the average orientation of the D_{4h} anions in $(n\text{-Bu}_4\text{N})_2[\text{Pt(CN)}_4]$ is the same as found[10] in $(n\text{-Bu}_4\text{N})_2[\text{Ni(CN)}_4]$. This assumption is supported by polarized infrared spectral measurements on crystals of the two compounds.[10] The inverse matrix is[10]

$$\begin{pmatrix} A_\pi \\ A_\sigma \end{pmatrix} = \begin{pmatrix} 3.564 & -2.564 \\ -0.038 & 1.038 \end{pmatrix} \begin{pmatrix} A_\parallel \\ A_\perp \end{pmatrix}$$

In-plane and out-of-plane components in the polarized electronic spectra of Pt(CN)_4^{2-} are shown in Figure 1. Regions marked I, II, III, and IV correspond to bands observed in solution.[8,9] The positions of the band systems in the crystal spectra are in excellent agreement with solution results. For example, band I peaks at 35 400 cm^{-1} in aqueous solution at 300 K,[8] whereas the maximum is observed at 35 520 cm^{-1} in a crystal of $(n\text{-Bu}_4\text{N})_2[\text{Pt(CN)}_4]$ at 5 K.

Table I. Excited States Derived from $d \rightarrow a_{2u}(p_z, \pi^*\ \text{CN})$ MLCT Transitions in Pt(CN)_4^{2-}

One-electron transition	Excited-state symmetry
$a_{1g}(d_{z^2}) \rightarrow a_{2u}$	$A_{1u}(^3A_{2u})$, $E_u(^3A_{2u})$, $A_{2u}(^1A_{2u})$
$e_g(d_{xz}, d_{yz}) \rightarrow a_{2u}$	$A_{1u}(^3E_u)$, $A_{2u}(^3E_u)$, $B_{1u}(^3E_u)$, $B_{2u}(^3E_u)$, $E_u(^3E_u)$, $E_u(^1E_u)$
$b_{2g}(d_{xy}) \rightarrow a_{2u}$	$B_{2u}(^3B_{1u})$, $E_u(^3B_{1u})$, $B_{1u}(^1B_{1u})$

Table II. Electronic Spectral Data for $(n\text{-Bu}_4\text{N})_2[\text{Pt(CN)}_4]$ at 5 K

System	nm	cm^{-1}	Polarizn	$^1A_{1g}\rightarrow$
I	281.5	35 520	σ	$E_u(^3A_{2u})$
II	263.0	38 020	π	$A_{2u}(^3E_u)$
	257.2	38 880	σ	$E_u(^3E_u)$
	255.5	39 140	π	
III	243.5	41 070	$\sigma > \pi$	*a*
IV	(225.5)[b]	(44 350)	(π)	
	220.8	45 290	π	$A_{2u}(^1A_{2u})$
	218.8	45 700	σ	$E_u(^1E_u)$

[a] $E_u(^3B_{1u})$ or $E_u(^3E_u) + \bar{\nu}(\text{C}{\equiv}\text{N})_{a_{1g}}$. [b] Shoulder.

The ground state of D_{4h} Pt(CN)_4^{2-} is $^1A_{1g}(b_{2g}{}^2e_g{}^4a_{1g}{}^2)$.[1] If spin–orbit coupling is included, there are 12 excited states derived from MLCT transitions of the type $d \rightarrow a_{2u}$ (Table I). We shall concentrate our attention, however, on transitions to E_u and A_{2u} states, as these are allowed (polarized σ and π, respectively). Assuming an occupied d-level ordering of $a_{1g}(d_{z^2}) > e_g(d_{xz}, d_{yz}) > b_{2g}(d_{xy})$, which is well-established for Ni(CN)_4^{2-},[4,11] theory predicts[4,8,12] that the energies of the E_u and A_{2u} excited states should increase according to $E_u(^3A_{2u}) < A_{2u}(^3E_u) < E_u(^3E_u) < E_u(^3B_{1u}) < A_{2u}(^1A_{2u}) \leq E_u(^1E_u)$.

Band positions, polarizations, and suggested transition assignments for Pt(CN)_4^{2-} are summarized in Table II. Band I is σ polarized, in accord with expectation for the $^1A_{1g} \rightarrow E_u(^3A_{2u})$ transition. The relatively small intensity of the band and the observation of a positive MCD $\mathcal{A}$ term[4,8] are also consistent with the assignment. The transition cannot be $^1A_{1g} \rightarrow E_u(^3E_u)$, as in that case the π-polarized $^1A_{1g} \rightarrow A_{2u}(^3E_u)$ would necessarily fall in the same region, and band I is strongly σ polarized. Thus we may conclude, with confidence, that the lowest transition observed in absorption is in fact $^1A_{1g} \rightarrow E_u(^3A_{2u})$, as first proposed by Piepho et al.[4]

Systems II and IV both contain strong π- and σ-polarized bands. The intense π-polarized features at 38 020 and 45 290 cm^{-1} are attributed to $^1A_{1g} \rightarrow A_{2u}(^3E_u)$ and $^1A_{1g} \rightarrow A_{2u}(^1A_{2u})$, respectively. The weak π-polarized band in system II (39 140 cm^{-1}), which occurs in a region of strong σ polarization, could represent a component of a vibronically

