the unusual reactivity of the dimers.[20] In particular, the nature of the contribution of the sulfur p orbitals to the LUMO of the Mo(IV) complexes is consistent with the extensive reactivity of the sulfido ligands in these dimers with hydrogen and with unsaturated molecules. The studies reported here confirm the validity of the molecular orbital description of these systems. The electronic and EPR spectra and the cyclic voltammetric data for the Mo(III)/Mo(IV) tetrasulfur-bridged derivatives provide evidence for delocalization of the unpaired electron over two equivalent molybdenum ions. The EPR results for the anionic Mo(III)/Mo(IV) complexes, which show hyperfine coupling to the counterions presumably as a result of the ions' interaction with sulfido ligands, provide the first spectral corroboration for the proposed description of the reactive b_{2g} frontier molecular orbital in these dimers.

Experimental Section

Materials. Tetrahydrofuran was distilled from calcium hydride prior to use. Dichloromethane was distilled over P_2O_5 or passed through an activated alumina column. Acetonitrile was dried over calcium hydride, filtered, and distilled from P_2O_5. Spectral grade acetone and methanol were used without further purification. Potassium graphite was obtained from Alfa, and dry NaH was purchased from Aldrich.

Physical Measurements. EPR spectra were recorded on a Varian E-109 X-band spectrometer. The *g* values were measured relative to solid DPPH ($g = 2.0036$). Air-sensitive solutions of $(MeCpMo)_2(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2$, $[(MeCpMo)(\mu\text{-}SCH_3)(\mu\text{-}S)]_2^-$, and $[MeCpMo(\mu\text{-}S)]_2S_2CH_2^-$ were transferred to an EPR tube fitted with a ground-glass stopper under a nitrogen atmosphere in a Vacuum Atmospheres glovebox. EPR spectra were recorded immediately. The simulated EPR spectra were generated with use of a first-order spin Hamiltonian. The absorption spectra due to the various isotopic and spin possibilities were superimposed with the appropriate population factors. A Lorentzian line shape function (line width 1 G for $(I^-)Na^+$, line width 2.6 G for $(I^-)K^+$) was used. Finally the absorption spectra were numerically differentiated to obtain the spectra plotted in Figures 4 and 5.

Electronic spectra were obtained in matched cells with Cary 14 and Cary 219 spectrophotometers. Air-sensitive solutions were transferred to a cell fitted with a Kontes high-vacuum valve under a nitrogen atmosphere in a Vacuum Atmospheres glovebox. Spectra were recorded immediately.

Syntheses. The syntheses of the Mo(IV),[2-4] Mo(III),[4,8,13] and cationic[8,13] and neutral[4] mixed-valence dimers were carried out according to literature methods. The anionic mixed-valence dimers were generated in solution as described below.

$[MeCpMo(\mu\text{-}S)(\mu\text{-}SCH_3)]_2K$ ($(III^-)K^+$). THF and CH_3CN Solutions of the title complex were generated in a glovebox by reduction of solutions of $[MeCpMo(\mu\text{-}S)(\mu\text{-}SCH_3)]_2$ (III) with excess KC_8. The reduced teal blue solutions were filtered through a glass wool plug before spectral analysis. Comparison of the visible absorption spectra for the neutral and anionic derivatives served as a check on the completeness of reduction. The purity of the anion was inferred from its spectroscopically observed quantitative oxidation to the neutral starting material upon exposure to air.

$[MeCpMo(\mu\text{-}S)]_2S_2CH_2^-$ (I^-). THF and CH_3CN solutions of the title anion were generated in a glovebox by reduction of solutions of $[MeCpMo(\mu\text{-}S)]_2S_2CH_2$ (I) with excess KC_8 or NaH. The green solutions were filtered through a glass wool plug before spectral analysis. Exposure of THF solutions of the anion to air resulted in oxidation to neutral starting material. However, under these conditions the starting material undergoes partial further oxidation to an unidentified yellow complex. Since the starting material was not regenerated quantitatively, it was difficult to determine whether or not a small amount of air oxidation of the anion had taken place before electronic spectra were recorded. The reported extinction coefficients are lower limits, with estimated errors of <20%.

