Inorg. Chem. **2007**, *46*, 3798–3800

Inorganic Chemistry
Communication

Optical Memory and Multistep Luminescence Thermochromism in Single Crystals of $K_2Na[Ag(CN)_2]_3$

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Received February 3, 2007

Single crystals of the layered compound $K_2Na[Ag(CN)_2]_3$ exhibit a dual emission with high-energy (HE) and low-energy (LE) phosphorescence bands at 313 and 402 nm, respectively. Remarkably, the crystals exhibit "optical memory", in which a new emission band with intermediate energy (IE) at 380 nm is generated upon laser irradiation ($\lambda_{ex} = 266$ nm) at cryogenic temperatures. The irradiated crystals reinstate their original luminescence spectrum upon heating to room temperature and then recooling. In addition to these unusual "write/read/erase" changes, the crystals also exhibit multistep luminescence thermochromism such that the LE/HE intensity ratio increases between 17 and 80 K but then decreases upon further heating. The unprecedented occurrence of both novel phenomena in one compound has been related to reversible photophysical changes instead of irreversible photochemical changes.

Molecular materials that can exhibit reversible changes in their optical, magnetic, and/or electrical properties via application of external stimuli are invaluable for many applications. For example, data storage applications have been suggested for organic films that exhibit "write/read/erase" properties by redox switching[1] and for transition-metal cluster complexes whose magnetic moments reverse sign by only slight changes in the applied field strength.[2] Coordination compounds of the d^{10} monovalent ions of group 11 constitute a promising class of molecular materials for the aforementioned applications because of the remarkable changes that they exhibit in their structure, bonding, and optomagnetoelectronic properties upon population of their low-lying excited states. For example, Zink and co-workers reported an "optical memory" effect for Cu^+- and Cu^+/Ag^+-doped β-alumina, in which the crystal "remembers" which part of it had been irradiated.[3] Ford and co-workers, on the other hand, showed that the clusters $Cu_4L_4X_4$ (L = aromatic amine; X = halide) exhibit "luminescence thermochromism" such that their luminescence color is reversibly altered with temperature due to changes in the relative intensities of X → L charge transfer and Cu_4-cluster-centered phosphorescence bands.[4] Here we show drastic reversible changes in both aforementioned phenomena in single crystals of one compound, $K_2Na[Ag(CN)_2]_3$.

The synthesis and crystal growth of $K_2Na[Ag(CN)_2]_3$ were performed by the reaction of a stoichiometric mixture of NaCN, KCN, and AgCN in an aqueous suspension followed by slow evaporation, following a published literature procedure.[5] The details of the luminescence experiments are described elsewhere.[6]

Figure 1 shows the changes in luminescence spectra of $K_2Na[Ag(CN)_2]_3$ crystals upon irradiation. Prior to laser irradiation, the crystals exhibit two emission bands with maxima at 313 and 402 nm, henceforth referred to as the HE (high energy) and LE (low energy) bands, respectively. Following exposure to 266 nm laser light for 20 min, a new emission band at an intermediate energy (IE) is generated with a maximum at 380 nm. This is accompanied by a significant decrease in the intensity of the HE band, while the LE band becomes no longer discernible. Remarkably, the luminescence excitation spectra (see the Supporting Information) undergo no change in their profile as a result of this experiment, suggesting that the ground-state structure of the crystals remains intact after irradiation. Hence, the changes in the luminescence spectra are deemed photophysical as opposed to photochemical in nature such that the structural changes resulting from irradiation last only for the lifetime of the excited states. Even more remarkable is that the crystals exhibit full hysteresis of their original lumines-

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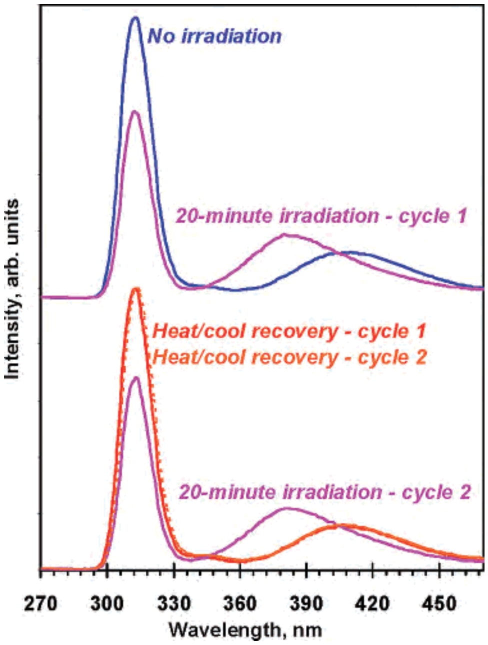

Figure 1. Luminescence spectra of $K_2Na[Ag(CN)_2]_3$ single crystals at 70 K before and after irradiation with 266 nm laser light. The results of a repetition of the same experiment are shown after the same sample was heated to room temperature and then cooled again to 70 K in the dark.

cence spectra after they are heated to ambient temperature and then cooled. Another cycle of irradiation → heating → cooling generated the same remarkable changes with a full recovery (Figure 1). Therefore, the "memory" effect exhibited by the irradiated crystals is "erased" upon heating to ambient temperature. These observations are reminiscent of those in doped materials of d^{10} systems reported by the Zink group in β-alumina[3] and by us in KCl matrixes.[6] The optical changes we report here have two important distinctions from the aforementioned precedents: (1) the active species are in single crystals of a pure material as opposed to being impurities in doped crystals, and (2) a new excimeric band is generated upon irradiation instead of changes in existing luminescence bands as the situation was in both the Zink work and our previous work on doped crystals.

