Significant structural differences exist between the poly-[Zn(vbpy)$_3$]$^{2+}$ and poly-[M(vbpy)(COD)]$^+$ films which apparently arise from differences in the structural demands imposed by the metal complex sites. That is, the poly-[M(vbpy)(COD)]$^+$ films are necessarily linear-strand polymers while the poly-[Zn(vbpy)$_3$]$^{2+}$ films can be extensively cross-linked. These structural differences are expressed in the coordination chemistry of the metal ion free films. For example, less than 10% incorporation of Fe^{II} sites occurs in metal-free films prepared from poly-[Rh(vbpy)(COD)]$^+$. Conversely, less than 30% incorporation of Rh^I sites occurs in metal-free films prepared from poly-[Zn(vbpy)$_3$]$^{2+}$. Thus, the use of an electropolymerizable metal precursor of a given coordination geometry creates a permanent structural template in the film that results only in rapid exchange of metal ions with similar coordination properties.

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Interlamellar Liebig Titration Based on Photoluminescence. Reaction of Silver Uranyl Phosphate with Hydrogen Cyanide Gas

Sir:

The photoluminescence (PL) exhibited by the lamellar solid hydrogen uranyl phosphate, $HUO_2PO_4 \cdot 4H_2O$ (HUP), and its derivatives is proving to be a valuable probe of intercalation chemistry and host–guest interactions.[1,2] An important feature of the structure of HUP is that it consists of wafflelike layers of $(UO_2PO_4)_n^{n-}$ that are separated by sheets of water, which contain the charge-balancing protons.[3] It occurred to us that these sheets are essentially two-dimensional aqueous acidic solutions that might mediate acid–base/precipitation chemistry.

In this paper, we demonstrate the interlamellar equivalent of the Liebig titration:[4] AgCN can be precipitated from the solid–gas reaction of $AgUO_2PO_4 \cdot 3H_2O$ (AgUP) with HCN. Moreover, the AgCN undergoes hydrolysis with the reaction medium to establish an equilibrium whose equilibrium constant can be estimated from changes in PL accompanying the reaction.

As reported previously, AgUP is nonemissive at 295 K.[1,5] When AgUP is exposed to gaseous HCN, the solid emits the characteristic yellow-green color of HUP[1] with an intensity that increases with partial pressure, P_{HCN}.[6] The PL lifetime increases with P_{HCN} and approaches that of HUP,[1] suggesting the presence of Ag-substituted HUP. The emissive changes are reversible: removal of the HCN gas causes the PL to vanish over a period of several hours.

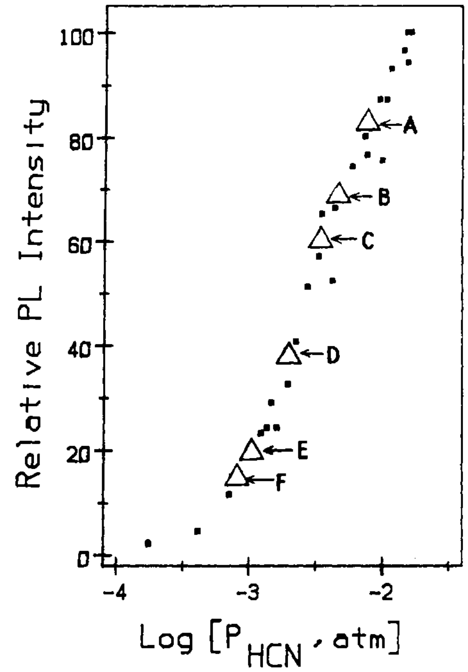

Figure 1. PL intensity at 525 nm of a sample of silica-dispersed $AgUO_2PO_4$ as a function of the partial pressure of HCN gas. Data, represented by the squares, were obtained in random order and are plotted relative to the maximum PL value observed at high P_{HCN}. Points labeled A–F are "doped" samples of $H_{1-x}Ag_xUO_2PO_4$ whose compositions are given in Table I. Their placement on the plot is described in the text.

Under a partial pressure of HCN, an X-ray powder diffraction pattern[7] exhibits broad, weak reflections of AgCN[8] and confirms the presence of an HUP-like phase: the interlamellar spacing increases from its value of 8.47 Å in AgUP to 8.70 Å, the value observed for HUP.[1] Intermediate spacings are observed for solids prepared by partial intercalation of Ag^+ ions into HUP, indicating the formation of hydrated solid solutions, $H_{1-x}Ag_xUO_2PO_4$.