Acknowledgment. This work has been supported by the National Institutes of Health, by the National Science Foundation, and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. M.R.D. is grateful for a fellowship from the John Simon Guggenheim Foundation, 1984–1985. We are grateful to A. K. Rappé for providing us with the EPR simulation program.

Registry No. I, 85565-70-4; $(I^-)Na^+$, 99510-47-1; $(I^-)K^+$, 99495-31-5; II, 99510-48-2; $(II^+)I^-$, 99510-49-3; $(II^-)K^+$, 99495-28-0; III, 99495-27-9; $(III^-)K^+$, 99495-22-4; IV, 99495-29-1; $(IV^+)BF_4^-$, 99495-24-6; V, 99495-30-4; $(V^+)BF_4^-$, 99495-26-8.

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Host-to-Guest, Excited-State Energy Transfer in Lamellar Solids. Photoluminescent Properties of Hydrated Europium Uranyl Phosphate

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Received July 23, 1985

Hydrogen uranyl phosphate (HUP) undergoes complete exchange with Eu^{3+} ions to yield a hydrated, lamellar solid of approximate composition $Eu_{1/3}UO_2PO_4$ (EuUP). An X-ray powder pattern of the solid indicates the presence of a single phase, which indexes in tetragonal symmetry with an interlamellar spacing of ~10.2 Å. Exclusive excitation of the host UO_2^{2+} chromophore leads to photoluminescence (PL) from both excited UO_2^{2+} and Eu^{3+}, indicative of host-to-guest, excited-state energy transfer. From radiative quantum yields and time-resolved PL measurements, energy transfer is estimated to occur with nearly unit efficiency at a rate of $\sim 2 \times 10^5$ s^{-1}. High-resolution PL data obtained at 12 K indicate that the Eu^{3+} ions can occupy multiple lattice sites in EuUP.

Introduction

The rich diversity of intercalation chemistry[1] has prompted us to explore the excited-state properties of lamellar solids. We recently reported on the photoluminescence (PL) of the layered compound hydrogen uranyl phosphate (HUP), $HUO_2PO_4 \cdot 4H_2O$, and of solids derived therefrom by cationic substitution.[2-4] A partially substituted solid, $H_{0.7}[Cr(NH_3)_6]_{0.1}UO_2PO_4 \cdot 6H_2O$ (HCrUP), provided evidence for efficient host-to-guest energy transfer: excitation of the host UO_2^{2+} chromophore yielded PL and an aquation reaction characteristic of the guest Cr(III) complex.[3,4]

Our results with HCrUP prompted us to examine whether other classes of trivalent cations capable of involvement in energy-transfer processes could be incorporated into lamellar solids derived from HUP. Lanthanon ions are attractive candidates in this regard. Our initial choice for such studies was Eu(III), since energy transfer from UO_2^{2+} to Eu^{3+} ions is well documented in a variety of media including solutions,[5] solids having the perovskite

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(1) For an overview, see: "Intercalation Chemistry"; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982.

(2) Olken, M. M.; Biagioni, R. N.; Ellis, A. B. *Inorg. Chem.* **1983**, *22*, 4128.

(3) Olken, M. M.; Ellis, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 7468.

(4) Olken, M. M.; Verschoor, C. M.; Ellis, A. B. *J. Lumin.* **1984**, *31/32*, 552.

