

in copper chloride predict an absorption maximum at 575 nm, which is, in fact, very close to the observed maximum under visible irradiation. The formation of copper colloids is thus proposed. The possibility of copper colloid formation is supported by work on photochemical disproportionation in the  $\text{CuCl}(s)\text{-H}_2\text{O}(l)$  system in which the induced spectrum has been identified as copper colloids (18-30 Å, oblate).<sup>12</sup> It is important to note that copper colloids formed within a copper halide crystallite will be gray-brown in color as opposed to the red color shown by copper colloids in a glassy matrix due to the higher refractive index of the copper halide crystallite. In the glasses, however, the presence of colloids has been difficult to establish. No optical bleaching of the darkened glass is observed at accessible wavelengths into the near infrared nor does darkening with a polarized source produce any observable dichroism. The phenomenon of polarizability helps to establish the colloidal nature of the absorbing species in darkened silver

halides.<sup>13</sup> The colloidal nature of the darkened copper halide photochromics is nonetheless supported by the spectral data and fade characteristics.

### Conclusions

All present evidence indicates that the copper halide containing glasses give rise to a unique photochromic glass system. The photochromic behavior is particularly notable from the standpoint of the low-temperature dependence of darkening, including the darkening observed at temperatures near 60 °C.

These glasses as described do not equal the performance of silver halide containing photochromic glasses with respect to speed of darkening and fading; however, applications may exist where the cost and/or availability of silver would restrict the use of silver halide photochromism.

**Registry No.**  $\text{SiO}_2$ , 7631-86-9;  $\text{B}_2\text{O}_3$ , 1303-86-2;  $\text{Na}_2\text{O}$ , 1313-59-3;  $\text{Li}_2\text{O}$ , 12057-24-8;  $\text{K}_2\text{O}$ , 12136-45-7;  $\text{CuO}$ , 1317-38-0;  $\text{Cl}$ , 7782-50-5;  $\text{Br}$ , 7726-95-6;  $\text{WO}_3$ , 1314-35-9;  $\text{As}_2\text{O}_3$ , 1327-53-3.

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## Laser-Excited Luminescence Study of the Chain Compound $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$

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Luminescence studies from 5 to 290 K on single crystals of the chain compound  $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  show the presence of a short-lived component (<10 ns) centered at about  $26 \times 10^3 \text{ cm}^{-1}$  and a long-lived (2 ms at 5 K) component at about  $19 \times 10^3 \text{ cm}^{-1}$ . The  $26 \times 10^3 \text{ cm}^{-1}$  transition shows a strong temperature dependence which is shown to result from the changing metal-metal separation. Differences of lifetimes and emission energies between palladium and platinum chain compounds are explained as a result of the smaller spin-orbit coupling for palladium. Comparison to  $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  suggests that the palladium salts will not be good candidates for one-dimensional-like conductors.

### Introduction

Recent years have seen much interest in the square-planar platinum tetracyanide compounds. The best known example of these is KCP ( $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ ), which exhibits extremely anisotropic electrical conductivity and also displays a prototypical Peierls distortion-like phase transition at low temperatures.<sup>1</sup> In an effort to better understand the role of bonding in KCP, a number of studies, particularly by Yersin and co-workers,<sup>2-5</sup> have been carried out on a series of non-conducting platinum chain compounds which can serve as prototypes to KCP. The effect of metal-metal interactions on the spectroscopic properties have been quantified, and the role of the structure on the conductivity properties has become better understood.

Palladium tetracyanides are also known to form chain compounds,<sup>6</sup> and it becomes interesting to ascertain whether the observations and concepts for the  $5d^8$  platinum compounds carry over to the  $4d^8$  palladium compounds. In this work we have studied  $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  which is one of these linear

chain compounds. According to early X-ray studies<sup>7</sup> it crystallizes in a monoclinic space group  $C_{2h}^2$  and has chains of  $\text{Pd}(\text{CN})_4^{2-}$  anions separated by 3.37 Å at room temperature. This is an intermediate distance with respect to platinum compounds where the distances have ranged approximately from 2.87 to 3.67 Å.

