

Single Crystal Luminescence of Dimeric Cis-bis(2-phenylpyridine)platinum(II) at High Pressure

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The emission spectrum of single-crystal cis-bis(2-phenylpyridine)-platinum(II) has been measured at room temperature under high pressures up to 60 kbar. The observed red shift of the emission is on the order of $-15 \text{ cm}^{-1}/\text{kbar}$ and can be explained by a reduction of the Pt–Pt distance in the dimeric units with increasing pressure.

1. Introduction

The complex cis-bis(2-phenylpyridine)platinum(II) (=CBPPP) contains a d^8 -central ion and deprotonated 2-phenylpyridine as an anionic ligand [1]. In the crystal the molecules form dimeric units with essentially parallel planes. At ambient conditions the intra-dimeric Pt–Pt distance, R , is 3.53 Å, whereas the platinum ions of different dimers are more than 4.5 Å apart.

From several crystalline platinum(II) compounds with quasi-one dimensional structure such as the tetracyanoplatinates(II) it is well known that the optical properties depend significantly on the intra-columnar Pt–Pt coupling [2]. Thus, application of high pressure shifts the optical transition energies of these compounds in the order of $\Delta\bar{\nu}/\Delta p \approx -100 \dots -400 \text{ cm}^{-1}/\text{kbar}$ due to the pressure induced reduction of the intra-columnar Pt–Pt distance [2, 3].

The structure of the solid CBPPP is characterized by the dimeric units, and therefore, it differs essentially from the columnar structure of the tetracyanoplatinates(II) with its equidistant (or nearly equidistant) arrangement of the metal ions along the columns. Since the luminescence and the optical absorption of single crystal CBPPP can be assigned to electronic transitions in the binuclear center of the dimeric unit [4], it should be worthwhile to vary the intra-dimeric Pt–Pt distance by application of high pressure and to

look for the corresponding changes of the luminescence properties.

2. Experimental

Single crystals of CBPPP were prepared according to [1].

The measurements of the luminescence at high pressure were performed by a special spectrometer with a modified sapphire cell of Bridgeman's opposed anvil type [5]. The isotropic pressure within the cell was determined by the pressure shift of the R lines ($-0.76 \text{ cm}^{-1}/\text{kbar}$ at room temperature) of small ruby crystals [6].

3. Results

Figure 1 shows the luminescence spectrum of single crystal CBPPP at room temperature for several pressures. The spectrum consists of one broad band with a half-width of $\approx 2200 \text{ cm}^{-1}$, and it is independent of the orientation of polarization. With increasing pressure the maximum of the emission is shifted from $15\,550 \pm 100 \text{ cm}^{-1}$ at $p = 1 \text{ bar}$ to lower energies.

The wave number of the emission maximum as function of the applied pressure up to $p = 60 \text{ kbar}$ is given in Figure 2. Between $p = 1 \text{ bar}$ and 10 kbar the pressure-induced energy shift is nearly linear with a slope of $\Delta\bar{\nu}/\Delta p \approx -20 \text{ cm}^{-1}/\text{kbar}$. Increase of the pressure from $p = 10 \text{ kbar}$ to 20 kbar yields no percep-

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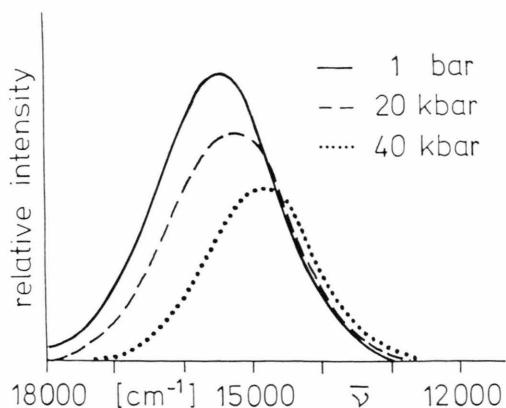


Fig. 1. Emission spectra of single crystal CBPPP at $p = 1$ bar, 20 kbar, and 40 kbar. $T = \text{room temperature}$. $\lambda_{\text{exc}} = 364$ nm.