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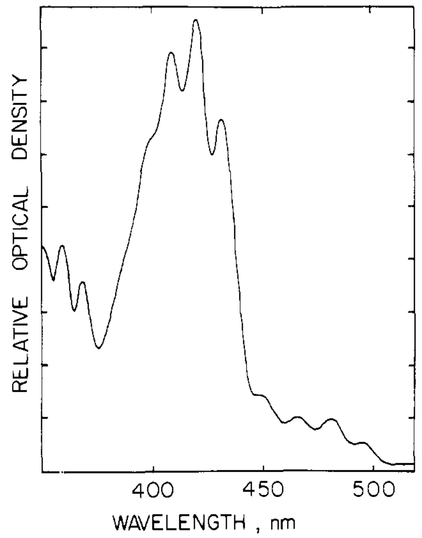

Figure 1. Absorption spectrum of EuUP. The absorption spectrum was obtained by spreading a silicone grease mull of the solid on filter paper; silicone grease on filter paper served as a reference.

structure,[6] glasses,[7] and zeolites.[8]

We report in this paper that HUP can be fully substituted with a trivalent lanthanon ion to yield a layered solid, hydrated $Eu_{1/3}UO_2PO_4$ (EuUP), with novel emissive properties. Specifically, we find that this compound exhibits efficient host-to-guest, excited-state energy transfer, with excitation of the UO_2^{2+} chromophore leading to PL characteristic of the intercalated Eu^{3+} ion. Moreover, high-resolution, 12 K PL spectra reveal that Eu^{3+} ions can occupy multiple lattice sites in EuUP.

Results and Discussion

Powdered samples of EuUP are readily prepared and characterized under ambient conditions. In sections below, we describe the synthesis and structure of this solid and its 295 and 12 K PL properties.

Synthesis and Structure. Samples of EuUP were prepared by slurrying HUP in an aqueous $Eu(NO_3)_3$ solution at 40 °C for several hours. After workup, the resulting yellow solid was characterized by an X-ray diffraction powder pattern. The pattern could be indexed in tetragonal symmetry and indicated the presence of a single phase. The *a*-lattice value of 6.99 Å matches that of single-crystal HUP;[9] the interlamellar spacing, however, is 10.2 Å, indicative of swelling relative to the HUP lattice (8.69-Å spacing[2,9]). An IR spectrum of the solid (KBr pellet) also supports retention of the lamellar structure: a strong band at 1000 cm^{-1}, characteristic of the waffle-like $[UO_2PO_4]_n^{n-}$ sheets of HUP and its derivatives, is observed. An elemental analysis of the solid shows it to be hydrated with a U:Eu ratio of 3:1, corresponding to full substitution of Eu^{3+} for H^+. The sites that the Eu^{3+} ions occupy in EuUP are not presently known, although 12 K PL data show that multiple sites exist in the lattice at that temperature (vide infra).

With regard to hydration, elemental analysis indicated the presence of at least four waters of hydration. The exact quantity varied among samples but resulted in only modest variations in excited-state properties. Attempts to dehydrate the solid by heating above ~45 °C resulted in loss of the lamellar structure.

An electronic spectrum of EuUP at 295 K is displayed in Figure 1. The spectrum exhibits vibronic structure characteristic of the UO_2^{2+} moiety and is similar in appearance to the HUP spectrum.[2] Interestingly, however, the band maximum at ~420 nm is somewhat blue-shifted relative to its position at 428 nm in HUP, perhaps reflecting a local distortion about the uranyl ion caused by the intercalated Eu^{3+} ions. We were unable to directly observe the weak absorption bands of the lanthanon ion.

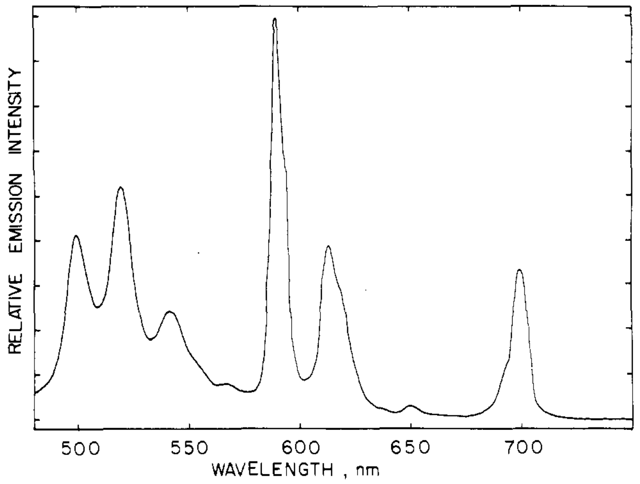

Figure 2. Uncorrected PL spectrum of EuUP at 295 K. The front-surface PL was obtained for the solid by exciting at 436 nm.