### Experimental Section

Single crystals of  $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  were grown by slow evaporation of aqueous solutions. These crystals were either mounted in an Air Products Helitran for variable-temperature measurements down to 5 K or immersed in small quartz liquid-nitrogen Dewars for 77 K. Care was taken to avoid dehydration which can occur easily for these crystals. Luminescence excitation was generally at 337.1 nm by a Molelectron Model UV14 nitrogen laser. Emission was detected by an RCA 31034 A-20 response phototube mounted on a McPherson scanning monochromator.

Lifetime measurements were made with a Princeton Applied Research Model 162 boxcar integrator. Excitation was provided by the pulsed nitrogen laser with pulses approximately 5 ns in length. Shorter lifetimes than this could normally be expected to be deconvoluted, but electronic drift precluded accurate lifetime measurements less than 10 ns.

### Observations

No emission from  $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  was apparent at room temperature but cooling to 77 K yielded visually intense luminescence. A typical spectrum obtained at 7 K is shown in

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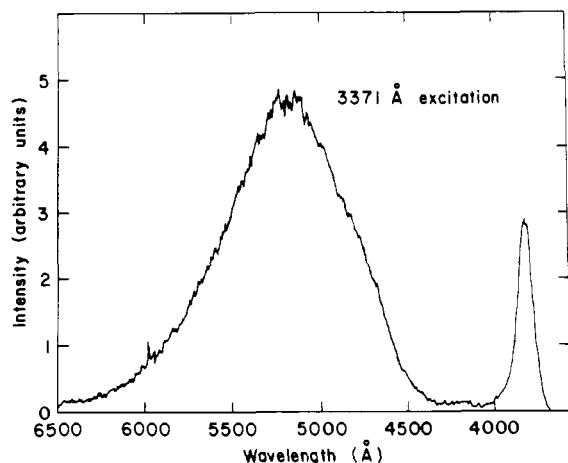


Figure 1. Luminescence spectrum from BaPd(CN)<sub>4</sub>·4H<sub>2</sub>O at 7 K. A nitrogen laser was used for excitation.

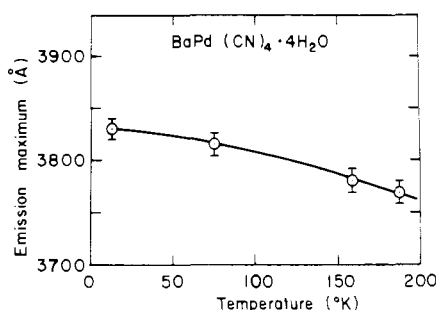


Figure 2. Emission maximum of  $26 \times 10^3 \text{ cm}^{-1}$  band vs. temperature. The curved line is a guide to the eye.

Figure 1. Two well-separated maxima are seen at this temperature, a higher energy band at about 382 nm ( $26\,000 \text{ cm}^{-1}$ ) with a width of  $900 \text{ cm}^{-1}$  fwhm and a lower energy band at 512 nm ( $19\,500 \text{ cm}^{-1}$ ) with width  $3300 \text{ cm}^{-1}$ . The relative intensities of the two maxima should not be compared because the crystal was not oriented and no account was taken of the polarization of the laser and of the monochromator system. Figure 2 shows the temperature dependence of the emission wavelength maxima. This peak shifted smoothly to lower energy as the temperature decreased. The width also decreased but was still  $900 \text{ cm}^{-1}$  at 5 K. No structure in either band was observed at the lowest temperatures of these measurements (5 K).

