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Triboluminescence, Photoluminescence, and High-Pressure Spectroscopy of Tetracyanoplatinate Salts. Determination of the Pressure at Triboluminescent Sites

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Triboluminescence spectra, photoluminescence spectra of single crystals and of powders at atmospheric pressure, and high-pressure photoluminescence spectra of crystals of the tetracyanoplatinate salts (MCP) $KLiCP\cdot 2H_2O$, $KNaCP\cdot 3H_2O$, $Cs_2Ca(CP)_2\cdot nH_2O$, and $Cs_2CP\cdot H_2O$ are obtained. These compounds exhibit large pressure-dependent shifts of their luminescence maxima under hydrostatic high-pressure conditions (up to 320 cm^{-1}/kbar) and are thus sensitive probes of the pressure at crystal sites giving rise to triboluminescence. The pressure-dependent shifts are measured. The positions of the peak maxima and the bandwidths at half-height of the triboluminescence and photoluminescence spectra are measured. The positions of the peak maxima in the triboluminescence experiments are the same within experimental error as those in the 1-atm photoluminescence experiments. The pressure of the emitting site during triboluminescence is 1 atm. Similarly, the temperature dependences of the peak maxima are used to show that the temperature at the emitting site is the same as that of the bulk crystal. The triboluminescence takes place at sites where the stress is relaxed and not at the tips of cracks under high-pressure conditions. The mechanistic implications of the pressure results and the correlation of triboluminescence activity with polar space groups are discussed.

Introduction

Triboluminescence (TL), the emission of light caused by the application of mechanical stress on solids, is known for a number of metal complexes and salts. The main focus of past research has been the spectroscopic identification of the emitting excited states responsible for TL, the fracture mechanics giving rise to TL, and the structural properties required for TL activity.[1,2]

The detailed mechanism by which TL is excited by mechanical energy is less clearly understood, but several aspects of the excitation mechanism can be deduced from the spectroscopic, structural, and mechanical studies. TL is associated with polar space groups of molecular crystals and generally originates from excited states of molecules comprising the crystals and/or of molecular nitrogen from the surrounding atmosphere. Crystal fracture is required for TL activity in molecular crystals, and the rise and decay of the TL intensity is directly related to the creation and annihilation of mobile cracks.[3] These observations suggest that electrical charging of the newly created surfaces in molecular crystals under stress causes molecular excitation by electron impact (i.e., inelastic energy transfer from electrons accelerating across a potential difference in the crack) and/or by electric field induced electron-hole formation followed by pair recombination.

Experimental determination of the pressure that exists at the actively emitting site in the TL experiment is needed to verify the electrical mechanism and perhaps to help discriminate between electron-impact excitation vs. electron-hole pair recombination. Both mechanisms suggest that the TL emission should take place at the surface of newly created fracture surfaces. Thus, the local pressure at the TL site should be low compared to that at the tip of the mobile crack. Furthermore, electron-impact excitation can occur after the crack faces have become well separated, i.e., by more than several molecular diameters. Under these conditions, the local pressure will be near atmospheric pressure. Recombination luminescence would be more probably nearer the crack tip, where the piezoelectric charging would be greatest and pressures on the order of several kilobars can exist.

An ideal probe of the pressure at the TL site could be provided by a substance that has a large pressure-dependent shift of its luminescence maximum. The position of the maximum could be measured as a function of carefully controlled hydrostatic high pressure. The position of the maximum in the TL spectrum could then be compared to that in the photoluminescence spectrum at the known pressures, and the pressure extent during the TL emission could be determined.

We report here the pressure dependence of the photoluminescence spectra of four tetracyanoplatinates(II), $M_x[Pt(CN)_4]\cdot nH_2O$ (MCP), with M_x = KLi, KNa, Cs_2Ca, and Cs_2. MCP's tend to crystallize in quasi-one-dimensional (1-D) structures in which the square-planar $[Pt(CN)_4]^{2-}$ units are stacked in columns.[4,5] The intracolumnar Pt–Pt distance is short compared to the separation from column to column, resulting in a strongly anisotropic interaction between the complex ions.[6-8] MCP's show large pressure-dependent shifts of the optical emission maxima.[9,10]

TL spectra and 1-atm photoluminescence spectra are obtained under identical optical and geometrical conditions. The pressure at the active TL sites are determined, and the mechanistic consequences of the results are discussed.