PL Properties at 295 K. The color of EuUP PL varies considerably with gross changes in hydration. Upon air-drying, EuUP displays weak yellow PL under a blacklight. Heating the solid to ~45 °C to induce dehydration produces reddish PL, albeit with loss of the lamellar structure (vide supra). The 295 K PL spectrum of air-dried EuUP, Figure 2, provides evidence for host-to-guest energy transfer. With exclusive excitation of the UO_2^{2+} chromophore, the spectrum is a composite of structured host UO_2^{2+} (~500–550 nm) and guest Eu^{3+} (~580–710 nm) luminescence; the PL from Eu^{3+} is characteristic of the ion, with the bands assignable to transitions from the ^5D excited state to the ^7F ground state.[10] Besides expression in the PL spectrum, energy transfer is also evident from an excitation spectrum for Eu^{3+} PL (monitored at 690 nm), which exhibits UO_2^{2+} vibronic bands matching those in the EuUP absorption spectrum.

Radiative quantum yields, ϕ_r, and lifetimes, τ, also demonstrate guest quenching of host PL. A typical value of ϕ_r for UO_2^{2+} PL is 0.02 with 436-nm excitation, a substantial reduction from the HUP value of ~0.7.[2] For Eu^{3+} PL in EuUP, we measured ϕ_r to be ~0.01–0.02.

Lifetime data, acquired with 450-nm excitation from a N_2-pulsed dye laser, evidence guest quenching comparable to that inferred from ϕ_r results. Thus, τ for UO_2^{2+} PL, monitored at 515 nm, is ~6 μs compared to ~450 μs in HUP.[2] The exponential decay observed permits calculation of the radiative (ϕ_r/τ) and nonradiative ($\tau^{-1} - \phi_r\tau^{-1}$) unimolecular rate constants as being $\sim 3 \times 10^3$ and 2×10^5 s^{-1}, respectively. The radiative constant is similar to that of HUP and several of its mono- and divalent-substituted derivatives.[2] For HUP, the nonradiative rate constant is $\sim 7 \times 10^2$ s^{-1}. Assuming that this value, like its radiative counterpart, is unaffected by the presence of Eu^{3+} ions, the energy-transfer rate can be estimated as being essentially the calculated nonradiative rate, $\sim 2 \times 10^5$ s^{-1}. As the dominant rate for decay of the excited UO_2^{2+} ion, this value implies that energy transfer approaches unit efficiency and that the Eu^{3+} PL is relatively inefficient. The low ϕ_r value for Eu^{3+} PL likely reflects effective nonradiative relaxation via the interlamellar water molecules.[10] Temporal features of the Eu^{3+} PL in EuUP, shown in Figure 3, provide evidence of this relaxation as well as of energy transfer. We find that the Eu^{3+} PL initially rises after pulsed excitation, then decays with a lifetime of ~120 μs, a value in the range observed for other solids in which Eu is coordinated to at least six H_2O molecules.[11] The rise time of Eu^{3+} PL is ~6 μs,

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(5) Tanner, S. P.; Vargenas, A. R. *Inorg. Chem.* **1981**, *20*, 4384 and references therein.
(6) Blasse, G.; Krol, D. M. *J. Lumin.* **1981**, *22*, 389.
(7) Reisfeld, R.; Lieblich, N.; Boehm, L.; Barnett, B. *J. Lumin.* **1976**, *12/13*, 749.
(8) Suib, S. L.; Carrado, K. A. *Inorg. Chem.* **1985**, *24*, 200.
(9) Morosin, B. *Phys. Lett. A* **1978**, *65A*, 53.
(10) Horrocks, W. DeW., Jr.; Albin, M. *Prog. Inorg. Chem.* **1984**, *31*, 1.
(11) Horrocks, W. DeW., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334.