The luminescence decay curves for each maxima were measured to provide information on the emission lifetimes. At all temperatures, the higher energy peak displayed a lifetime which was shorter than the effective instrumental resolution. The resolution was on the order of 10 ns, but the actual lifetime may be much shorter than this. The lifetime of the lower energy emission was found to be longer and easily measurable. The temperature dependence of this lifetime is shown in Figure 3. At 0 K the lifetime can be estimated to be about 2.5 ms and decreases by approximately a factor of 2 for each 30 K temperature rise. Some effort was made to characterize the polarization characteristics of the emission. The palladium anion chains run parallel to the crystal needle axis.<sup>6</sup> This direction will subsequently be referred to as the *z* direction. There was considerable polarization leakage with the particular experimental setup, but the results indicated that the 382-nm band was polarized in the *z* direction while the 520-nm band was polarized perpendicular to *z*.

## Discussion

As indicated earlier, much of the significance in the study of BaPd(CN)<sub>4</sub>·4H<sub>2</sub>O lies in making a comparison to the results seen for the series of analogous platinum salts. The important

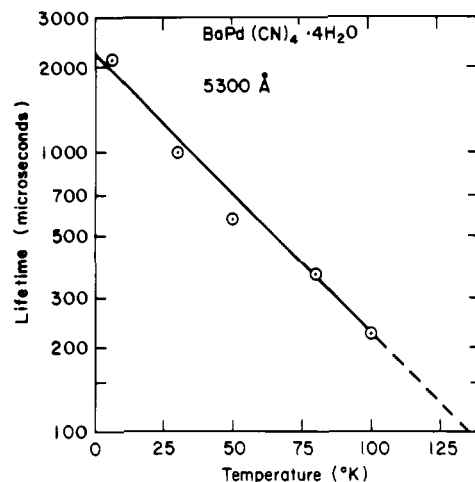


Figure 3. Lifetime of  $19 \times 10^3 \text{ cm}^{-1}$  band vs. temperature. The dashed line is extrapolation to higher temperatures.

features in both cases are those that can be related in a quantitative way to the metal-metal distance in the solid state.

The emission from the crystalline palladium salt has been found to consist of two components, one of which we will now call the fluorescence band and the other the phosphorescence band. The fluorescence band is the higher energy one, appearing at about 382 nm at 77 K and polarized along *z* perpendicular to the anion planes. The numerical value of the lifetime of this band was too small to be determined with the given experimental apparatus.

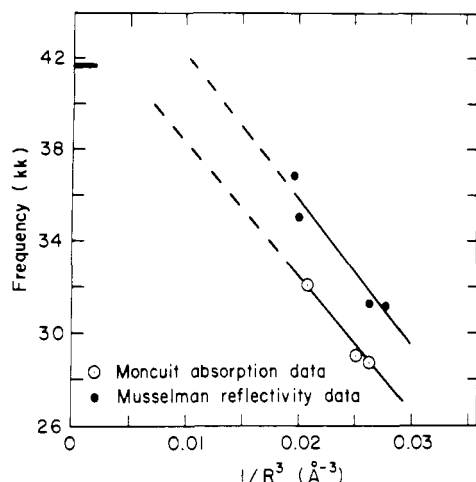
The fluorescence can be correlated with the lowest energy solid-state absorption band which has been measured to lie at  $31 \times 10^3 \text{ cm}^{-1}$  by Moncuit<sup>8</sup> and at  $31.2 \times 10^3 \text{ cm}^{-1}$  by reflectivity.<sup>9</sup> This represents a Stokes shift of approximately  $5000 \text{ cm}^{-1}$  which is comparable to that seen in many similar materials.<sup>10</sup> The lowest energy absorption band in solution lies at about  $41 \times 10^3 \text{ cm}^{-1}$ .<sup>6</sup> The present absorption and emission are characteristic of the solid state and have their origins in the interaction of neighboring intrachain metal atoms. The absorption band has earlier been found to be polarized along *z* and is relatively intense with an absorption coefficient of about  $1000 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The short lifetime observed for the fluorescence here is numerically consistent with having its origin in such an allowed transition. Thus the short lifetime, polarization character, and proximity to the absorption band are consistent with the fluorescence being related to the "solid-state" absorption band.

