# Pressure Effect on the Optical Spectra of Some One-Dimensional Pt-Complexes

Yoji HARA, Ichimin SHIROTANI, Yukako OHASHI, Katsuyuki ASAUMI, and Shigeru MINOMURA

*The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106*

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The absorption and luminescence spectra of the polycrystalline magnesium, barium, and potassium salts of tetracyano platinate (II) were measured at hydrostatic pressures up to 5.4 kbar. These three salts showed an anomalously large red shift with pressure in both the absorption and luminescence spectra. The X-ray powder diffraction measurement was carried out for the magnesium salt up to 70 kbar. At 70 kbar the Pt–Pt distance decreased from 3.16 Å to 2.93 Å, 7.3% in linear compressibility. In the low pressure region up to ~20 kbar, the Pt–Pt distance was observed to decrease greatly. The intramolecular transition 5dz$^2$→6pz energy was calculated as a function of the Pt–Pt distance. By comparing the calculated and observed values, such a large red shift in the absorption spectra was tentatively explained in terms of electrostatic stabilization of the intramolecular transition 5dz$^2$→6pz due to the decrease of the intermolecular distance and due to the consequent increase of the 5dz$^2$→6pz intermolecular CT character.

In a previous paper,[1] we partly reported the optical behavior of quasi-one-dimensional solids under high pressure, such as potassium tetracyano platinate (II); $K_2Pt(CN)_4 \cdot 3H_2O$, magnesium tetracyano platinate (II); $MgPt(CN)_4 \cdot 7H_2O$, barium tetracyano platinate (II); $BaPt(CN)_4 \cdot 4H_2O$. When pressure was applied up to 5.4 kbar, the Mg-salt showed the largest red shift of the absorption peak that we had ever known, including organic compounds.

The optical properties of square planar complexes of platinum (II), which are composed of quasi-one-dimensional Pt-chains, at high pressures have long been a subject of interest. Through X-ray diffraction studies,[2] it has been shown that $MgPt(CN)_4 \cdot 7H_2O$, $BaPt(CN)_4 \cdot 4H_2O$, and many of their related compounds have the one-dimensional columnar stacking structure of $Pt(CN)_4{}^{2-}$.

Interrante and Bundy have investigated the X-ray diffraction patterns for $K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$,[3a] $Pt(NH_3)_4 \cdot PtCl_4$ (Magnus' green salt, MGS) and $Ir(CO)_2(acac)$[3b] at high pressures and found that the lattice constant and the metal-metal distance in d$^8$ metal complexes decrease with increasing pressure.

Yamada studied the polarized absorption spectra of $K_2Pt(CN)_4 \cdot 3H_2O$, $MgPt(CN)_4 \cdot 7H_2O$, $BaPt(CN)_4 \cdot 4H_2O$, and related compounds and found the existence of weak bonding between adjacent Pt ions.[4] Polarization spectral measurements for the Mg-, Ca-, Sr-, and Ba-salts led Moncuit and Poulet to assign the absorption band in the visible region to the intramolecular transition 5dz$^2$→6pz, polarized along the Pt-chain (c axis).[5]

Krogmann assigned the band to the transition from the 5zd$^2$ band to the 6pz band formed by adjacent Pt ions.[6] Zahner *et al.*[7] considered the visible absorption band in nickel dimethylglyoxime ($Ni(DMG)_2$) and its related compounds to be the intramolecular transition 3dz$^2$→4pz. They also suggested that the electrostatic interaction between the adjacent metal ions was responsible for the red shift which they had observed for such compounds.

Ohashi *et al.* quantitatively explained the polarized spectra of $Ni(DMG)_2$ and its related compounds.[8]

In this paper, the optical properties of the tetracyano platinate (II) solids at high pressures will be shown. The Pt–Pt distance of the Mg-salt as a function of pressure was investigated by the X-ray diffraction study, and the result will also be shown. A calculation was tried to know the nature of the large red shift with pressure, since neither a qualitative nor semi-quantitative investigation has been carried out for the $MPt(CN)_4 \cdot nH_2O$ type solids. We show the results of the calculation for the absorption energy (5dz$^2$→6pz in the central Pt ion) as a function of Pt–Pt distance. These results will be compared with the experimental one.

