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Note

Light-induced electron transfer in lead(II)gold(I) dicyanide

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Abstract

Photoluminescence studies of Pb[Au(CN)$_2$]$_2$ are reported. Laser excitation of 337 nm for Pb[Au(CN)$_2$] at 78 K results in a decrease in luminescence intensity with increasing laser exposure time indicating the creation of non-luminescing species. Increasing the sample temperature to 300 K results in the non-luminescing species going back to the original Pb[Au(CN)$_2$]$_2$. Light-induced electron transfer in which Au(I) is reduced to Au(CN)$_2^{2-}$ is assigned as the principal process responsible for the decrease in luminescence intensity of Pb[Au(CN)$_2$]$_2$ with increasing laser exposure at 78 K.

Keywords: Photoluminescence studies; Photochemical reaction; Electron transfer process; Pb(II)Au(I) dicyanide complex

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1. Introduction

The d^{10} Au(I) salts, MAu(CN)$_2$ (M = K$^+$, Cs$^+$, Tl$^+$, etc.) have a structure consisting of layers of Au(CN)$_2^-$ linear ions alternating with layers of M^{n+} ions. The intralayer Au–Au distances vary with the counterion M^{n+}. The photoluminescence properties of the two-dimensional compounds KAu(CN)$_2$ and CsAu(CN)$_2$ have been found to be dictated by the extent of gold–gold covalent interactions [1–3]. In TlAu(CN)$_2$ the presence of both Tl–Au and Au–Au covalent interactions shifts both the absorption and emission energies to lower values compared to the otherwise iso-structural CsAu(CN)$_2$ [4–6].

We have recently reported [7] the excited state properties of the layered compounds M[Au(CN)$_2$]$_3$ and M[Ag(CN)$_2$]$_3$ with M = Eu^{3+}. Exclusive excitation of the Au(CN)$_2^-$ and Ag(CN)$_2^-$ ions leads to photoluminescence from the Eu^{3+} ion, indicating excited-state energy transfer. The Au(CN)$_2^-$ and Ag(CN)$_2^-$ emissions are totally quenched for a wide range of temperatures. In this paper we report the excited state properties of the yellow colored compound, Pb[Au(CN)$_2$]$_2$. Laser excitation at 337 nm for this Pb(II) salt at 78 K results in a decrease in luminescence intensity which is reversed by heating the sample in the dark to 300 K and then recooling to 78 K. The formation of a non-luminescing species is interpreted in terms of an excited-state electron transfer process in which Au(CN)$_2^-$ in an excited electronic state is reduced to Au(CN)$_2^{2-}$ which then decomposes to Au and 2CN$^-$. This process is reversed upon heating to 300 K.

2. Experimental

The compound, Pb[Au(CN)$_2$]$_2$ was prepared by mixing a solution of Pb(NO$_3$)$_2$ with a solution containing a stoichiometric amount of KAu(CN)$_2$. A precipitate of Pb[Au(CN)$_2$]$_2$ appeared as a fine, light yellow powder.

For this study, the luminescence spectra were first measured with a Perkin Elmer MPF44A spectrofluorimeter. A 120 W xenon lamp served as the light source. Later luminescence work utilized a Molectron UV series 14 pulsed nitrogen laser as the excitation source with a McPherson model 2051 monochromator and a RCA31034 photomultiplier tube.

In order to achieve the low temperature needed, a model Lt-3-110 Heli-Tran apparatus was used. Liquid nitrogen was used as the coolant. The samples were mounted on a polished copper plate with a glue named Colloidion. Experiments were carried out which showed

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that the polished copper plate and the Colloidion glue did not give any background signal to the measured luminescence spectra. The exposure to the excitation light source was kept to a minimum during temperature dependence studies. A nitrogen gas stream was used to prevent moisture buildup on the sample sheath.

Scans of the spectra were taken with monochromator slits between 1.0 and 2.5 nm on the spectrophotometer and between 0.4 and 1.0 nm on the laser apparatus. Scan rates for the spectra were 50 and 60 nm/min for the laser and the spectrophotometer, respectively.