Further evidence for the above assignment can be found in the interesting behavior found for the temperature dependence of the emission wavelength as was shown in Figure 2. As the temperature was decreased, the energy of the fluorescent band also decreased. This will be shown below to be related to the effects of thermal contraction. As the crystal cools, the intrachain metal-metal separation becomes smaller, causing the orbital overlap and interaction to increase. The results of such effects have been investigated by Yersin et al.,<sup>3,4</sup> who have reported both experimental and theoretical results of a related study on linear chain platinum compounds. Experimentally, the platinum-platinum separation *R* along the linear chains was systematically varied by them over the range 3.1–3.7 Å by substitution of different cations in the compound or by the application of pressure to a given compound. In both cases, the effect was the same as above with the absorption and

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**Figure 4.** Plots of reflectivity and absorption maxima for lowest energy band of  $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  vs.  $R^{-3}$ . Straight lines and extrapolations are guides to the eye only.

emission moving to lower energy with decreasing separation. Plots of the data showed that the energy varied linearly as  $R^{-3}$ . Calculations<sup>2</sup> with a two-band model using a (Pt  $5d_{z^2}$ ,  $6s$ ) hybrid ground-state orbital and a (Pt  $6p_z$ ,  $\text{CN}\pi^*$ )-like orbital for the conduction band also yielded an  $R^{-3}$  dependence for the energy gap. It is important to see if a similar analysis can be applied to the experimental data from a series of palladium chain compounds, although very little data are presently available on such compounds. Figure 4 shows the reflectivity and absorption results for this limited number of compounds plotted as a function of  $R^{-3}$ . There is obviously scatter, but the trends are nevertheless there. As the metal-metal separation increases, the absorption energy trends toward higher values. Straight lines have been drawn through the data as guides to the eye to give what must be considered qualitative results. Extrapolation of the lines to the left of the graph yield values for the absorption energy that could be expected for infinite separation of the metal neighbors. In solution  $\text{Pd}(\text{CN})_4^{2-}$  molecules are far apart, and there is no metal-metal bonding. The extrapolated absorption for infinite separation of metal-metal spacing should correspond to the absorption energy expected for a solution. Both lines extrapolate to values of energy which are similar to those found for intense solution transitions<sup>6</sup> but higher than the lowest transition energy (41 kK).

Figure 4 can be used to give a crude estimate of the thermal contraction in a crystal of  $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ . By use of the data in Figure 2, it can be estimated that the emission energy decreases by approximately  $700 \text{ cm}^{-1}$  from room temperature down to 5 K. At room temperature, the crystal has a metal-metal separation of  $3.37 \text{ \AA}$ , and the absorption energy is  $31.0 \times 10^3 \text{ cm}^{-1}$ . With these values and on the assumption that the emission and absorption show the same  $700\text{-cm}^{-1}$  shift, it can be estimated that the separation  $R$  at 5 K should be about  $3.32 \text{ \AA}$ . This would be a contraction of about 1.5% which is not unreasonable. For comparison, it would be interesting to make an X-ray determination of the thermal expansion to see if there is agreement. A study<sup>2</sup> of several tetracyanoplatينات has shown successful analysis along these lines.

The reflectivity and absorption data shown in Figure 4 do not fit a straight line nearly as well as might have been expected in comparison to the excellent fits found for platinum. It seems likely that new measurements on an expanded set of palladium chain compounds would yield results similar to those for platinum chain compounds.