Collectively, these data are consistent with eq 1, omitting waters of hydration; eq 1 is idealized in that the lamellar compounds are

$$AgUO_2PO_4(s) + HCN(g) \rightleftharpoons HUO_2PO_4(s) + AgCN(s) \qquad (1)$$

$H_{1-x}Ag_xUO_2PO_4$ solid solutions. The X-ray powder data suggest that AgCN has precipitated onto the surface of the crystallites. That HCN can coax the Ag^+ ions from the interlamellar region of AgUP is not surprising, given the known mobility of Ag^+ and the high ionic conductivity of HUP and its derivatives.[9]

The PL changes accompanying eq 1 permit the construction of a titration curve, relating PL intensity to P_{HCN}; in order to increase the surface area of AgUP, thereby increasing the reaction rate, we dispersed the solid by grinding it with silica.[10] Figure 1 presents typical titration data at 295 K. These data permit extraction of the equilibrium constant for eq 1, K_1, once the residual concentration of Ag^+ ions in the lattice has been determined for points on the curve. This is accomplished by preparing

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(1) Olken, M. M.; Biagioni, R. N.; Ellis, A. B. *Inorg. Chem.* **1983**, *22*, 4128.
(2) Rosenthal, G.; Ellis, A. B. *J. Am. Chem. Soc.* **1987**, *109*, 3157.
(3) Morosin, B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3732.
(4) See, for example: Butler, J. N. *Ionic Equilibrium, A Mathematical Approach*; Addison-Wesley: Reading, MA, 1964; p 280.
(5) Anal. Calcd for AgH_6O_9PU($AgUO_2PO_4 \cdot 3H_2O$): Ag, 20.47; P, 5.88. Found (Schwarzkopf): Ag, 20.08; P, 5.97.
(6) All experiments were conducted in a glass and Tygon flow system. The partial pressure of HCN (Matheson; 1.62% HCN in N_2 mixture) was varied by adjusting the tank flow rate as it was mixed with a stream of pure N_2. Both gas streams were saturated with water vapor to prevent sample dehydration. PL spectra were recorded with an Aminco-Bowman spectrophotofluorimeter.
(7) A Nicolet I2 powder diffractometer was employed; the sample was sealed under a polypropylene cover.
(8) "JCPDS Powder Diffraction File, Inorganic Phases"; International Center for Diffraction Data: Swarthmore, PA, 1986; File 23-1404.
(9) Pham-Thi, M.; Colomban, Ph. *Solid State Ionics* **1985**, *17*, 295 and references therein.
(10) An ~0.1-g 1:1 mixture of AgUP and silica (325 mesh; Sargent-Welch) was employed.

Table I. Properties of $H_{1-x}Ag_xUO_2PO_4$ Samples[a]

sample	$10^4X_{Ag^+}$[b]	10^3P_{HCN},[c] atm	$10^{-6}K_1$,[d] atm^{-1}
A	0.87	8.2	1.4
B	1.1	4.6	2.0
C	1.9	4.0	1.3
D	2.3	2.1	2.0
E	6.7	1.1	1.1
F	9.2	0.89	1.2

[a] Samples of the "doped" solids were prepared by intercalative ion-exchange reactions, described in ref 1. [b] The silver content of the doped solids, expressed as a mole fraction, was determined from PL properties after acid dissolution, as described in ref 11. [c] The partial pressure of HCN that produces the same relative amount of PL intensity in a $AgUO_2PO_4$ (AgUP) sample as observed in the doped sample, thereby providing an estimate of the residual Ag^+ content in the AgUP sample (see text). The values of P_{HCN} corresponding to the doped samples have been labeled in Figure 1. [d] The equilibrium constant for eq 1, calculated by using eq 2 and the corresponding values in the table.

a family of standards, $H_{1-x}Ag_xUO_2PO_4$, having known small concentrations of Ag^+.