During the experiments on photochemical decay, each sample in a vacuum was cooled to 77 K with no laser exposure prior to the first scan taken. Thereafter scans were taken every 10 min with constant laser exposure. When 70 min of exposure time had passed, the laser exposure was cut off and the samples warmed over a 100 min period (5 W heating power) up to 280 K. The sample was then lowered to 77 K over a 10 min period and allowed an additional 10 min to come to thermal equilibrium. The laser exposure began again and the recovery spectra was immediately taken. About 4 cycles of 77 K excitation and 300 K heating were required to leave the sample totally non-emitting.

3. Results

3.1. Photoluminescence spectra

At 77 K, the luminescence spectra of the $Pb[Au(CN)_2]_2$ showed two large, sharp peaks when excited at a wavelength of 399 nm as shown in Fig. 1. One peak occurred at 463 nm, and the second peak was at 547 nm. Three separate peaks appeared in the excitation spectra with the main sharp 399 nm peak, a weaker sharp peak at 373 nm and a low, broad peak around 330 nm. The excitation peak at 399 nm increased in intensity slowly up to the peak maximum as the wavelength increased, but dropped away sharply at shorter wavelengths. Excitation at 393, 373 or 330 nm resulted in the same emission spectrum shown in Fig. 1.

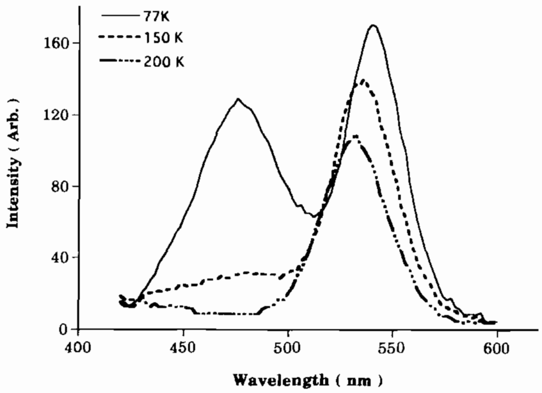

Fig. 1. Temperature dependent luminescence spectra of $Pb[Au(CN)_2]_2$ with 399 nm excitation at 77, 150 and 200 K.

Fig. 2 shows the temperature dependence of the luminescence intensity for both the high energy peak at 463 nm and the low energy peak at 547 nm of $Pb(Au(CN)_2)_2$. The luminescence peak intensity for the 463 nm peak decreased very sharply with increasing temperature, but the peak intensity for the 547 nm peak fell much more slowly. The 463 nm peak disappeared entirely above 180 K. Fig. 3 shows that, as the temperature is increased, the 547 peak at 78 K shifted to 523 nm at 290 K.

3.2. Laser excitation spectra

The luminescence spectra obtained by the xenon lamp source were also observed with laser excitation. A drop in intensity with laser exposure time was also observed. This decrease in intensity was noticeable only

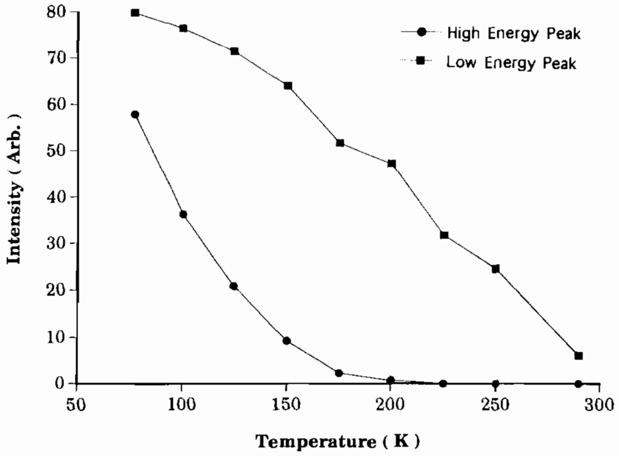

Fig. 2. Temperature dependence of the luminescence intensity for both the high energy peak at 463 nm and the low energy peak at 547 nm.