The lower energy band at about  $19.5 \times 10^3 \text{ cm}^{-1}$  exhibited different properties from the fluorescent band. At 5 K, the

width was approximately  $3300 \text{ cm}^{-1}$  as compared to about  $900 \text{ cm}^{-1}$  for the higher energy band. The polarization analysis indicated a transition perpendicular to  $z$ . Another major difference was in the lifetime of the emission. The extrapolated value at 0 K is about 2.5 ms which suggests a spin-forbidden process. A rapid decrease in the lifetime of this component was found upon increasing the temperature, and this presumably shows simply the increasingly important effects of non-radiative processes. The natural radiative lifetime may be substantially longer than experimentally observed. Given the value of 2.5 ms for  $\tau$  and the  $3300\text{-cm}^{-1}$  width, a rough upper limit for the integrated molar extinction coefficient can be estimated to be only on the order of 1. This follows because the oscillator strength is given approximately by<sup>11</sup> eq 1, where

$$f = \frac{g_u}{g_l \tau_0 (\bar{\nu})^2} \quad (1)$$

$g_u$  and  $g_l$  are the upper and lower electronic state degeneracies,  $\tau_0$  is the radiative lifetime, and  $\bar{\nu}$  is the emission maximum. Also, using eq 2 and taking the bandwidth  $\Delta\bar{\nu}$  for the ab-

$$f = 4.6 \times 10^{-9} \int \epsilon(\bar{\nu}) d\bar{\nu} = 4.6 \times 10^{-9} \epsilon_{\text{max}} (\Delta\bar{\nu}) \quad (2)$$

sorption band to be the bandwidth of the emission, we can estimate  $\epsilon_{\text{max}}$ . If the transition is also broad in absorption, this would make its experimental observation difficult.

The long lifetime and perpendicular polarization for this lower energy band completes the analogy to the platinum systems where similar states were reported and assigned as triplet states.<sup>2</sup> The difference between the two systems lies in the separation of the triplet and singlet states. For the palladium salt where the palladium-palladium distance is about  $3.37 \text{ \AA}$ , the separation is about  $7000 \text{ cm}^{-1}$ . The largest separation experimentally determined<sup>2</sup> for any of the platinum compounds was about  $3000 \text{ cm}^{-1}$  for  $\text{Na}_2\text{Pt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  with a platinum-platinum spacing of  $3.67 \text{ \AA}$ . Smaller spacings led to an approach of the two levels until they were essentially coincident at about  $3.0 \text{ \AA}$ . Qualitatively, it can be inferred that the fluorescent state with its parallel polarization is more sensitive to the effects of the intrachain metal-metal overlap than in the phosphorescent state. It can also be pointed out that for the same metal-metal separation the phosphorescence levels for the platinum and palladium compounds are not that different while the fluorescence level for palladium is significantly higher energy than for platinum. For example, the levels for  $\text{CaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  with a spacing of  $3.38 \text{ \AA}$  are  $20\,500$  and  $22\,500 \text{ cm}^{-1}$  for phosphorescence and fluorescence, respectively.<sup>2</sup> For  $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  at about  $3.35 \text{ \AA}$ , the energies are  $19\,000$  and  $26\,000 \text{ cm}^{-1}$ .

Yersin et al.<sup>3</sup> have studied the emission energies of a number of  $\text{Pt}(\text{CN})_4^{2-}$  compounds with varying Pt-Pt distances. The extrapolated transition energy for KCP with a Pt-Pt distance of  $2.89 \text{ \AA}$  is about  $10\,000 \text{ cm}^{-1}$  and from Figure 4, which shows a plot of reflectivity and absorption maxima as a function of  $R^{-3}$  for  $\text{Pd}(\text{CN})_4^{2-}$ , we infer that the metal-metal distance needed to obtain a low transition energy as in KCP is unrealistically short. So the higher energies that characterize the states in palladium make it unlikely that compounds can be prepared which will have properties similar to those found for KCP. Mixed crystals with  $\text{Pd}(\text{CN})_4^{2-}$  and  $\text{Pt}(\text{CN})_4^{2-}$  making up the chains can also be prepared and these might be expected to show interesting properties. However, the reflectance work of Musselman<sup>6</sup> indicates that amalgamated states form, and in this case, the energies will tend toward values higher than for the pure platinum case, and this is not the desired direction.