The points labeled A–F in Figure 1 are samples of HUP that have been "doped" with Ag^+[1,11] and then exposed to HCN gas. The relative increase in PL intensity in passing from $P_{HCN} = 0$ to the saturation value[12] of P_{HCN} serves to locate the point on the curve of Figure 1. An expression for K_1,[13] eq 2, is obtained for these standards from P_{HCN} and the H^+ and Ag^+ mole fractions; for our PL data, X_{H^+} can be approximated as unity. Substitution of the Figure 1 data into eq 2 yields a consistent value for K_1 of $\sim 1.5 \times 10^6$ atm^{-1}, as shown in Table I.

$$K_1 = X_{H^+}(P_{HCN}X_{Ag^+})^{-1} \qquad (2)$$

It is instructive to compare K_1 with solution data. Equation 1 can be obtained by adding eq 3 and 4, where the compounds

$$Ag^+(aq) + HCN(g) \rightleftharpoons H^+(aq) + AgCN(s) \qquad (3)$$

$$AgUO_2PO_4(s) + H^+(aq) \rightleftharpoons HUO_2PO_4(s) + Ag^+(aq) \qquad (4)$$

in eq 4 are $H_{1-x}Ag_xUO_2PO_4$ solid solutions. Reported values of K_{eq} for eq 3, K_3, range from 6.6×10^5 to 7.4×10^7 atm^{-1}.[14,15] We have measured K_{eq} for eq 4, K_4, to be ~ 0.3,[16] so that reasonable agreement is obtained between K_1 and K_3K_4.

In summary, the reaction of AgUP with HCN gas illustrates the ability of a lamellar solid to serve as a medium for a classical analytical titration and to act as a chemical sensor. The techniques described herein should permit a broad variety of aqueous acid-base/precipitation reactions to be mimicked in a lamellar matrix.

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(11) The mole fraction of Ag^+ in the doped samples was determined by dissolving them in HNO_3, measuring their PL intensity and lifetime, and comparing these values to those of standards that fit Stern–Volmer quenching behavior. Quenching of UO_2^{2+} PL in solution by Ag^+ ions has been reported previously: see Marcantonatos, M. D. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2252.

(12) The saturation value was the tank HCN concentration of $\sim 1.6 \times 10^{-2}$ atm; however, the PL intensity did not increase noticeably even when the system was exposed to pure HCN.

(13) We treat the solid as an ion-exchange host. See: Bard, A. J. *Chemical Equilibrium*; Harper & Row: New York, 1966; p 143.

(14) Rossini, F. D. "Selected Values of Chemical Thermodynamic Properties"; Circular 500; U.S. Government Printing Office: Washington, DC, 1952; pp 222, 229, 594.

(15) *CRC Handbook of Chemistry and Physics*, 65th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1984; p D-51.

(16) After samples of HUP had come to equilibrium with aqueous $AgNO_3$ solutions, the concentration of Ag^+ remaining in solution was measured with a Ag ion electrode.

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Articles

Contribution from the Departments of Chemistry, Faculty of Education, Mie University, Tsu, Mie 514, Japan, and Nara University of Education, Takabatake-cho, Nara, Japan

Binuclear Complexes of Ruthenium and Osmium Bridged by 2,2′-Bibenzimidazolate: Preparation, Electrochemistry, and Formation of Mixed-Valence Complexes

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The preparation and spectroscopic and electrochemical properties of new 2,2′-bibenzimidazolate- (BiBzIm-) bridged binuclear complexes of the general formula $[(bpy)_2M(BiBzIm)M'(bpy)_2]^{n+}$ (M = Ru, Os; M′ = Ru, Os, Co, Ni) are reported. The Os(II)–Os(III) mixed-valence complex shows multiple intervalence-transfer (IT) absorption bands at 4800 and 8180 cm^{-1} in the near-infrared region, which can be attributed to the orbital splitting of optically prepared Os(III) site by tetragonal distortion and spin–orbit coupling. The Ru(II)–Os(III) and Ru(II)–Ru(III) mixed-valence complexes also exhibit multiple IT bands. The bandwidths at half-intensity for IT bands are narrower than those expected from Hush's theoretical treatment. These new mixed-valence complexes belong to Robin and Day's class II. The comproportionation constant K_{com} for the complex M = M′ = Ru greater than that for the complex M = M′ = Os is observed. This result, contrary to the trends reported so far, is discussed in terms of the orbital mixing between metal sites and BiBzIm. The anionic BiBzIm bridging ligand can cause stabilization of the mixed-valence complex by reducing the positive charge on the complex. The comparison of a BiBzIm-bridged complex with a bpm-bridged one is also discussed in terms of the donor–acceptor property of the ligand.

Introduction

Binuclear transition-metal complexes have received much attention in recent years. Many types of binuclear complexes with bridging ligand have been synthesized and utilized in the studies of electron-transfer processes and metal–metal interactions.[3] The

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(1) Mie University.

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(3) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. (c) Taube, H. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 481. (d) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *23*, 87.