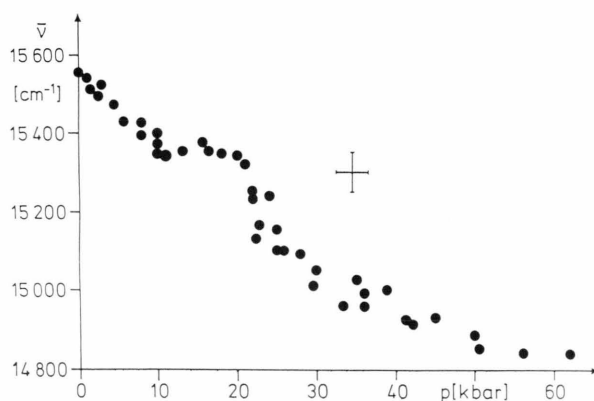


Fig. 2. Wave number of the emission maximum of single crystal CBPPP at room temperature as function of the applied pressure. $\lambda_{\text{exc}} = 364$ nm.

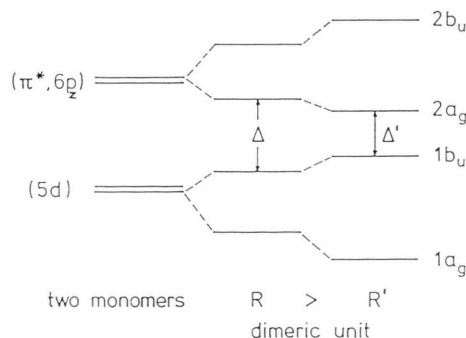


Fig. 3. Proposed energy level diagram for CBPPP (schematic). Left-hand side: two monomers. Middle part and right-hand side: dimeric unit with normal and reduced Pt-Pt distance, respectively. (5d) represents schematically the Pt states $5d_{z^2}$, $5d_{yz}$, and $5d_{x^2-y^2}$ of the two monomers.

tible change of the emission energy, the graph $\bar{\nu}(p)$ exhibits a distinct plateau. With further increase of the pressure the emission is red shifted again. After a strong red shift beyond the high pressure side of the plateau the slope $\Delta\bar{\nu}/\Delta p$ becomes smaller with increasing pressure and reaches a value of $\approx -8 \text{ cm}^{-1}/\text{kbar}$ at $p = 35$ kbar.

The half-width of the emission band is nearly constant over the whole pressure range investigated. With increasing pressure between $p = 1$ bar and 60 kbar the emission intensity decreases by a factor of ≈ 2 .

4. Discussion

The observed pressure effects can be explained by the electronic properties of the binuclear center of the dimeric unit. The single complex has cis-configuration. Each of the platinum ions is surrounded by two carbon and two nitrogen atoms. Since the two complexes of a dimer are related to each other by an inversion center, the symmetry of the dimer can be described by the point group C_{2h} (double group C'_{2h}).

For each single complex the HOMO is composed mainly of a metal 5d-orbital. Which 5d-orbital acts as HOMO, cannot be stated clearly, since the energy order of the orbitals $d_{x^2-y^2}$, d_{xz} , d_{yz} , and d_{z^2} is not known definitely [7–16]. (The z axis is oriented perpendicularly to the plane of the complex. The x axis and the y axis bisect the angles N–Pt–C and N–Pt–N, respectively.) The LUMO has uneven parity and is a mixture of the π^* orbital of the ligand system and the metal $6p_z$ orbital, see the left-hand side of Figure 3.

On forming the dimer (symmetry C_{2h}), the MO's of the single complexes will interact. Since each of the pairs of complex orbitals d_{z^2} , d_{yz} , $d_{x^2-y^2}$ gives rise to dimer orbitals of symmetry a_g (bonding) and b_u (anti-bonding), the HOMO of the dimer has symmetry b_u and is a superposition of d_{z^2} -, d_{yz} -, and $d_{x^2-y^2}$ -components. The LUMO's of the two single complexes yield the dimer orbital set $2a_g$ and $2b_u$. These orbitals can interact with the lower lying dimer orbitals of corresponding symmetry. Thus, the HOMO $1b_u$ and the LUMO $2a_g$ of the dimer are stabilized and destabilized, respectively, see the middle part of Figure 3.

The splitting widths of both sets and, therefore, the energy gap Δ between the states $1b_u$ and $2a_g$ depend on the intra-dimer Pt–Pt distance R . By reduction of this distance the inter-complex overlap of the involved

orbitals will increase, and as a result the energy gap Δ will be lowered, see the right-hand side of Figure 3.