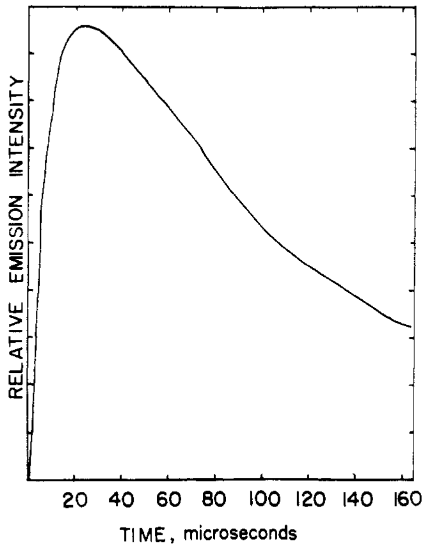

Figure 3. Plot of (PL intensity) vs. time for solid EuUP. The sample was excited at 450 nm, and Eu^{3+} PL was detected at 690 nm.

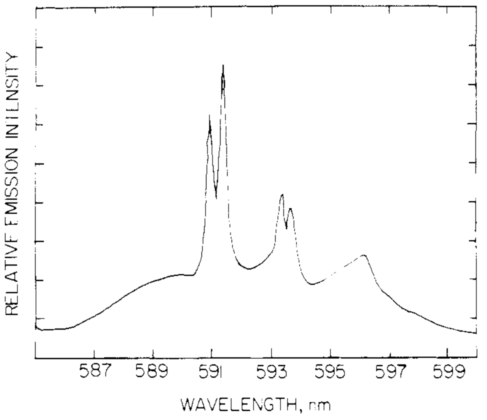

Figure 4. Uncorrected PL spectrum of EuUP ($^5D_0 \rightarrow {}^7F_1$ spectral region) at ~12 K. The front-surface PL was obtained for the solid by exciting at 457.9 nm.

virtually identical with the decay time of UO_2^{2+} PL, as expected for host-to-guest energy transfer.

PL Properties at 12 K. At 12 K, the Eu^{3+} PL displays resolvable fine structure, shown in Figure 4 with excitation of the UO_2^{2+} chromophore at 457.9 nm, which, in principle, permits an assessment of the number and symmetry of lattice sites occupied by the Eu^{3+} ions in EuUP.

The region between 585 and 599 nm shown in Figure 4 corresponds to the $^5D_0 \rightarrow {}^7F_1$ transition. For a given lattice site, such a transition will be characterized by one, two or three bands as the site symmetry descends from cubic to hexagonal (or tetragonal) and then to lower symmetries.[12] The pattern shown in Figure 4, which contains five resolvable bands, thus corresponds to multiple lattice sites in EuUP. We attempted to more precisely identify the number of lattice sites and their symmetries by exciting between 525 and 527 nm, the region corresponding to the $^7F_0 \rightarrow {}^5D_1$ absorption bands of Eu^{3+} sites. However, our excitation source was of insufficient resolution (3 Å) to carry out the site-selective excitation experiments which can be used to determine band groupings. The $^5D_0 \rightarrow {}^7F_0$ transition provides another means for identifying the number of Eu^{3+} sites, since only a single transition will be observed for each site. These transitions are weak, however, and we were unable to observe them in EuUP with our instrumentation. Thus, in the absence of better spectroscopic data, all that we can conclude at this point is that at least two Eu^{3+} lattice sites are present in EuUP at 12 K.

