Transition energy tuning from 3.3 to 1.4 eV in the system $M_x[Pt(CN)_4] \cdot mH_2O$

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(Received 16 June 1978)

The electronic transition energies of the $M_x[Pt^{2+}(CN)_4] \cdot mH_2O$ compounds, crystallizing in columnar structures, depend strongly on the Pt-Pt distance R in the direction of the columns. R can be varied by substituting M and/or by application of high pressure. Using three different compounds {$Na_2[Pt(CN)_4] \cdot 3H_2O$, $Ca[Pt(CN)_4] \cdot 5H_2O$, $Mg[Pt(CN)_4] \cdot 7H_2O$} and applying hydrostatic pressures up to 38 kbar it is possible to adjust the emission energy continuously from 3.3 to about 1.35 eV. The pressure-induced energy shift is unusually large with values between -320 and $-140 cm^{-1}$/kbar.

Square planar $[Pt(CN)_4]^{2-}$ complexes have the tendency to crystallize in linear stacks with relatively short Pt-Pt distances R in the direction of the columns.[1] Single crystals of $M_x[Pt(CN)_4] \cdot mH_2O$ are available with R values between 3.67 and 3.15 Å depending on the type of the cation M (e.g., Na, Ca, Ba, Mg, ...) and the content of crystal water which somewhat isolate the different columns from each other. As a consequence of the structure these nonconducting compounds have very anisotropic electronic properties which have been investigated by different methods of polarized spectroscopy as absorption, reflectivity, and luminescence measurements.[2,3] Main emphasis has been given to the luminescence properties since all the tetracyanoplatinates (II) emit light with a relatively high quantum efficiency. This emission is highly polarized and thus reflects the anisotropy of the compounds.[2-6]

The transition energies $\bar{\nu}$ depend strongly on the in-chain Pt-Pt distance R and can be correlated to a simple empirical R^{-n} power law (with $n = 3.0 \pm 0.4$).[3,4,7] A substitution of the cations leads to different R values and conseqently it is possible to "adjust" the transition energies in a range of about 3.3 to 2.1 eV (emission peaks at 295 K). This adjustment, however, is a *discontinuous* one. Application of high pressure as an additional method permits to reduce R to intermediate values and thus to shift the transition energies *continuously*.[5,6] Therefore it is expected that a combined method of high pressure application and substitution of cations allows to "tune" the transition energies from the near uv to the ir.

For the high-pressure investigations we used a modified sapphire cell of Bridgeman's opposed anvil type which allows measurements under hydrostatic conditions with polarized light. The pressure was determined by the R line shift of ruby pieces placed around the sample. The spectrophotometer and the high-pressure cell are described in Ref. 5. It is important to fit the excitation wavelength and polarization to the highly allowed transition of the tetracyanoplatinates. This has been achieved using a tunable dye laser.

Figure 1 reproduces the results of a series of measurements at 295 K. The emission peak energies $\bar{\nu}$ are given for three individual tetracyanoplatinates versus pressure p. The polarization of the electric field vector $\vec{E}$ is either parallel or perpendicular to the chain axis (c axis). The compounds NaCP and MgCP were chosen since they represent, to our knowledge, those single crystals of the tetracyanoplatinates (II) with the largest and the shortest in-chain metal-metal distances, respectively. The CaCP R-value lies in between. The different diagrams of the figure have separate pressure scales which are adjusted along the abscissa in a way that the $\bar{\nu}$ plots are connected continually. At 38 kbar the peak energy ($\vec{E} \perp \vec{c}$) of NaCP equals the CaCP value recorded under ambient conditions. (It was not possible to measure the NaCP emission peak energy with $\vec{E} \parallel \vec{c}$ between 25 and 38 kbar.) The CaCP energies ($\vec{E} \parallel \vec{c}$ and $\vec{E} \perp \vec{c}$) at 30 kbar are the same as those of MgCP at 1 atm.