In the electronic ground state of the dimer the orbitals $1b_u$ are fully occupied, yielding a 1A_g ground state term. From the first excited electron configuration $(1b_u)^1(2a_g)^1$ the terms 1B_u and 3B_u result. The low energy emission corresponds to the transition $^1A_g \leftarrow ^3B_u$. A detailed analysis of the emitting states with 3B_u parentage is given in [4]. (In [4] the symmetry of the dimer is approximated by D_{4h} , thus $^3B_u(C_{2h})$ corresponds to $^3A_{2u}(D_{4h})$).

The pressure dependence of the emission may be understood in terms of these properties. With increasing pressure from $p = 1$ bar to 10 kbar the intra-dimer Pt–Pt distance decreases. As a result the energy gap $2a_g - 1b_u$ and, thus, the energy difference $^3B_u - ^1A_g$ become smaller, and a pressure induced red shift of the emission ensues.

Between $p = 10$ kbar and 20 kbar the emission energy does not vary, indicating that the intra-dimer Pt–Pt distance remains constant. For several crystalline tetracyanoplatinates(II) which show similar plateaus in their $\bar{\nu}(p)$ graphs, structural transformations have been established in the corresponding pressure region [2, 3, 17]. It is likely that between $p = 10$ kbar and 20 kbar also in the CBPPP crystal a structural transformation takes place, consisting possibly in a rearrangement of the whole dimers and/or in a deformation of the outer parts of the ligand system, but without a change of the intra-dimer Pt–Pt distance.

At $p = 20$ kbar this structural transformation is completed and a pressure increase yields a further shortening of the intra-dimer Pt–Pt distance, accompanied by a further red shift of the emission. At very high pressures ($p > 35$ kbar) this effect becomes smaller, most likely because of the decrease of the dimer compressibility.

The slope $\Delta\bar{\nu}/\Delta p$ for CBPPP is one order of magnitude smaller than the corresponding slopes found for crystalline tetracyanoplatinate(II) of comparable intra-columnar Pt–Pt distance [2]. This large difference can be traced back to at least two factors. First, following

Hückel's MO theory the resonance splitting for a linear chain has the maximum value $4|\beta|$, whereas the splitting for a dimer amounts to $2|\beta|$. Thus, the energy gaps for a linear chain and for a dimer are $\Delta_{ch} = \delta_{ch} - 2(\beta_d + \beta_p)$ and $\Delta_{di} = \delta_{di} - (\beta_d + \beta_p)$, respectively, with δ the energy gap of the corresponding monomer. β_d and β_p designate the absolute values of the resonance integrals for the $5d$ and the π^* , $6p_z$ wavefunctions, respectively. A pressure induced reduction of the inter-complex distance R yields an increase of the resonance integrals, $\Delta\beta_d$ and $\Delta\beta_p$. Therefore the corresponding change of the gap for the dimer is only half that for the linear chain, $(\Delta' - \Delta)_{di} \approx \frac{1}{2}(\Delta' - \Delta)_{ch}$. Second, this effect will be strengthened, if the HOMO of CBPPP contains a distinct admixture of d_{yz} and $d_{x^2-y^2}$. Since the valence band of crystalline tetracyanoplatinate(II) has mainly d_{z^2} character [2], it follows that $(\Delta\beta_d)_{di} < (\Delta\beta_d)_{ch}$ and, finally, $(\Delta' - \Delta)_{di} < \frac{1}{2}(\Delta' - \Delta)_{ch}$, which explains that the pressure induced red shift of the CBPPP emission is much smaller than that of the tetracyanoplatinates(II).

Perhaps these two factors cannot explain completely the total difference between the pressure induced red shifts of CBPPP and of systems with chain structure like tetracyanoplatinate(II). Therefore, as an additional factor the possibility should be considered that the pressure dependence of the Pt–Pt distance R in the dimeric unit of CBPPP is smaller than in the chains of tetracyanoplatinate(II), $|dR/dp|_{di} < |dR/dp|_{ch}$, in that CBPPP has a lower compressibility than tetracyanoplatinate(II) and/or in that the intra-dimeric force constant of CBPPP is stronger than the inter-dimeric one. A definitive answer on that point is expected from measurements of the corresponding structure parameters at high pressures.

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