## Experimental

*X-Ray Measurement.* For high pressure X-ray powder diffraction studies, the Bridgman type apparatus with moving tungsten carbide anvils was used, where pressure was cramped. The samples were put in a hole of 0.3 mm diameter in the center of a boron disk of 3 mm diameter and 0.3 mm thickness. The radiation used was Mo*Kα* with 0.7107 Å wavelength. A Zr filter was used. Camera diameter was 75.74 mm. The pressure was determined from measurements of the (200), (220), (222), (400), (420), and (422) reflections caused by the NaCl, using the pressure *vs.* compression values calculated by Decker.[9] As the Mg-salt was reactive with NaCl, it was measured solely without mixing with NaCl. It follows that no absolute determination of pressure values could be obtained.

The Mg-salt has the tetragonal structure.[10] The lattice constants "c" and "a" at each pressure were determined from measurements of the (022) and (232) reflections.

*Spectral Measurement.* The absorption spectra were measured as a function of pressure. The pressure was generated by an intensifier using white gasoline medium up to 5.4 kbar. The absorption and emission spectra were measured with nujol mulls and in the polycrystalline state held tightly between glasses, respectively. The optical measurements were performed with a Shimadzu double beam spectrophotometer.

*Preparation of Samples.* The K-, Mg-, and Ba-salts[11] were prepared as described in the literature. Attention was paid to the preservation of the Mg-salt so as to keep it in an atmosphere with a high vapor pressure of water.

## Results and Discussion

*Absorption and Luminescence Spectra.* *$MgPt(CN)_4 \cdot 7H_2O$*: The Mg-salt is composed of one-dimensional Pt-chains with tetragonal crystal structure and has a

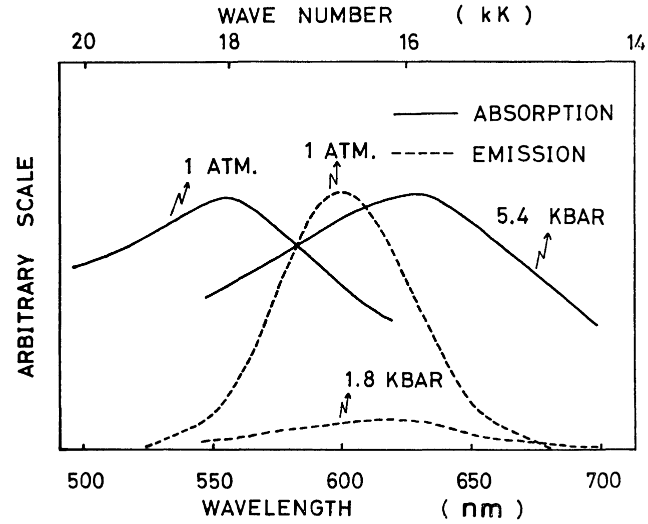

Fig. 1. Pressure effect on the absorption and luminescence spectra of polycrystalline $MgPt(CN)_4 \cdot 7H_2O$.

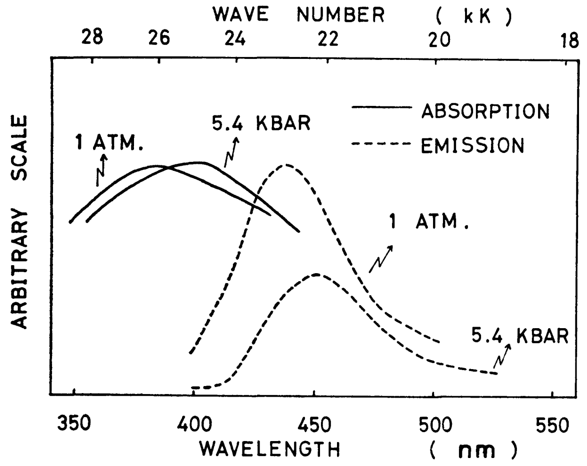

Fig. 2. Pressure effect on the absorption and luminescence spectra of polycrystalline $K_2Pt(CN)_4 \cdot 3H_2O$.