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For BaPd(CN)<sub>4</sub>, in contrast to the Pt salt, the emission lifetimes should be more characteristic of a <sup>1</sup>A<sub>2u</sub> → <sup>1</sup>A<sub>1g</sub> electric-dipole spin-allowed transition and a <sup>3</sup>A<sub>2u</sub> → <sup>1</sup>A<sub>1g</sub> spin-forbidden transition because of a smaller spin-orbit constant. Thus, the spin-allowed lifetime should be shorter than with Pt and the spin-forbidden lifetime for Pd longer than for Pt; again, this is in agreement with experimental data.

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## Luminescence Spectra of Some Substituted Group 6B Metal Carbonyls in Methane and Argon Matrices at 12 K

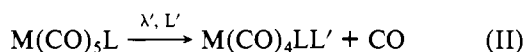
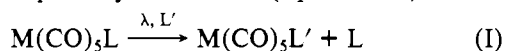
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The importance of the matrix-isolation technique for the measurement of emission and excitation spectra of M(CO)<sub>5</sub>L complexes (M = Mo and W; L = pyridine, 3-bromopyridine, pyridazine, piperidine, NH<sub>3</sub>, PMe<sub>3</sub>, and PCl<sub>3</sub>) has been demonstrated. For the first time both fluorescence and phosphorescence emission have been detected. Only phosphorescence was found for Mo(CO)<sub>5</sub>py, and for the Cr complexes no luminescence was obtained. The fluorescence band shifted to higher energy upon going from N-donor to P-donor complexes corresponding to the shift of the lowest-lying d-d transition in the UV-visible absorption spectrum. W(CO)<sub>5</sub>pyr, which has a low-lying MLCT transition, showed no detectable luminescence in contrast to emission studies in glasses at 77 K.

### Introduction

Photochemistry of substituted group 6B metal carbonyls both in solutions<sup>1-10</sup> and in matrices at 12 K has been the subject of several papers.<sup>11-19</sup> For these complexes two photochemical pathways are found (eq I and II). The



pathways are dependent on the wavelength of irradiation, the metal, and the ligand L. A higher quantum yield of CO ejection was found after short wavelength irradiation and/or in going from M = W to Mo and Cr.<sup>7</sup> A drastic reduction of quantum efficiency is found when a MLCT transition is lowest in energy for ligands having low-lying π\* orbitals.<sup>4</sup> For the photochemical processes I and II the total reaction quantum yield was less than unity, showing that radiative and nonradiative deactivation processes must be involved. Information about such deactivation processes is sparse, and only for a few substituted metal carbonyl complexes, e.g., XRe(CO)<sub>3</sub>L (X = Cl, Br, I; L = 9,10-phenanthroline and related ligands),<sup>20-22</sup> W(CO)<sub>4</sub>(substituted pyridine)<sub>2</sub>,<sup>23,24</sup> M(CO)<sub>4</sub>bpy (M = Cr, Mo, W),<sup>25</sup> and W(CO)<sub>5</sub>L (L = donor ligands (amines, ethers, ketones, and phosphines))<sup>1,3-5,8-10</sup> has luminescence been reported, mostly in glasses at 77 K. Matrix isolation has been very successful in characterising the intermediates and elucidating the photochemical pathways. However, in going from solutions at room temperature to matrices at 12 K, the photochemical behavior changes.<sup>19</sup> For a more detailed understanding of the photochemistry of substituted metal carbonyls it is therefore necessary to investigate deactivation processes.

In this paper we describe the results of luminescence measurements of a series of M(CO)<sub>5</sub>L complexes (M = Mo and

W; L = pyridine, 3-bromopyridine, pyridazine, piperidine, PMe<sub>3</sub>, and PCl<sub>3</sub>) in Ar and CH<sub>4</sub> matrices at 12 K; some preliminary results have been reported earlier.<sup>26</sup>

### Results

**A. UV-Visible Spectra.** The UV-visible absorption spectra of the W(CO)<sub>5</sub>L complexes (L = amine, imine) show one

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