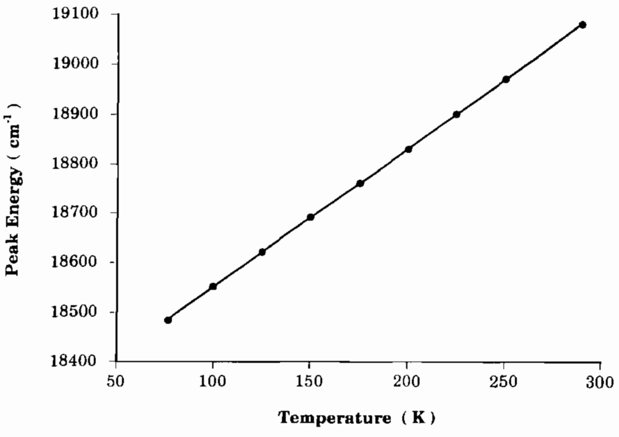

Fig. 3. Temperature dependence of the low energy luminescence peak energy vs. temperature.

at low temperatures (77 K) and could not be observed to any noticeable degree with the xenon lamp source.

In all cases the decrease in intensity was noticeable within a few minutes of laser exposure and continued throughout the experiments. The luminescence intensity could be brought back by warming the sample to room temperature and 'erasing' the laser's effects.

In the laser luminescence spectrum we again find peaks at 463 and 547 nm. The intensity of both peaks decreases with increasing laser exposure as shown in Fig. 4. The intensity after heating and cooling, the recovery intensity, was only 79% of the original intensity, and only 2% higher than the intensity after 60 min of exposure.

4. Discussion

4.1. Spectral assignments

For the $Pb[Au(CN)_2]_2$ luminescence spectra the 463 nm peak has been assigned as a Pb^{2+} ($6p \rightarrow 6s$) transition because of its similarity to the luminescence spectra for $Pb(NO_3)_2$. The 547 nm peak has been assigned as a $Au(CN)_2^-$ transition because of its resemblance [4] to the luminescence spectrum for $TlAu(CN)_2$.

Extended Hückel molecular orbital calculations [4] have been carried out for $Pb[Au(CN)_2]$ and are in agreement with the above luminescence peak assignments. Fig. 5 obtained from the EHMO calculations gives a plot of the potential energy of $Pb[Au(CN)_2]_2$ vs. the Pb–Au separation for a linear Au–Pb–Au geometry. The minimum in the potential energy curve shows that weak covalent Pb–Au interactions exist in this system as in $Tl[Au(CN)_2]_2$ [4]. X-ray studies are being carried out to determine the crystal space group of $Pb[Au(CN)_2]_2$.

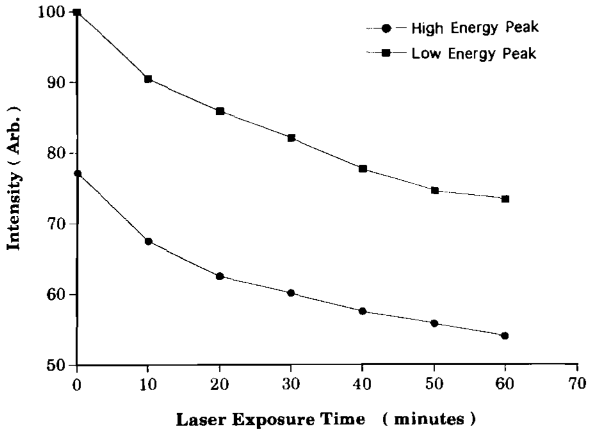

Fig. 4. Variation in the luminescence intensity of both the low energy and high energy peaks with increasing laser exposure for 337 nm excitation at a sample temperature of 78 K.