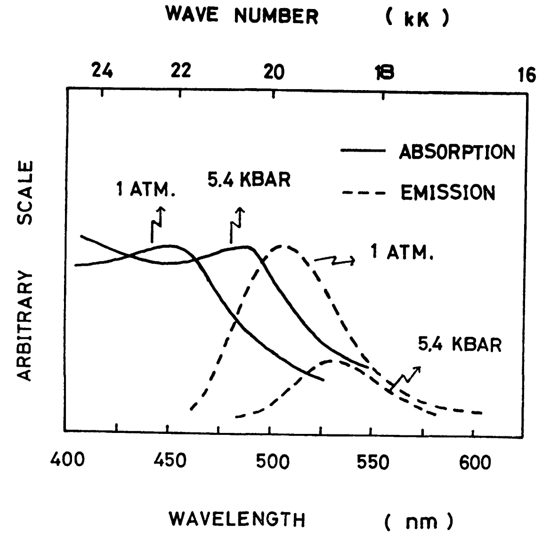

Fig. 3. Pressure effect on the absorption and luminescence spectra of polycrystalline $BaPt(CN)_4 \cdot 4H_2O$.

crimson color. The Pt–Pt distance was reported to be 3.16 Å.[2a] The effect of pressure on the absorption and on the luminescence spectra of the polycrystalline Mg-salt is shown in Fig. 1. The absorption peak of 555 nm (18.0 kK) showed an anomalously large red shift up to 629 nm (15.9 kK) at 5.4 kbar with increasing pressure, in a rate of $-389$ cm$^{-1}$/kbar.

The emission band of 600 nm (16.7 kK) at atmospheric pressure shifted to 620 nm (16.1 kK) at 1.8 kbar, in a rate of $-320$ cm$^{-1}$/kbar. The red shift observed both in the absorption and in the luminescence spectra was the largest so far detected by the present authors. The emission intensity decreased sharply with increasing pressure and was almost completely extinguished at pressures over 5 kbar.

*$K_2Pt(CN)_4 \cdot 3H_2O$*: In Fig. 2 the pressure effect on the absorption and luminescence spectra of the polycrystalline K-salt is displayed. The absorption peak of 382 nm (26.2 kK) showed a large red shift up to 402.5 nm (24.85 kK) at 5.4 kbar with increasing pressure, in a rate of $-250$ cm$^{-1}$/kbar.

The emission band of 437.5 nm (22.9 kK) at atmoshperic pressure shifted to 450 nm (22.2 kK) at 5.4 kbar, in a rate of $-130$ cm$^{-1}$/kbar.

*$BaPt(CN)_4 \cdot 4H_2O$*: The Ba-salt has the monoclinic crystal structure and a yellow-green color.[2b] The Pt–Pt distance is predicted to be 3.32 Å. Figure 3 shows the pressure effect on the absorption and luminescence spectra of the polycrystalline Ba-salt. The absorption peak of 450 nm (22.2 kK) showed a large red shift up to 488 nm (20.5 kK) at 5.4 kbar with increasing pressure, in a rate of $-315$ cm$^{-1}$/kbar. The emission band of 505 nm (19.8 kK) at atmospheric pressure shifted to 530 nm (18.9 kK) at 5.4 kbar, in a rate of $-167$ cm$^{-1}$/kbar. These results are summarized with those for the Mg- and K-salts in Table 1.