Experimental Section

1. Sample Preparation. KLiCP, Cs_2CP, and $Cs_2Ca(CP)_2$ were prepared according to literature methods.[11] KNaCP was prepared by dissolving equimolar amounts of K_2CP and Na_2CP in water, slowly reducing the volume of the mixture on a water bath, and collecting the yellow crystals. Excellent elemental analyses for C, H, and N were obtained for all compounds except $Cs_2Ca(CP)_2$. For the latter compound, the number of waters of hydration is not known. The crystals used in this study analyzed for 9.63% C, 1.20% H, and 11.62% N.

2. Triboluminescence and Atmospheric-Pressure Photoluminescence Spectroscopy. Triboluminescence and 1-atm spectra were obtained under identical optical and geometric conditions by using a vidicon detection system. In a typical series of experiments, an ensemble of randomly oriented small crystals of the sample to be studied was placed in a glass sample holder mounted in front of the collection lens. Photoluminescence of the crystals was excited with a Lambda-Physik Model M1000 nitrogen laser. Triboluminescence was then excited by grinding the crystals with a glass rod. Photoluminescence of the resulting powder was then excited with the nitrogen laser. All spectra are uncorrected for the instrument response.

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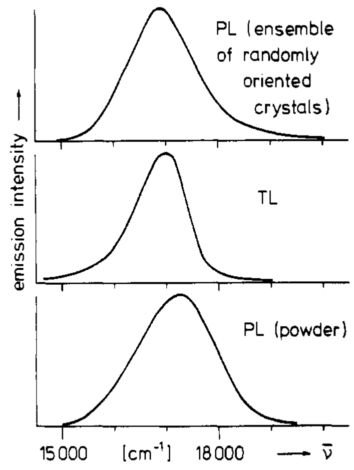

Figure 1. Photoluminescence (PL) and triboluminescence (TL) spectra of $KLi[Pt(CN)_4]\cdot 2H_2O$ (T = 295 K; p = 1 atm; λ_{ex} = 337 nm).

Table I. Energies of the Peak Maxima ($\bar{\nu}_{max}$, cm^{-1})[a] and the Widths at Half-Height ($\Delta\bar{\nu}_{1/2}$, cm^{-1})

compd	triboluminescence		photoluminescence (randomly oriented crystals)		photoluminescence (powder)	
	$\bar{\nu}_{max}$	$\Delta\bar{\nu}_{1/2}$	$\bar{\nu}_{max}$	$\Delta\bar{\nu}_{1/2}$	$\bar{\nu}_{max}$	$\Delta\bar{\nu}_{1/2}$
$KLi[Pt(CN)_4]$	16 910	1150	16 920	1350	17 200	1650
$KNa[Pt(CN)_4]$	17 780	1110	17 800	1520	18 110	1660
$Cs_2Ca[Pt(CN)_4]_2$	21 450	1180	21 490	2030	21 540	2230
$Cs_2[Pt(CN)_4]$	22 490	2910	22 450	2410	22 320	3020

[a] The experimental uncertainty in the peak maximum is about ±100 cm^{-1}.

The detection system consisted of a quartz collecting lens that focused the emitted light onto the slit of a $^1/_4$-m B&M Spektronik Model 25/25 polychromator equipped with a 150 line/mm grating blazed at 5000 Å. The detector was a B&M Spektronik SIT vidicon system with a cooled target. All spectra were obtained from 10 scans, each with a 1-s collection time. Because of the "lag effect" of the cooled target, the integrated intensities of many individually weak triboluminescence pulses were collected and measured.