Figure 2 shows the emission spectra of $K_2Na[Ag(CN)_2]_3$ vs temperature. The excitation spectra yield maxima near 290 and 250 nm regardless of the λ_{em} being monitored (see the Supporting Information). The temperature behavior of the two emission bands illustrates striking luminescence thermochromism that reverses its direction at ~80 K (Figure 2). Thus, the LE/HE intensity ratio increases upon heating in the 17 → 80 K range but decreases upon further heating. Multiple factors have been considered for the explanation of the striking changes in the luminescence spectra of $K_2Na[Ag(CN)_2]_3$ crystals upon temperature variation. Although the ~7300 cm^{-1} energy separation between the HE and LE bands is on the order of the S−T splitting for the Ag^+ ion[7] and although fluorescence and phosphorescence can both be exhibited simultaneously in d^{10} complexes,[8] we rule out the possibility of intersystem crossing from a singlet HE state

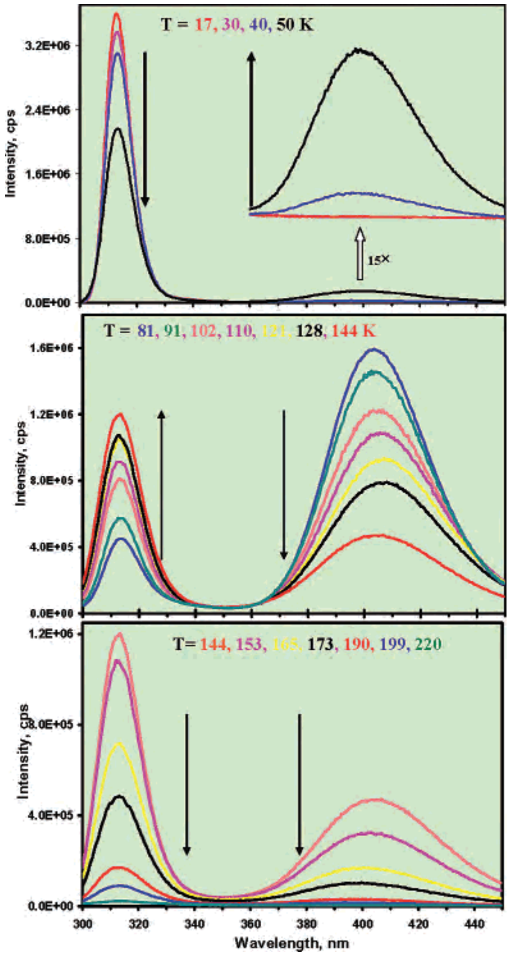

Figure 2. Luminescence spectra of $K_2Na[Ag(CN)_2]_3$ single crystals vs temperature.

to a triplet LE state because both bands exhibit microsecond lifetimes at all temperatures (e.g., $\tau_{86K} = 5.3 \pm 0.1$ and 20.8 $\pm$ 0.1 μs for HE and LE, respectively). Delayed fluorescence is also ruled out because such an emission usually exhibits the same lifetime as the corresponding phosphorescence while the emission bands here give rise to significantly different lifetimes at the same temperature and even different temperature dependence for each lifetime (see the Supporting Information for further lifetime data). Then we consider thermal contraction of Ag···Ag distances. Although such contractions are common for low-dimensional materials of closed-shell transition metals,[9] they usually lead to gradual and small red shifts for the same band upon cooling, while the changes here are in the relative intensities of two bands. Another reasonable cause considered is a discrete structural change (phase transition) near 80 K, the temperature at which the direction of the luminescence thermochromism trend changes. However, this possibility is ruled out based on a prior study for $K_2Na[Ag(CN)_2]_3$, in which no peak in the specific heat data vs temperature was seen.[10] Temperature-dependent neutron diffraction and Raman data suggest a