Table 1. Absorption and emission maxima in the visible region, red shift, and Pt–Pt distance

| Material | Absorption maximum nm (kK) | Red shift (cm$^{-1}$/kbar) | Emission maximum nm (kK) | Red shift (cm$^{-1}$/kbar) | Pt–Pt distance (Å) |
|---|---|---|---|---|---|
| $K_2Pt(CN)_4 \cdot 3H_2O$ | 382<br>(26.2) | −250 | 437.5<br>(22.9) | −130 | >3.35[a] |
| $BaPt(CN)_4 \cdot 4H_2O$ | 450<br>(22.2) | −315 | 505<br>(19.8) | −167 | 3.32[b] |
| $MgPt(CN)_4 \cdot 7H_2O$ | 555<br>(18.0) | −389 | 600<br>(16.7) | −320 | 3.16[b] |

a) S. Yamada, *Kagaku*, **41**, 651 (1971). b) Ref. 6.

The fact that the ratio of the quantum yield at each pressure to that of 1 atmosphere increased in the order K>Ba≫Mg might be explained in terms of the difference of the mixing of the intermolecular charge transfer $5dz^2 \rightarrow 6pz$ into both excited and ground state,[4] which will be discussed in more detail in a later part of the paper.

Moncuit *et al.* tentatively assigned the emission band to vibronically induced d–d transitions.[5] However, it is doubtful that such d–d transition may show such large red shift with pressure. It might be possible to assign it to the allowed $6pz\ (a_{2u}) \rightarrow 5dz^2(a_{1g})$ intramolecular transition.

*X-Ray Diffraction.* $MgPt(CN)_4 \cdot 7H_2O$ has a tetragonal unit cell with the metal chain axis aligned along the "c" unit cell direction with the "a" perpendicular to it. The lattice constants for the "c" and "a" unit cell dimensions are 6.32 and 14.54 Å, respectively.[2a] Figure 4 illustrates the pressure effect on the X-ray powder diffraction of the Mg-salt up to 70 kbar. Both the "c" and "a" unit cell dimensions decrease continuously over the pressure range. In the low pressure region up to ~20 kbar, the Pt–Pt distance, which is the half of the "c" unit cell dimension, was observed to decrease greatly. At 20 and 70 kbar the Pt–Pt distance decreased by 4.7% (3.01 Å) and 7.3% (2.93 Å) in linear compressibility, respectively. At 70 kbar the "a" unit cell dimension decreased to 14.11 Å, 2.9% in linear compressibility. These results are compared with those given by Interrante *et al.* in Table 2.

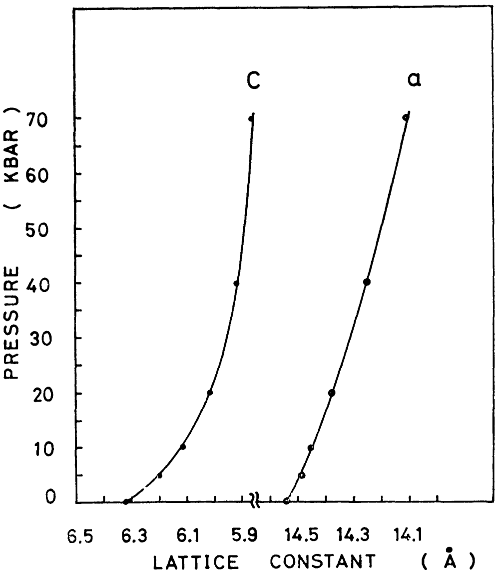

Fig. 4. Change in the "c" and "a" unit cell dimensions of $MgPt(CN)_4 \cdot 7H_2O$ with pressure.