3. High-Pressure Photoluminescence Spectroscopy. The high-pressure instrumentation has been described previously.[10] A single crystal of the sample to be studied and several ruby chips were placed in the high-pressure cell. The high-pressure medium, liquid paraffin, was introduced. The pressure was calibrated by using the pressure-induced shift of the R_1 ruby line[12] relative to the 6965-Å line of an argon lamp. All measurements were carried out at 295 K. The excitation light was directed perpendicular to a face of the single crystal and polarized parallel to the crystallographic c axis ($\vec{E}\|c$).

Results

1. Triboluminescence and Photoluminescence at Atmospheric Pressure. Three types of spectra were recorded: triboluminescence excited by mechanically grinding crystals, photoluminescence of ensembles of randomly oriented small crystals excited by a nitrogen laser, and photoluminescence of finely ground powders excited by a nitrogen laser. All atmospheric-pressure spectra were obtained under identical geometric and optical conditions using the same optics and detector. The three spectra of a typical sample, that of KLiCP, are shown in Figure 1. The energies of the peak maxima and the full widths at half-height of the TL and PL emissions are compared in Table I.

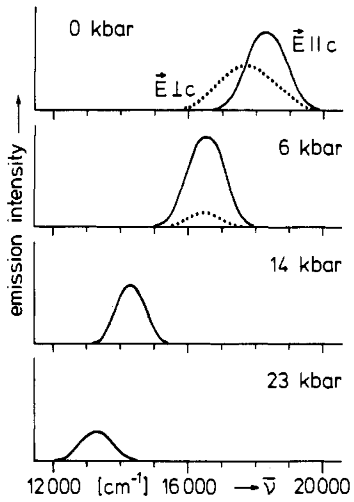

Figure 2. Polarized photoluminescence spectra of $KLi[Pt(CN)_4]\cdot 2H_2O$ single crystals for different pressures (T = 295 K; λ_{ex} = 364 nm).

The relative intensities of the TL of the samples studied decrease in the order KNaCP > KLiCP > $Cs_2Ca(CP)_2$ > CsCP. The TL spectra are the averaged spectra of at least 20 individual measurements. The experimental uncertainties in the measurement of the positions of the TL and PL band maxima are ±100 cm^{-1}. In the case of CsCP, where the relative TL intensity is the weakest, the uncertainties of the band maxima and the bandwidths may be slightly larger.

The position of the band maxima in all three types of spectra (TL, PL of randomly oriented small crystals, PL of powders) is the same within experimental error for Cs_2CP and for $Cs_2Ca(CP)_2$. For the KNaCP and KLiCP salts, the band maxima of the TL spectra and those of the PL spectra of randomly oriented small crystals have equal energies but the band maxima in the powder PL spectra are shifted to higher energies.

The bandwidths at half-height of the TL bands of KLiCP, KNaCP, and $Cs_2Ca(CP)_2$ are smaller than those of the PL bands of randomly oriented small crystals. The latter are narrower than the bandwidths of the PL spectra of powders. The larger bandwidth in the TL spectrum of Cs_2CP is probably a result of the larger experimental uncertainty caused by the weak TL intensity of this compound.

2. Hydrostatic High-Pressure Effects on the Photoluminescence Spectra. The pressure dependence of the photoluminescence band of oriented single crystals of the four compounds under investigation was measured between atmospheric pressure and 30 kbar. All four compounds exhibited a relatively large shift of the emission maximum to lower energies with increasing pressure. All measurements were made at room temperature.

The polarization of the pressure-dependent spectra was measured when such measurements were possible. In the cases of KLiCP and KNaCP, the polarizations of the emission were measured up to pressures of 7 and 11 kbar, respectively. Above those pressures the positions of both of the bands under both polarization directions were identical. For the $Cs_2Ca(CP)_2$ and the Cs_2CP salts, the $\vec{E}\perp c$-allowed bands contain practically the whole emission intensity at atmospheric pressure. Thus only the unpolarized spectra were measured for these two systems.