Summary

HUP can be fully substituted with a trivalent lanthanon ion, Eu^{3+}. The resulting solid, EuUP, exhibits PL characteristic of excited Eu^{3+} and UO_2^{2+} from excitation of the host UO_2^{2+} chromophore. Energy transfer to Eu^{3+} ions proceeds with nearly unit efficiency at 295 K at a rate of $\sim 2 \times 10^5$ s^{-1}. At 12 K, high-resolution spectroscopic data indicate that the Eu^{3+} ions occupy multiple lattice sites in EuUP.

Experimental Section

Materials and Syntheses. All chemicals were analytical reagent grade and were used as received. Starting materials included $UO_2(NO_3)_2 \cdot 6H_2O$ from Fisher, H_3PO_4 from Mallinckrodt, and $Eu(NO_3)_3 \cdot 5H_2O$ from Aldrich. All manipulations were carried out in air. HUP was prepared as described previously from $UO_2(NO_3)_2 \cdot 6H_2O$ and H_3PO_4.[2] This compound underwent ion exchange with Eu^{3+} ions by modification of a literature procedure.[13] In a typical synthesis, EuUP was prepared by slurrying ~2 g of HUP in 100 mL of a 0.3 M aqueous $Eu(NO_3)_3$ solution at 40 °C for ~2 h. The resulting yellow solid was washed with triply distilled water, air-dried for ~6 h, and then stored in a tightly stoppered vial. Microanalyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. The analysis shows the product to be a hydrated solid with a U:Eu ratio of 3:1 (two samples yielded ratios of 3.07 and 3.05:1; a partially dehydrated sample gave a ratio of 3.00:1), corresponding to essentially full substitution of Eu^{3+} for H^+. An X-ray diffraction powder pattern of the solid, obtained as described previously,[2] was indexed in tetragonal symmetry with a *c*-lattice value derived from 00*l* data of ~10.2 Å; the *a*-lattice value was 6.99 Å, the value reported for single-crystal HUP.[9]

Spectra. IR spectra were taken on a Beckman Model IR 4250 instrument using KBr pellets. Electronic absorption spectra were obtained on a Cary 17D UV–vis–near-IR spectrophotometer by spreading a silicone grease (Dow-Corning high-vacuum grease) mull of the solid on filter paper; silicone grease on filter paper served as a reference. Uncorrected 295 K emission and excitation spectra at low resolution (6 nm) were acquired with an Aminco-Bowman spectrophotofluorimeter and red-sensitive PMT, which used "head-on" excitation with the instrument's Xe lamp, as described previously.[2] Uncorrected 12 K PL spectra at higher resolution (0.4 nm) were obtained with the 457.9-nm line of an Ar^+ laser, an Air Products Displex Model CSW-202 closed-cycle cryocooler, a McPherson Model 270 0.35-m monochromator, equipped with both a grating blazed at 500 nm and an R928 PMT, and a Keithley picoammeter. Spectra were displayed on a Houston Model 2000 X-Y recorder. The PL signal was fed to the McPherson monochromator by a fiber optic cable. Samples were enclosed in sealed Pyrex tubes to prevent exposure to vacuum. Low incident intensities were used to minimize sample heating.

Emissive Quantum Yields and Lifetimes. Values of ϕ_r for both the Eu^{3+} and UO_2^{2+} PL of EuUP were obtained with the Aminco-Bowman instrument by using techniques described previously.[2] Values of τ were acquired at 295 K with 450-nm excitation from an NRG N_2-pulsed dye laser system.[2]

Acknowledgment. We are grateful to the National Science Foundation for support of this work. Professors J. C. Wright and H. G. Brittain, Dr. Mark Valentini, John Wietfeldt, and Christine Capitano are thanked for experimental assistance and helpful discussions.

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(12) Wybourne, B. G. "Spectroscopic Properties of Rare Earths"; Interscience: New York, 1965; p 179.

(13) Weigel, F.; Hoffmann, G. *J. Less-Common Met.* **1976**, *44*, 99.