The high-pressure tuning of the transition energies is compared to the discontinuous effect obtained just by cation substitution, inserting the emission peak
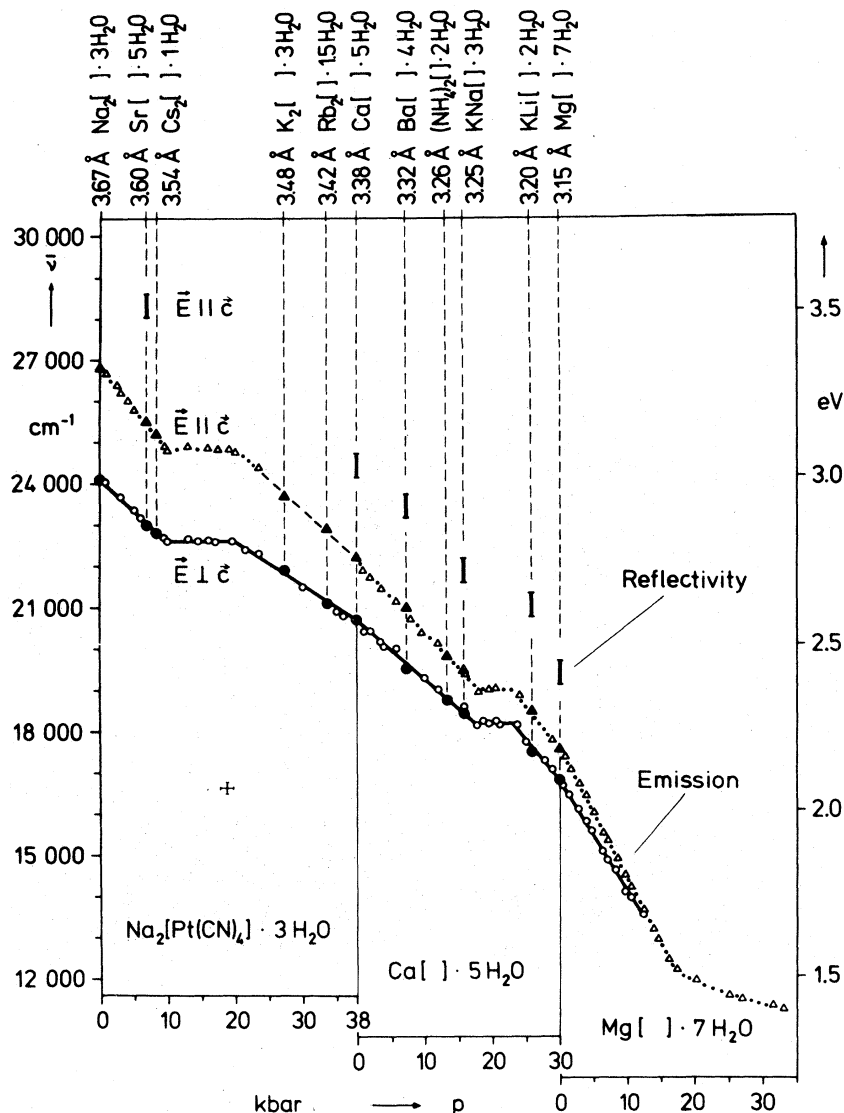
FIG. 1. Peak energies of the polarized emission for single-crystal $Na_2[Pt(CN)_4] \cdot 3H_2O$ (NaCP), $Ca[Pt(CN)_4] \cdot 5H_2O$ (CaCP), and $Mg[Pt(CN)_4] \cdot 7H_2O$ (MgCP) at 295 K vs. pressure. Emission and reflectivity peak energies of various other tetracyanoplatinates(II) with different in-chain Pt-Pt distances are also inserted (emission: $\vec{E} \parallel \vec{c}$ ▲; $\vec{E} \perp \vec{c}$ ●, reflectivity: $\vec{E} \parallel \vec{c}$ I). The experimental uncertainty is represented by the cross in the left-hand side diagram. (It is mentioned that for platinum dimethylglyoxime a comparable red shift has been found.[13])

energies ($\vec{E} \parallel \vec{c}$, $\vec{E} \perp \vec{c}$) and reflectivity maximum energies ($\vec{E} \parallel \vec{c}$)[2,3] of a series of other tetracyanoplatinates (at $p = 1$ atm) into the diagram. These energies fit well into the plots. The in-chain Pt-Pt distances are given on the upper scale.

The results show that the red shift of the transition energies with high-pressure application is equivalent to the red shift found by cation substitution. This allows the conclusion that mainly the in-chain Pt-Pt distance determines the transition energies while the surroundings of the $[Pt(CN)_4]^{2-}$ stacks are of minor importance.

The transitions, polarized with $\vec{E} \parallel \vec{c}$ are identified with strongly allowed interband transitions (reflectivity between 50% and 80%). A two-band model calculation gives quantitatively the transition energies, taking into account only in-chain interactions between hybrid molecular orbitals (Pt $5d_{z^2}, 6s$) and between modified excited (Pt $6p_z$) oribtals. The red shift induced by a reduction of R is explained by an increase of the band splittings which leads to a decrease of the gap energy. The selection rules are also displayed correctly in terms of a modified factor group analysis.[3,4]

TABLE I. Pressure-dependent energy shift $\Delta\bar{\nu}/\Delta p$ (1 atm) and emission-peak energies for various tetracyanoplatinates(II) at 1 atm and 20 kbar[a] (at 295 K).