The polarized spectra of KLiCP at four different pressures are shown in Figure 2. The intensity of the $\vec{E}\perp c$-polarized band decreases rapidly with increasing pressure. The intensity of the $\vec{E}\|c$ band decreases more slowly. At a pressure of greater than 23 kbar it was too weak to be measured. At pressures greater than 7 kbar the positions of both of the bands in both polarization directions are identical.

The plot of the energy of the emission maximum of KLiCP as a function of pressure is shown in Figure 3. A decrease in the energy of the maxima of the bands in both polarization directions up to a pressure of about 12 kbar is found. The slopes of the plots of energy vs. pressure are 320 cm^{-1}/kbar for the $\vec{E}\|c$ band and

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[12] Noack, R. A.; Holzapfel, W. B. "High-Pressure Science and Technology"; Plenum Press: New York, 1979; Vol. 1.

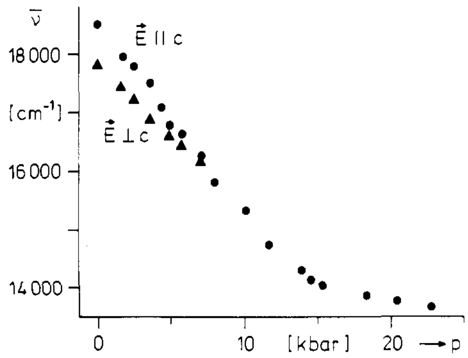

Figure 3. Emission peak energies for a single crystal of KLi[Pt(CN)$_4$]·2H$_2$O vs. pressure (T = 295 K; λ_{ex} = 364 nm).

Table II. Experimental Values of the Pressure-Induced Shift of the Photoluminescence Emission Maxima

	$\Delta\bar{\nu}/\Delta p$, cm^{-1}/kbar		
compd	$\vec{E} \parallel c$	$\vec{E} \perp c$	unpolarized
KLiCP	320	220	270
KNaCP	210	120	165
Cs$_2$Ca(CP)$_2$			90
Cs$_2$CP			115

220 cm^{-1}/kbar for the $\vec{E} \perp c$ band. At pressures above 15 kbar the slopes are much smaller. It is possible that at ~15 kbar a phase transition occurs.[13]

Similar high-pressure data were obtained for the other three compounds. The changes in the energies of the emission maxima as a function of pressure for all of the compounds studied are given in Table II. The slopes in all cases are those determined between atmospheric pressure and about 10 kbar. In the case of Cs$_2$CP and KNaCP at about 10 kbar, the slope decreases significantly, possibly due to phase transitions. For the KNaCP salt between ~11 and ~15 kbar, increasing the pressure does not shift the emission peak energies within the limits of experimental error. Phase transformations occur in this region with no or only small changes of the Pt–Pt distances.[6] In the case of Cs$_2$Ca(CP)$_2$, the plot of the energy maximum of the emission as a function of pressure is nearly linear up to a pressure of 30 kbar.

In comparison with the PL band of randomly oriented, small KLiCP crystals, the single-crystal emissions of this salt with $\vec{E} \perp c$ and $\vec{E} \parallel c$ polarization seem blue-shifted by ~500 and ~1500 cm^{-1}, respectively. Measurements with other MCP salts show that this blue shift becomes smaller as the in-chain Pt–Pt distance increases. This effect is due to self-absorption of the emitted light by the crystals. As mentioned above, the single-crystal emission was excited by $\vec{E} \parallel c$-polarized light, yielding maximum absorption within a thin surface layer, because of the high $\vec{E} \parallel c$ extinction.[6] Other orientations of $\vec{E}$, as given in an ensemble of randomly oriented crystals, result in an excitation inside the crystals enlarging the self-absorption process. The stronger the overlap of absorption and emission bands and the smaller the emission intensity ratio $I(\vec{E} \perp c)/I(\vec{E} \parallel c)$, the larger the integral self-absorption and the larger the red shift of the remaining emitted light of randomly oriented small crystals. Just these facts are realized for MCP's with decreasing Pt–Pt distance.

