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ON THE LUMINESCENCE LIFETIMES AND THEIR PRESSURE EFFECT OF SOME ONE-DIMENSIONAL Pt-COMPLEXES

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The luminescence lifetimes in $K_2Pt(CN)_4.3H_2O$, $BaPt(CN)_4.4H_2O$ and $MgPt(CN)_4.7H_2O$ were measured at 1 atom. and higher hydrostatic pressures up to 7.2 kbar at room temperature. Two longer components lengthen anomalously by a factor of $\sim$ 30 with a decrease in the Pt-Pt distance from 3.50 to 3.16 Å.

A lot of studies on optical, electrical, magnetic, Mössbauer and X-ray diffraction have been done for one-dimensional Pt-complexes. In previous papers,[1),2)] the author and co-workers found that the luminescence intensity of the visible luminescence band ($6pz \rightarrow 5dz^2$) in $MgPt(CN)_4.7H_2O$(MgCP), $BaPt(CN)_4.4H_2O$(BaCP) and $K_2Pt(CN)_4.3H_2O$(K_2CP) anomalously decreased with a decrease in the Pt-Pt distance, suggesting a considerable contribution of the intermolecular $6pz \rightarrow 5dz^2$ transition to the intramolecular one. Murata and Morita[3)] also observed that at 4K the visible luminescence band of above complexes shifted to red and decreased in intensity by the change of excitation energy. Therefore the lifetime measurement will be helpful to know the nature of such a phenomenon.

In this paper, the lifetime and the time-resolved spectra in MgCP, BaCP and K_2CP will be presented.

The Pt-complexes were prepared as described in the literature.[4)]

With pulsed molecular nitrogen laser, the luminescence is detected through appropriate filters and lenses by a 1P28 photomultiplier, displayed on a oscilloscope, and subsequently photographed. The pressures are generated by an intensifier with white gasoline medium up to 7.2 kbar.

In Table 1, the lifetimes observed are listed. Two longer components in each

Table 1.

The lifetimes observed

Material	Lifetime (μsec)	Pt-Pt distance (Å)
$MgPt(CN)_4 \cdot 7H_2O$ (MgCP)	61.1 13.6 0.50	3.16[5]
$BaPt(CN)_4 \cdot 4H_2O$ (BaCP)	3.11 0.70 0.20	3.32[5]
$K_2Pt(CN)_4 \cdot 3H_2O$ (K_2CP)	1.98 0.59 0.20	3.50[6]

Table 2.

The lifetime of the longest component and the total relative intensity in $BaPt(CN)_4 \cdot 4H_2O$ at various hydrostatic pressures

Pressure (KBAR)	0	1.8	3.6	7.2
τ (μsec)	3.11	13.4	17.1	29.6
Total Relative Intensity	1	0.83	0.66	0.29

complex are seen to be significantly influenced by the Pt-Pt distance. This significant increase in delocalization of a electron in the excited state suggests the considerable contribution of the intermolecular $6pz \rightarrow 5dz^2$ transition to the ground state.

In Table 2, the lifetime of the longest component in BaCP is shown as a function of pressure. It lengthens greatly with pressure. This trend is also found for MgCP and K_2CP. It is seen from Table 2 that the longest components in each complex are due to the same origin. The total relative intensity at 2.7, 4.5 and 5.4 kbar is 0.72, 0.56 and 0.48, respectively. Then it seems to change

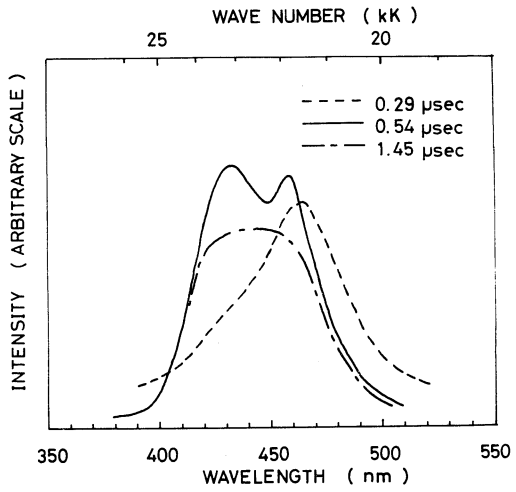

Figure 1.

The time-resolved spectra of polycrystalline $K_2Pt(CN)_4 \cdot 3H_2O$.

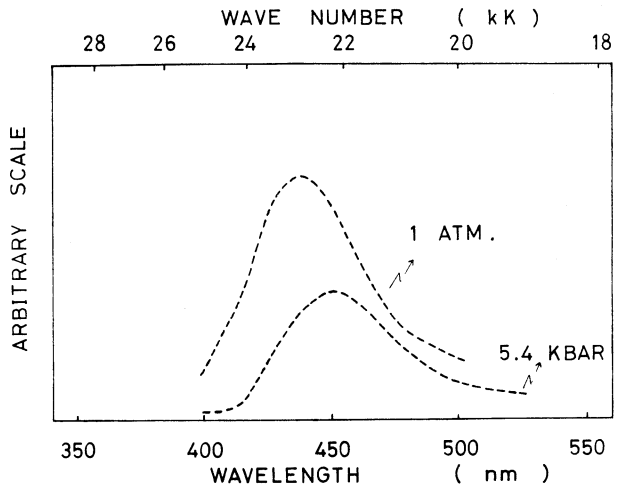

Figure 2.

The pressure effect on the luminescence spectra of polycrystalline $K_2Pt(CN)_4 \cdot 3H_2O$.

linearly with pressure.

Figure 1 exhibits the time-resolved spectra of K_2CP. It exhibits triple appearance, and similar ones are also found for MgCP and BaCP. The results are in good agreement with that measured by Moucuit and Poulet.[7] The triple bands observed have been attributed to the vibronical transitions due to intramolecular

$6pz \rightarrow 5dz^2$ one; two A_{2u}'s and a Eu.[3),7)] With the significant dependensy on the Pt-Pt distance into account, it is reasonable to assume that the longer two components correspond to A_{2u} states (parallel to the Pt-Pt bonding derection), and the rest to an Eu one (perpendicular to it).

Figure 2 exhibits the decrease in luminescence intensity of K_2CP with an increase in pressure. A similar result is obtained for MgCP and BaCP. The result is reversible and reproducible.

The quantum yield η is simply given by

$$\eta = \frac{1}{1 + \tau_r/\tau_n}$$

Here, τ_n and τ_r express the lifetime due to a nonradiative transition and to a radiative one. It should be noted that η decreases with a value of τ_r/τ_n. Then, the intensity decrease is closely related to a great increase in radiative lifetime.

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