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monoclinic-to-pseudohexagonal gradual phase change but at temperatures >220 K (at which the solid does not luminesce); this is a new type of phase transition reported for the first time in ref 10. We adopt a change in the photophysical relaxation pathways between the HL and LE states as the correct model for the luminescence thermochromic changes. To further characterize this kinetic model, we have analyzed the changes in the intensity ratios (relative peak areas) with temperature and found that they follow an exponential behavior. Therefore, Arrhenius plots of ln(intensity ratio) vs $1/T$ give linear behavior with good correlation ($R^2 = 0.997$), from which an activation energy (E_a) of 268 cm^{-1} is calculated for the HE → LE forward relaxation up to 80 K. Similar plots for the LE → HE reverse relaxation above 80 K give R^2 and E_a values that depend on the upper temperature limit. Thus, we obtain $R^2 = 0.982$ and $E_a = 326\ \mathrm{cm}^{-1}$ for the entire 80−190 K data, while a better fit ($R^2 = 0.998$) with $E_a = 242\ \mathrm{cm}^{-1}$ is obtained when the analysis is limited to the 80−128 K data, probably because of less competition by multiphonon deexcitation to the ground state because such a process becomes more dominant at higher temperatures. Radiationless processes from lower-energy to higher-energy states are not uncommon in luminescent materials at relatively high temperatures.[11] The LE state is more amenable to multiphonon deexcitation to the ground state than the HE band (Energy Gap Law considerations), which is likely a contributing factor in the reversal of the luminescence thermochromism in the highest-temperature range. It is surprising, however, that the E_a value for the LE → HE process is much lower than the energy difference between the HE and LE states (~7000 cm^{-1}). We propose that the radiationless HE $\leftrightarrow$ LE relaxation processes occur from the vertical Franck−Condon states instead of the potential minima. The accompanied curve crossing at the Franck−Condon states of the HE and LE bands is consistent with the spectral observation that the excitation spectra monitoring either emission are rather similar (Figure S2 in the Supporting Information). The low E_a values above (~300 cm^{-1}) are easily surmountable, even by some single phonons in this system (e.g., $\nu_{\mathrm{C-N}}$ ~2300 cm^{-1}), which facilitates the interesting spectral changes observed.

The unstructured emission profile, even for crystals at 17 K, and the large separation from the excitation bands, combined with the general band assignments that we established in numerous publications for $[\mathrm{Ag(CN)_2}]^-$ materials,[6,12] lead us to assign the emission bands of $\mathrm{K_2Na[Ag(CN)_2]_3}$ crystals to excimeric $^*[\mathrm{Ag(CN)_2}^-]_n$ clusters with $n \geq 2$. The Ag−Ag bonding in the proposed excited-state structure is localized on excimeric clusters that are separated from one another, as opposed to having a uniform delocalized compression of Ag−Ag distances in all complexes in each two-dimensional sheet. Each of the HE, LE, and IE emission bands is, therefore, assigned to a different excimeric cluster with characteristic "n", geometry, and/or conformation. While the identity of the exact excimeric species responsible for each emission cannot be definitively assigned without a direct excited-state structural study, the structures in Figure 3 are consistent with those in our previous investigations, which suggest that the relative emission energies follow the order: linear trimer < bent trimer < dimer.[6,12] It is not unusual that oligomeric M−M-bonded excimeric species are responsible for the emission in a d^{10} solid material with packing due to extended M···M intermolecular interactions. Indeed, Coppens and co-workers have shown via time-resolved X-ray diffraction that discrete dimeric species are responsible for the phosphorescence of a trinuclear $\mathrm{Cu^I}$ complex that packs with extended Cu···Cu interactions in the ground state.[13] Thus, the model in Figure 3 is reasonable.

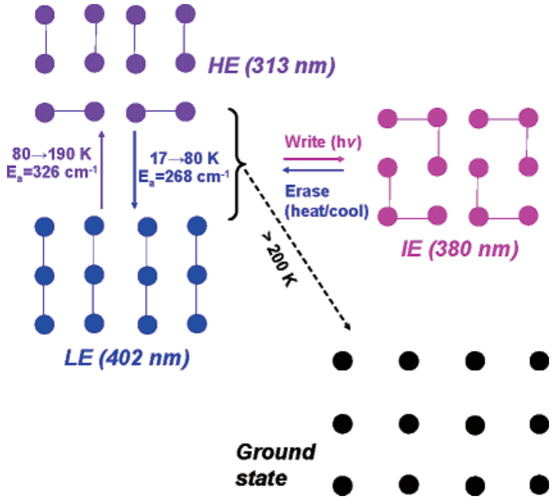

Figure 3. Proposed model for the changes in the molecular structure of Ag clusters in the relevant electronic states upon irradiation and temperature variation of $\mathrm{K_2Na[Ag(CN)_2]_3}$ crystals.

In summary, remarkable luminescence changes have been observed for the layered compound $\mathrm{K_2Na[Ag(CN)_2]_3}$ involving "optical memory" and luminescence thermochromic changes. Because these phenomena occur reversibly in pure (undoped) crystals of one compound, potential applications in data storage and temperature sensing are anticipated for $\mathrm{K_2Na[Ag(CN)_2]_3}$ and similar compounds we are pursuing that behave likewise.

Acknowledgment. This research is supported by NSF (Grant CHE-0315877 to H.H.P. and CAREER Award CHE-0349313 to M.A.O.), the Welch Foundation (Grant B-1542 to M.A.O.), and the Department of Energy (Award DE-FC26-06NT42856 to M.A.O.).

Supporting Information Available: Additional spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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