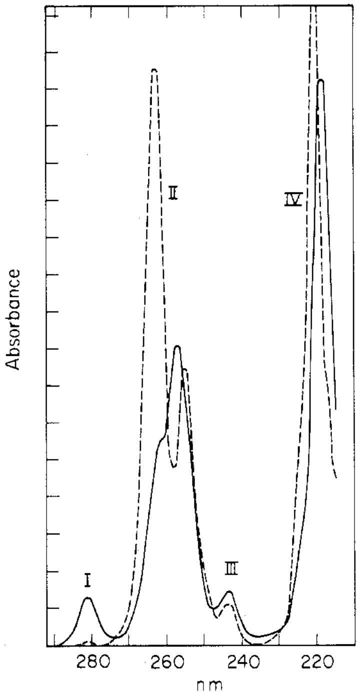

Figure 1. Polarized single-crystal absorption spectra of $(n\text{-Bu}_4N)_2[Pt(CN)_4]$ at 5 K: solid line, σ spectrum; dashed line, π spectrum.

allowed transition. A firm assignment for this feature, however, cannot be made at this time. The positions of ${}^1A_{1g} \rightarrow A_{2u}({}^3E_u)$ and ${}^1A_{1g} \rightarrow A_{2u}({}^1A_{2u})$ are in reasonably good agreement with calculations that take $\xi = 3$ kK.[8,12] To accord with theory, an interpretation based on transitions to $A_{2u}({}^3E_u)$ and $A_{2u}({}^1A_{2u})$ lying in the same region (at 38 020 and 39 140 cm^{-1}) would require an absurdly small ξ value ($<500\ cm^{-1}$),[12] and is therefore rejected.

The strong σ-polarized bands in systems II (38 880 cm^{-1}) and IV (45 700 cm^{-1}) may be assigned with confidence to the transitions ${}^1A_{1g} \rightarrow E_u({}^3E_u)$ and ${}^1A_{1g} \rightarrow E_u({}^1E_u)$, respectively. Positions of both A_{2u} and three of four E_u states, therefore, have been determined. Only the position of ${}^1A_{1g} \rightarrow E_u({}^3B_{1u})$ is in doubt. It is possible that the σ-polarized component of band III (41 070 cm^{-1}) is ${}^1A_{1g} \rightarrow E_u({}^3B_{1u})$ and that the π component represents a vibronically allowed transition either to B_{1u}, $B_{2u}({}^3E_u)$, or $B_{2u}({}^3B_{1u})$. Alternatively, the σ component could represent one quantum of the totally symmetric cyanide stretching vibration built upon the ${}^1A_{1g} \rightarrow E_u({}^3E_u)$ origin at 38 800 cm^{-1}, as 2190 cm^{-1} is a reasonable value for $a_{1g}(C{\equiv}N)$ in the $E_u({}^3E_u)$ state.

It is encouraging that there is now a high degree of consistency between interpretations of the electronic spectra of $Ni(CN)_4^{2-}$ [11] and $Pt(CN)_4^{2-}$. It has been verified experimentally, through both solution MCD and single-crystal polarized spectra, that the lowest MLCT excited states arise from the excitation $a_{1g}(d_{z^2}) \rightarrow a_{2u}$ and that spin–orbit effects are clearly not negligible. In $Ni(CN)_4^{2-}$, the two A_{2u} states are more strongly mixed via spin–orbit coupling than are the four E_u states,[11] whereas for $Pt(CN)_4^{2-}$ both A_{2u} and E_u sets appear to be thoroughly scrambled. The relatively large intensities of the bands attributed to singlet → "triplet" transitions are consistent with the high degree of excited-state mixing predicted by the calculations (e.g., the $A_{2u}({}^3E_u)$ state of $Pt(CN)_4^{2-}$ possesses about 40% $A_{2u}({}^1A_{2u})$ character, according to both recent theoretical estimates[8,12]). The d → a_{2u} band systems of $Pt(CN)_4^{2-}$ are distributed over a much wider energy range than those of $Ni(CN)_4^{2-}$, owing to the larger spin–orbit coupling in the 5d complex. This effect is illustrated by the positions of the A_{2u} states in the two cases, 38 020 and 45 290 cm^{-1} in $Pt(CN)_4^{2-}$ and 34 360 and 35 840 cm^{-1} in $Ni(CN)_4^{2-}$.[11]

The stabilization of MLCT excited states derived from $a_{1g}(d_{z^2}) \rightarrow a_{2u}$ relative to those corresponding to $e_g(d_{xz}, d_{yz}) \rightarrow a_{2u}$ or $b_{2g}(d_{xy}) \rightarrow a_{2u}$ transitions in $Pt(CN)_4^{2-}$ apparently is a consequence of the π-acceptor nature of cyanide ligands. Presumably, the e_g and b_{2g} orbitals in this complex possess some bonding character, whereas a_{1g} is nonbonding or slightly antibonding. It should also be mentioned that recent spectroscopic studies have shown that the lowest electronic excited states in planar $4d^8$ and $5d^8$ complexes containing phosphine and isocyanide ligands are also derived from the $a_{1g}(d_{z^2}) \rightarrow a_{2u}$ transition and that certain other similarities to the $Pt(CN)_4^{2-}$ spectrum appear to be present.[13-15] Thus it may be reasonable to expect the present version of the "spin–orbit d → a_{2u}" interpretation of the electronic spectrum of $Pt(CN)_4^{2-}$ to be a useful reference point in considering detailed assignments for MLCT bands in planar complexes containing heavy central metals and π-acceptor ligands.

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