Discussion

1. Excited-State Assignments. The emission properties of the four complexes investigated in this study are determined by the [Pt(CN)$_4$]$^{2-}$ ions. The energy level diagram of this complex ion is shown in Figure 4 (see ref 7). The ground state in D_{4h} symmetry including spin–orbit coupling is A$'_{1g}$ arising from the ^{1}A$_{1g}$ state from the (d$_{z^2}$)^2(d$_{xz}$,d$_{yz}$)^4(d$_{xy}$)^2 electron configuration. The first excited state is ^{3}A$_{2u}$ according to the electron transition 5d$_{z^2}$ → 6p$_z$, π^*(CN). The ^{3}A$_{2u}$ splits into a E$'_u$ and a A$'_{1u}$ when spin–orbit coupling is taken into account. The next higher spin–orbit state is A$'_{2u}$ with ^{3}E$_u$/^{1}A$_{2u}$ parentage. Transitions between the ground state and the excited states A$'_{2u}$ and E$'_u$ are electric dipole allowed with polarization $\vec{E} \parallel c$ and $\vec{E} \perp c$, respectively. The transition between A$'_{1g}$ and the lowest excited state A$'_{1u}$ is symmetry forbidden. However, when electron–phonon coupling with an e$_g$ and an a$_{2g}$ vibration is included, relatively weak transitions with $\vec{E} \perp c$ and $\vec{E} \parallel c$, respectively, are expected. In thermal equilibrium at room temperature practically the whole emission intensity is due to the transitions A$'_{1g}$ ← A$'_{2u}$ ($\vec{E} \parallel c$) and A$'_{1g}$ ← E$'_u$ ($\vec{E} \perp c$).

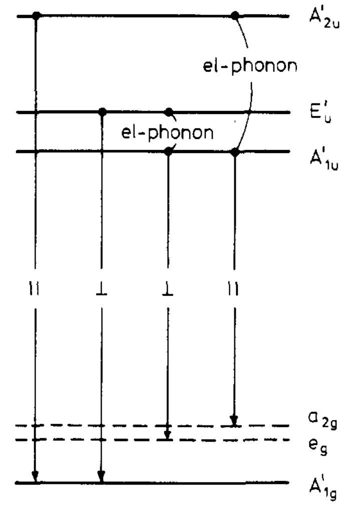

Figure 4. Energy level diagram for the emitting states of a [Pt(CN)$_4$]$^{2-}$ chain.

Table III. Relationship between Space Groups and Triboluminescence Activity in Tetracyanoplatinate Salts

compd	space group	polar space group	tribo-luminescent
Cs$_2$CP·H$_2$O	$P6_1$	+	+
KLiCP·2H$_2$O	$P2_1cn$	+	+
KNaCP·3H$_2$O	Cc	+	+
BaCP·4H$_2$O	$C2/c$	–	+
K$_2$Sr(CP)$_2$·6H$_2$O	$P2_1/m$	–	+
Na$_2$CP·3H$_2$O	$P\bar{1}$	–	–
K$_2$CP·3H$_2$O	$Pbcn$	–	–
Rb$_2$CP·H$_2$O	$Pncn$	–	–
CaCP·5H$_2$O	$Pcab$	–	–
SrCP·5H$_2$O	$C2/m$	–	–
La$_2$(CP)$_3$·18H$_2$O	$Pcan$	–	–
Dy$_2$(CP)$_3$·21H$_2$O	$Pcan$	–	–

2. Structure–Triboluminescence Relationships. It has already been proposed that triboluminescence activity can be strongly correlated with crystals having polar space groups. This correlation was originally proposed on the basis of studies of polymorphic forms of hexaphenylcarbodiphosphorane and anthranilic acid.[14] In the case of hexaphenylcarbodiphosphorane, two different crystalline forms of the same molecule were grown, one of which was triboluminescent while the other was inactive. In the case of anthranilic acid, three different polymorphic crystals were grown from the same molecule, one of which was triboluminescent while the others were inactive. The important structural feature that determined TL activity in these two systems was the existence of polar space groups in the triboluminescent crystals and nonpolar space groups in the inactive crystals. Surveys of families of crystals whose TL activities have been studied have shown that triboluminescence activity is strongly correlated with polar space groups.[15]

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(13) Yersin, H.; Gliemann, G.; Räde, H. S. *Chem. Phys. Lett.* **1978**, *54*, 111. See also ref 6.