Table 2. Comparison of the Pt–Pt distance of some one-dimensional Pt-complexes at 1 atm. and 70 kbar

| Compound | Pt–Pt | Overall change in "a" dimension (Å)[d] |
|---|---|---|
| $MgPt(CN)_4 \cdot 7H_2O$ | 3.16<br>2.93[d] (7.3)[e] | 0.43 |
| $Pt(NH_3)_4 \cdot PtCl_4$[a] (MGS) | 3.25<br>3.00 (7.7)[e] | ~0.47 |
| $Ir(CO)_2 \cdot (acac)$[a] | 3.23<br>2.89 (10.5)[e] | |
| $K_2Pt(CN)_4 \cdot Br_{0.3} \cdot 2.3H_2O$[b] | 2.89<br>2.78 (3.8)[f] | ~0.47 |

a) Ref. 3b. b) Ref. 3a. c) Data at 1 atm. d) Data at 70 kbar. e) Linear compressibility at 70 kbar. f) Linear compressibility at 50 kbar.

As is seen from Table 2, firstly the linear compressibility along the c axis at 70 kbar increases in the order, $Ir(CO)_2 \cdot (acac) > Pt(NH_3)_4 \cdot PtCl_4 \simeq MgPt(CN)_4 7H_2O > K_2Pt(CN)_4 \cdot Br_{0.3} \cdot 2.3H_2O$. Here, the charges on each metal are Ir(+1), Pt(+2) in the Mg-salt and MGS, and Pt(+2.3) in $K_2Pt(CN)_4 \cdot Br_{0.3} \cdot 2.3H_2O$. The Coulombic repulsion due to the plus charges on the central metal ion presumably reflects the relative tendency for the extent of the linear compressibility along the "c" axis. Secondly, the overall change in the "a" dimension up to 70 kbar seems to be independent of the kinds of ligands.

*Calculation.* Ohashi *et al.* calculated the intramolecular transition $(3dz^2 \rightarrow 4pz)$ energy of $Ni(DMG)_2$.[8] Here, we apply again the same method to the calculation of intramolecular transition($5dz^2$—$6pz$) energy of solid platinocyanide complexes and compare the calculated value with the observed one.

It was assumed,

(i) minus charge is located on the carbon atom and (ii) the Pt–C distance in the coordination plane was unchanged under pressure. The Pt–C distance was taken to be 2.06 Å, the same value as that of $K_2Pt(CN)_4 \cdot Br_{0.3} \cdot 2.3H_2O$.

We consider only the electrostatic effect on the 6pz and $5dz^2$ orbitals of the $Pt^+$ ion in the complex plane 1, due to $Pt^+$ ion in 2 and 3, and due to −3/4 charged CN ion in 1, 2, and 3, as is shown in Fig. 5. But we are compelled to neglect, for example, the CT effect and the electrostatic influence of the surrounding alkaline or alkaline earths cation, due to the lack of the corresponding data.

For each of the wave function $\phi_{5d}$ and $\phi_{6p}$, the Slater-type AOs' were used. The orbital exponent values necessary for the calculation were taken as $\xi_{5d}=3.8815$, given by Clementi *et al.*,[12] and $\xi_{6p}=1.9820$, extrapolated from the data of the former authors.

We introduced next equation, the same as that given by Ohashi *et al.*,[8]

$$E_l = E_l^v + \Delta_0 + \Delta(R)$$

Here, we put $\Delta(R) = \Delta(R_1) + \Delta(R_2)$, $E_l$ is the energy necessary for the local excitation of intramolecular transition $5dz^2 \rightarrow 6pz$. $E_l^v$ is the energy necessary for the transition from the $(5dz^2)^2$ valence state to the $(5dz^2, 6pz)$ one. These quantities were obtained from the analysis of the observed atomic spectra.[13] $\Delta_0$ is an electrostatic energy difference between 6pz and $5dz^2$ orbitals due to the formal charges on the atoms of the ligands in the complex plane 1, as is shown in Fig. 5. $\Delta(R_1)$ is the electrostatic energy difference between 6pz and $5dz^2$ orbitals of the Pt atom in the complex plane 1, due to the negative charges on the

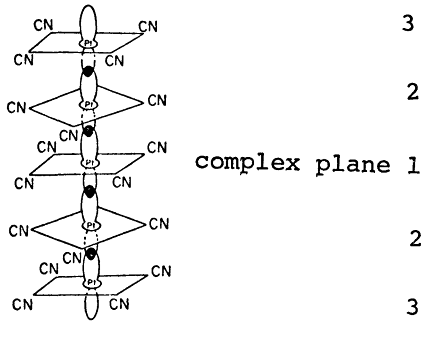

Fig. 5. The coordinate system used in the calculation on $[Pt(CN)_4{}^{2-}]_5$. Z axis is perpendicular to the complex plane. The complex plane numbers are also given.