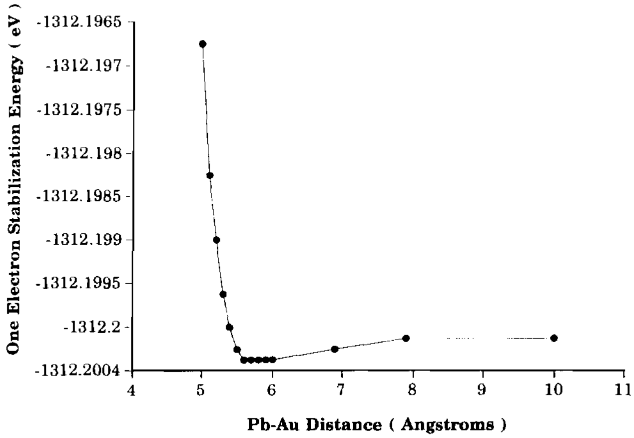

Fig. 5. A plot of the potential energy for $Pb[Au(CN)_2]_2$ vs. the Pb–Au separation distance.

4.2. Photochemical reaction

It is believed that laser excitation at 337 nm is resulting in a photochemical reaction with $Pb[Au(CN)_2]_2$. A non-luminescing species is created over a long period of laser exposure of 337 nm photons with a resulting decrease in luminescence intensity. We note that the peak assigned to Pb(II) decays along with the lower energy peak assigned to an Au transition. This indicates that both the Au(I) and the Pb(II) species are being changed to a non-luminescing form.

The mechanism proposed for the decrease in luminescence intensity with laser exposure time is as follows:

$$Au(CN)_2^- + h\nu(337\ \text{nm}) \longrightarrow Au(CN)_2^{x-} \qquad (1)$$

$$2Au(CN)_2^{x-} + Pb^{2+} \longrightarrow 2Au(CN)_2^{2-} + Pb^{4+} \qquad (2)$$

$$Au(CN)_2^{2-} \longrightarrow Au + 2CN^- \qquad (3)$$

The standard reduction potential of the system $Au(CN)_2^-/Au(CN)_2^{2-}$ is -0.6 V [8,9]. Upon excitation at 337 nm the excited $Au(CN)_2^-$ ion should be an extremely strong oxidizing agent ($E°$ for $Au(CN)_2^{x-}/Au(CN)_2^{2-} = 2.4$ V) sufficient to oxidize Pb^{2+} ($E°$ for $Pb^{4+}/Pb^{2+} \sim 1.7$ V) [10] in step (2). Step (3) of the mechanism [9] provides an irreversible step in the mechanism which prevents back-electron transfer in this solid state system at 78 K. Heating the solid to 300 K allows step (3) to become reversible and the result is that the original $Pb[Au(CN)_2]_2$ species can reform.

The importance of the reverse reaction rate for going back to the more stable initial species can be seen. At low temperatures the reverse rate is very slow compared to the photochemical decay step, leading to the creation of the normally unstable species. At higher temperatures, the reverse rate has increased to the point where it is so rapid no photochemical change can be seen to take place over several hours. Thus we can see that the slower the change at low temperatures, the quicker the recovery at higher temperatures due to the relative differences in reaction rates. The more unstable the species created the slower the photochemical decay and the quicker the recovery time.

5. Conclusions

In this study we synthesized the compound, $Pb[Au(CN)_2]_2$. Low temperature luminescence studies have been carried out for this compound. The luminescence peaks have been assigned based on comparison with the spectra of similar compounds and molecular orbital calculations.

The 337 nm laser excitation experiments have shown that photochemical effects occur for $Pb[Au(CN)_2]$ in which the Pb–Au luminescence intensity drops steadily with laser exposure at 77 K. The luminescence intensity can be recovered by increasing the temperature of the system to a point at which the stability of the non-luminescing species becomes unfavorable and reverts back to the original $Pb[Au(CN)_2]$ species. The photochemical reaction has been interpreted in terms of an electron transfer process in which Au(I) in an excited electronic state is reduced to Au(0). In the solid state lattice these species are stable unless the temperature is increased and, in this case, the original Pb(II) and Au(I) reforms.

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