Compound	$\bar{\nu}_{max}$ (1 atm) (cm^{-1})		$\bar{\nu}_{max}$ (20 kbar) (cm^{-1})		$(\Delta\bar{\nu}/\Delta p)p = 1$ atm (cm^{-1}/kbar)		Linear compressibility at $p = 1$ atm
	$\bar{E}\parallel\bar{c}$	$\bar{E}\perp\bar{c}$	$\bar{E}\parallel\bar{c}$	$\bar{E}\perp\bar{c}$	$\bar{E}\parallel\bar{c}$	$\bar{E}\perp\bar{c}$	κ_c (10^{-3} kbar^{-1})
Na$_2$[Pt(CN)$_4$]·3H$_2$O $R = 3.67$ Å	26750	24100	24800	22600	−200	−155	4.1
Ca[Pt(CN)$_4$]·5H$_2$O $R = 3.38$ Å	22250	20700	19000	18200	−170	−140	2.7
Ba[Pt(CN)$_4$]·4H$_2$O $R = 3.32$ Å	21000	19500	17550	16800	−280	−195	4.3
Mg[Pt(CN)$_4$]·7H$_2$O $R = 3.15$ Å	17550	16800	11200	···	−320	−270	4.2
Experimental error	±50		±150		±10%		±20%

[a]1 kbar = 10^9 dyn/cm^2 = 986.9 atm = 1020 kp /cm^2.

The emission with $\bar{E}\perp\bar{c}$ originates from an excited state of comparatively small oscillator strength and relatively long emission lifetime.[2,3,8] It can be shown by symmetry considerations and single complex ion calculations (including spin-orbit coupling) that the corresponding excited state wave function contains admixtures of several one-electron configurations.[9] Thus, for these transitions a two-band model calculation does not seem to be adequate. The smaller red shift of the transition with $\bar{E}\perp\bar{c}$ compared to that with $\bar{E}\parallel\bar{c}$ might be explained as consequence of different excited state charge structures. Further, the red shift of the $\bar{E}\perp\bar{c}$- emission peak energies with decreasing R is supposed to be modified by a lattice relaxation in the corresponding excited state.[3,8]

From the plot of Fig. 1 one can see that the NaCP and CaCP compounds show transformation regions where a pressure increase of about 10 and 6 kbar, respectively, does not shift the emission peak energies. The spectroscopic data do not allow a conclusive interpretation for this effect, however it seems to be a reasonable assumption that the in-chain Pt-Pt distances do not change appreciably in these regions (the emission peak energies would otherwise react very sensitively to such changes). It is likely that structural transformations occur, since before the onset of the transformation region a pressure induced reduction of the in-chain distance between adjacent complexes is as large as about 0.15 Å (Fig. 1). Consequently rearrangements of hydrogen bonds which link the nitrogens of the [Pt(CN)$_4$]$^{2-}$ complexes to the surroundings might result. The occurrence of structural transformations is corroborated by the observation that the crystals partly crack in these transformation regions, accompanied by a loss of the anisotropic emission properties.[6] The reduced red shift for MgCP above 20 kbar can be related to a decrease of the in-chain compressibility.[10]

Table I summarizes results of the high-pressure investigations. The linear compressibility data given in the Table result from $\Delta\bar{\nu}/\Delta p$ data by application of the empirical R^{-3} power law.[6] The MgCP compressibility thus determined is in good agreement with the value determined from the data given in Ref. 10.

The correlation between cation substitution and high-pressure application demonstrated by Fig. 1 does not exist for the emission quantum yield which decreases substantially with pressure increase, but there is no perceivable trend with cation substitution. Probably high pressure enhances the coupling between the electronic structure of the [Pt(CN)$_4$]$^{2-}$ columns and the three-dimensional phonon structure. This causes an increasing radiationless relaxation from the excited column states to the ground state.[11]

The adjustability of the electronic interband transition energies of the tetracyanoplatinates(II) over about 2 eV (≈ 16000 cm^{-1}) imparts to this class of compounds some interesting aspects. For example, it has been shown that energy is transferred by a radiationless process from the [Pt(CN)$_4$]$^{2-}$ columns (donors) to rare-earth cations (acceptors) which can be incorporated into the crystal structure.[12] These processes are strongly dependent upon the energetic positions of the relevant electronic states. The possibility of tuning the donor states relative to those of the acceptors supplies additional information about the energy-transfer process.

ACKNOWLEDGMENT

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