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The polar space group–triboluminescence activity correlation holds well for the tetracyanoplatinate(II) salts. The salts for which the space groups are known, their space groups, and the presence or absence of TL activity are listed in Table III. The two apparent exceptions to the correlation, $BaCP{\cdot}4H_2O$ and $K_2Sr(CP)_2{\cdot}6H_2O$, are both TL active but are expected to be inactive on the basis of their nonpolar space groups. A possible explanation for the TL activity may be the effect of hydration on the crystal lattice. The symmetry of local sites in the crystal can be reduced if water molecules are missing or if extra waters are present. Such perturbed local sites can have the polar properties required for TL activity. The importance of trace dopants in determining TL activity was proven in the case of saccharine. The pure crystal is TL inactive, but TL activity was induced by deliberately introducing dopants into the lattice. However, there is no reasonable view that the effect of hydration should be limited to the two tetracyanoplatinate salts mentioned above.

3. Local Pressure at the Triboluminescence-Active Site. The tetracyanoplatinate salts provide sensitive systems for the determination of the local pressure at the TL-active site because the change in the wavelength of the emission maximum is very pressure dependent.[11] Thus, the energy of the emission maximum can be measured as a function of calibrated hydrostatic high pressure and compared to the maximum observed in the triboluminescence experiment.

The dependence of the energies of the excited states of the tetracyanoplatinate salts on hydrostatic high pressure is well understood.[6] The position of the emission maximum (with units of cm^{-1}) follows the relationships

$$\vec{E}\parallel c: \quad \bar{\nu}_{max} = 42.9 \times 10^3 - (8.0 \times 10^5)R^{-3} \qquad (1)$$

$$\vec{E}\perp c: \quad \bar{\nu}_{max} = 36.8 \times 10^3 - (6.3 \times 10^5)R^{-3} \qquad (2)$$

where R is the platinum–platinum distance along the linear chain. This R^{-3} dependence has been experimentally proven by using a series of cations that cause variations in R of more than 0.9 Å. The R^{-3} rule holds not only for variations in the Pt–Pt distance caused by varying the cations but also for variations caused by changing the water of hydration content of the crystals, the temperature of the crystals, and the hydrostatic pressure on the crystals.

The best of the four studied compounds for determining the pressure at the TL-active site during triboluminescence is KLiCP because it exhibits the largest pressure-dependent shift of its emission maximum (Table II). The observed shift with unpolarized light is 270 cm^{-1}/kbar. Under identical experimental conditions of geometry, optics, and detector, the maximum of the triboluminescence spectrum (at 16910 ± 100 cm^{-1}) is identical with the peak maximum in the 1-atm pressure photoluminescence spectrum (at 16920 ± 100 cm^{-1}) within experimental error. Thus, the pressure at the emitting site in the TL experiment is 1 atm with an experimental uncertainty of about 0.7 kbar.

The pressure at the TL-active site for all of the compounds studied here is 1 atm. The experimental uncertainties in the pressure for the other compounds studied are larger than that for KLiCP discussed above because the pressure-induced shifts of the emission maxima are smaller (Table II). In the case of KNaCP, the shift of the emission maximum as a function of hydrostatic pressure is 165 cm^{-1}/kbar. The maximum of the triboluminescence spectrum is 17780 ± 100 cm^{-1} while that in the 1-atm photoluminescence spectrum is 17800 ± 100 cm^{-1}. The pressure at the emitting site in the TL experiments is thus 1 atm, with an experimental uncertainty of about 1.2 kbar. The pressure at the emitting sites in $Cs_2Ca(CP)_2$ and Cs_2CP is also 1 atm, with experimental uncertainties on the order of 1 kbar.