Table 3. Intramolecular transition $5dz^2 \rightarrow 6pz$ energy calculation for (A) $Pt^+$ and (B) $Pt^0$

| Pt-Pt distance | $E_l$ case (A) (kK)[a] | case (A) (kK) $\Delta(R_1)$ | $\Delta(R_2)$ | $E_l$ case (B) (kK) |
|---|---|---|---|---|
| 3.50 | 26.04 | −11.12 | − 6.70 | |
| 3.32 | 23.64 | −12.40 | − 7.82 | |
| 3.16 | 21.18 | −13.68 | − 9.01 | 8.91 |
| 3.13 | 20.58 | −14.00 | − 9.28 | 8.69 |
| 3.09 | 19.90 | −14.40 | − 9.57 | 8.39 |
| 3.00 | 18.20 | −15.28 | −10.38 | 7.85 |
| 2.89 | 16.06 | −16.32 | −11.49 | 7.09 |

a) calculated values are recorded in kilokaysers.

ligand carbon atoms in the complex plane 2 and 3, and $\Delta(R_2)$ is the electrostatic energy difference between 6pz and $5dz^2$ orbitals of the Pt atom in the complex plane 1, due to the positive charges on the Pt atoms in the complex plane 2 and 3. Furthermore, the calculation was carried out for the case of (A) $Pt^+$ and (B) $Pt^0$. The results are summarized in Table 3.

As is indicated in Table 3, (i) case (A) reproduces the observed value well, (see the symbol X in Fig. 7), (ii) though $|\Delta(R_1)|$ is larger than $|\Delta(R_2)|$ for case (A), the contribution to the red shift is almost the same between them. In other words, the 6pz orbital is almost equally stabilized relative to the $5dz^2$ orbital by the −3/4 charged carbon and +1 charged Pt in the complex plane 2 and 3 with decreasing Pt–Pt distance.

Figure 6 illustrates the electrostatic energy of the 6pz and $5dz^2$ orbitals as a function of the Pt–Pt distance. Within the limit of the calculation, it is clear that the relative stabilization of the 6pz orbital to the $5dz^2$ one causes the red shift.

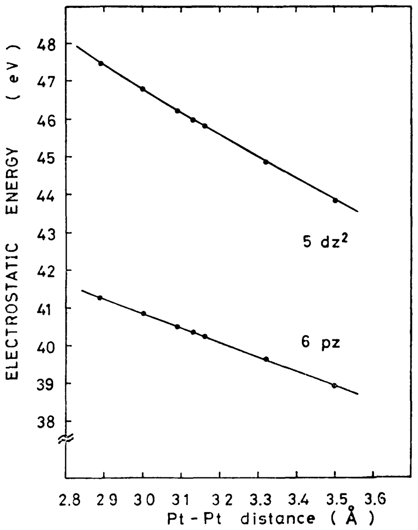

Fig. 6. The electrostatic energy dependence of the $5dz^2$ and 6pz orbitals of the central Pt ion on the Pt–Pt distance.