The similarities of the emission bandwidths in the TL and photoluminescence experiments are surprising. In the cases of KLiCP, KNaCP, and $Cs_2Ca(CP)_2$ the widths at half-height of the TL spectra are smaller than those in the PL spectra (Table I). For Cs_2CP, the TL line width is larger than that in the photoluminescence spectrum. In all of the above examples, the differences in the line widths are small but experimentally significant. The smaller TL line widths are surprising because the TL spectra might have been expected to represent a superposition of the emissions of molecules at a variety of sites under a distribution of local pressures and temperatures. If such a superposition occurred, the TL line widths would have been larger than those in the photoluminescence spectra of crystals at 1 atm of pressure.

The only other reported measurement of the pressure at the TL-active site used the pressure dependence of the relative intensities of photoluminescence bands.[16] In the reported study, a manganese salt that contains both tetrahedral and octahedral manganese complexes was used. Both the TL and the photoluminescence spectra exhibited simultaneous emissions from the two types of complexes. The intensity of the luminescence band from the octahedral manganese ion complex increased relative to that from the tetrahedral complex as the hydrostatic high pressure increased. Comparison of the emission intensities in the TL experiment relative to those in the high-pressure photoluminescence experiment showed that the TL spectrum is equivalent to the high-pressure photoluminescence spectrum at a pressure of less than 2 ± 1 kbar. Only an upper limit was determined in the study. The determination of the pressure based on the position of the peak maximum in this paper provides a definite value of the pressure (rather than an upper limit) with less experimental uncertainty.

Tetracyanoplatinate salts exhibit distinct temperature-dependent shifts of their luminescence maxima. The $\vec{E}\parallel c$ and $\vec{E}\perp c$ emission maxima of KLiCP at 1 atm are shifted to the blue by ~1700 cm^{-1} and ~2000 cm^{-1}, respectively, if the temperature is raised from 5 to 295 K.[17] The transition energies are nearly linear functions of the temperature. Since the maxima of the triboluminescence spectrum and of the 1-atm photoluminescence spectrum are identical, each with an experimental error of ±100 cm^{-1}, the "temperature" of the emitting site in the room-temperature TL experiment at 1 atm amounts to about 295 ± 30 K.

The similarities of the positions of the band maxima and of the line widths between the triboluminescence spectra and the 1-atm crystal photoluminescence spectra suggest that the TL emission occurs at crystal sites that are at atmospheric pressure and room temperature. Triboluminescence occurs from relaxed sites in the crystal and not from a site at or near the crack tip.

Summary

The large pressure-dependent shifts of the positions of the emission band maxima of tetracyanoplatinate salts make these compounds sensitive probes of the pressure at the sites in the crystals giving rise to triboluminescence emissions. The positions of the peak maxima in the triboluminescence experiments are the same within experimental error as those in the 1-atm photoluminescence experiments. In the most sensitive sample, KLiCP, the shift of the photoluminescence maximum with pressure is 270 cm^{-1}/kbar. When the experimental uncertainties are taken into account, it is concluded that the pressure at the emitting site during triboluminescence is 1 atm (about 10^{-3} kbar) with an experimental uncertainty of 0.7 kbar. The TL takes place at sites where the stress is relaxed and not at the tips of cracks under high-pressure conditions. The pressure results, together with the good correlation between polar space groups and TL activity, support the TL

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(15) Chandra, B. P.; Zink, J. I. *Inorg. Chem.* **1980**, *19*, 3098; *J. Phys. Chem. Solids* **1981**, *42*, 529; *J. Lumin.* **1981**, *23*, 363; *J. Phys. Chem.* **1982**, *86*, 4138.

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excitation mechanism based on electrical charging of newly created fracture surfaces. From the temperature dependence of the photoluminescence maximum the "temperature" of the TL site is estimated to be 295 K with an experimental uncertainty of 30 K.

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Registry No. KLi[Pt(CN)$_4$], 62728-87-4; KNa[Pt(CN)$_4$], 15318-78-2; Cs$_2$Ca[Pt(CN)$_4$]$_2$, 93645-96-6; Cs$_2$[Pt(CN)$_4$], 15747-35-0.

Notes

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Critical Deactivating Modes for the Metal-2,2'-Bipyridine or -1,10-Phenanthroline MLCT Excited States

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Relatively long-lived photoexcited states of transition-metal complexes have been utilized in a variety of interesting photoredox schemes.[1,2] It would clearly be of interest to understand the factors that affect excited-state properties and reactivities (lifetimes, ground- and excited-state redox potentials, absorption spectra, etc.) so that they could be systematically controlled to optimize the use of metal complexes as sensitizers. One class of chromophore that has been extensively studied consists of oxidizable metal centers bound to polypyridyl ligands like 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen).[2-4] The complexes have low-lying metal-to-ligand charge-transfer (MLCT) excited states that can be long-lived. Low-temperature emission spectra characteristically exhibit a short, poorly resolved vibrational progression with $\hbar\omega = 1350\ \text{cm}^{-1}$, which has been characterized as a framework stretch of the polypyridyl ligand.[4]

Recently, we have described a series of complexes of the type Os(B)L$_4^{2+}$ (B = bpy, phen; L = py, PR$_3$, NCMe, CO, etc.) which have relatively long-lived excited states whose properties can be tuned by systematic variations in L.[5] For this series, it was found that variations in both the radiative (k_r) and nonradiative (k_{nr}) decay rate constants could be understood quantitatively.[6] In particular, variations in k_{nr} are determined largely by the excited-state energy and differences in the equilibrium geometries of the ground and excited states in accordance with the "energy gap law".[7] From the vibrational structure of the emission spectra, the most important difference in equilibrium geometry occurs in the aforementioned 1350-cm^{-1} vibrational mode and it was demonstrated that this mode functions as the critical accepting vibration. Evidence was also obtained for less important contributions from a lower frequency mode (~400 cm^{-1}), presumably arising from metal-ligand skeletal vibrations. The purpose of the present work is (1) to consider the origin of the ~1350-cm^{-1} distortion in greater detail, and (2) to provide an electronic basis for a comparison between bpy vs. phen as the chromophoric ligand.

Experimental Section

CNDO/2 calculations[8] were carried out for bpy, phen, and their diprotonated forms H$_2$bpy^{2+} and H$_2$phen^{2+}. The coordinates for bpy and phen were taken from the structures for Ru(bpy)$_6^{2+}$[9] and Fe(phen)$_3^{2+}$.[10] For the diprotonated forms, the N-H bond length was taken to be 1.05 Å and the N-H vector was taken to bisect the C-N-C angle. Where comparable, the present results agreed fairly well with previously published results for bpy[11,12] and phen.[12,13]

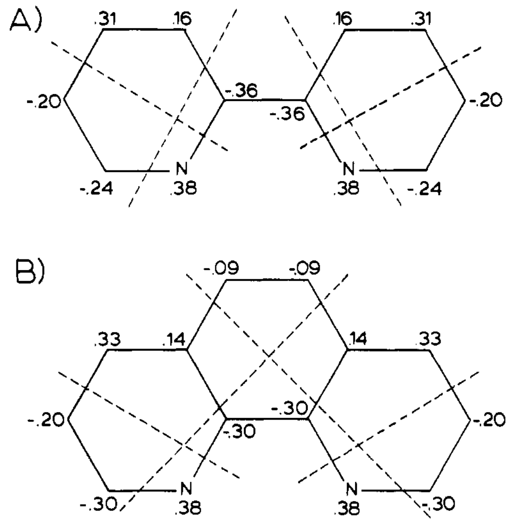

Figure 1. Calculated lowest energy π^* orbital of (A) H$_2$bpy^{2+} and (B) H$_2$phen^{2+}. The numbers indicate the contribution of the out-of-plane p orbital of the atom to the π^* orbital, and the dashed lines indicate the approximate nodal planes.

Results and Discussion

Our concern here is only with the lowest π^* orbital, and the discussion will be limited to it. Complete results are published

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