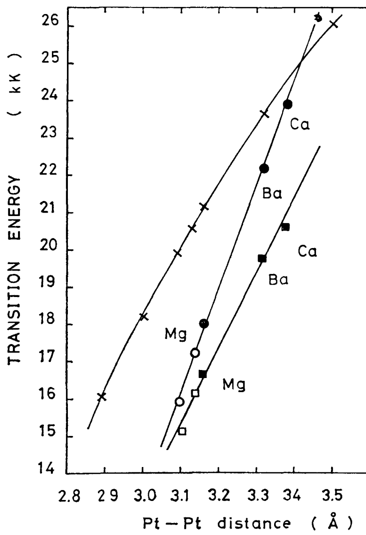

Fig. 7. The observed transition energy between $5dz^2$ and 6pz orbitals as a function of the Pt–Pt distance in various $Pt(CN)_4{}^{2-}$ derivatives:

Ca, $CaPt(CN)_4 \cdot 5H_2O$; Ba, $BaPt(CN)_4 \cdot 4H_2O$; Mg, $MgPt(CN)_4 \cdot 7H_2O$;

The symbols ●, ○ and ■, □ refer to data obtained from absorption and luminescence experiments respectively, where the symbols ○ and □ refer to the one obtained for the Mg-salt at high pressures. The Pt-Pt distance is 3.13 Å at 2.5 kbar, 3.1 Å at 5 kbar and $3.09_5$ Å at 5.4 kbar for the Mg-salt. The symbol X represents the calculated values of the intramolecular transition $5dz^2 \rightarrow 6pz$ energy for case (A) in Table 3.

These calculated values are compared with the observed values in Fig. 7. The results of spectral measurements on the Mg-salt at pressures up to 5.4 kbar evidence a direct relationship between the magnitude of these spectral shifts and the interionic distance in the solid. The calculated values will represent the observed values including the K-, Ca-, and Ba-salts. But when the Pt–Pt distance becomes less than that of the Ba-salt, 3.32 Å, the discrepancy between the calculated and observed values becomes larger. This discrepancy can be explained in terms of (i) the mixing effect of the $5dz^2 \rightarrow 6pz$ intermolecular charge transfer configuration between adjacent Pt ions into both of ground and excited state, (ii) the electrostatic effect of the surrounding alkaline or alkaline earths cations and (iii) the effect of a bond formation. According to our calculation, (ii) should decrease the intramolecular $5dz^2 \rightarrow 6pz$ energy by ~1.5 kK at most. Referring to the band calculation on MGS by Interrante *et al.*,[3c)] we tentatively evaluate (iii) to be $\sim$2 kK at 3.0 Å in the Pt–Pt distance. Ohashi *et al.*[8)] calculated the ground state stabilization energy due to (i) at 3.0 Å in the Ni–Ni distance of $Ni(DMG)_2$ to be $\sim$2 kK. At 3.0 Å the calculated value is more than the observed value by 4.7 kK. So on a rough estimation, the excited state stabilization energy at 3.0 Å of platinocyanide complexes should be $\sim$3.2 kK. Apart from this value, such mixing of CT character into the excited state should be closely related to the decrease of the emission intensity at high pressures (see the section for the Mg salt).

For the case of a single configuration coordinate Drickamer *et al.* obtained:[15)]

$$\frac{(h\nu_{1\mathrm{max}}-h\nu_{2\mathrm{max}})_{\mathrm{abs.}}}{(h\nu_{1\mathrm{max}}-h\nu_{2\mathrm{max}})_{\mathrm{emiss.}}}=\left(\frac{\omega'}{\omega}\right)^4$$

Here, the 1 and 2 refer to two different pressures. They assumed harmonic potential wells with different force constants $\omega$ and $\omega'$ for the ground state and excited state respectively.

In our study, the $\omega'/\omega$ values for the K-, Ba-salts at 5.4 kbar were found to be 1.178 and 1.172 respectively and 1.050 at 5.0 kbar for the Mg-salt. The smaller value for the Mg-salt is reasonable when one considers that the ground state mixes with the excited state through CT character much more in the Mg-salt than in the K- and Ba-salts. This is supported by the fact that the Mg-salt has a higher absorption intensity in the visible region than the other salts,[5)] which should be due to the larger transition moment between the $CT^-$ and $CT^+$ configuration than that between the ground and local excitation configurations for the intermolecular distance of $\sim$3 Å[8)].

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