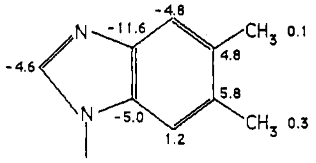
±20 ppm of this location. Decreasing the tip angle and increasing the delay between pulses (to allow for a slowly relaxing nucleus) also failed to resolve any resonance assignable to C-10.

The chemical shift pattern shown in III is quite reminiscent of that previously observed[15] for protonation of the 5,6-dimethylbenzimidazole moiety of the detached axial nuceloside (α-ribazole, IV) at N-3, except that in this case the shifts are more pronounced in this aromatic species. This similarity in chemical shift patterns suggests that protonation of the corrin nucleus at N-22 or N-23 should be considered. This possibility can be quickly dismissed, however, as it is extremely unlikely that the pK_a's for protonation at N-22 or N-23 would be so insensitive to the nature of the upper axial ligand (Table I) or that such protonation would follow an acidity function with such a small m^* value.[3,10] Thus, protonation of the corrin in aqueous sulfuric acid at C-10 seems most likely both because of the pattern of chemical shift changes (III) and our inability to observe a C-10 resonance, which is presumably broadened greatly by exchange as was the case for partial protonation of $^{13}CN^-$. In addition, protonation at C-10 is consistent with and explains previous observations of hydrogen-deuterium exchange of the C-10 proton in acidic, deuteriated media.[16,17]



IV

Considering the known electrophilic reactivity of the corrin C-10,[18-20] Pratt[21] has previously raised intriguing questions concerning this position including the reasons why it remains unmethylated in biosynthesis (in contrast to C-5 and C-15) and whether maintenance of an unmethylated bridging carbon has important chemical and/or biochemical consequences. Some attempts to answer these questions have already been made, but with conflicting results. Thus, while both the 10-chloro and 10-bromo derivatives of AdoCbl are active as coenzymes for bacterial diol dehydrase[22] (with K_m's virtually identical with that of AdoCbl and activities of 40% and 20% of the natural coenzyme for the chloro and bromo derivatives, respectively), the 10-chloro derivative is completely inactive with glutamate mutase.[23] Obviously much remains to be learned about this interesting biochemical system.

Acknowledgment. This work was supported by The Robert A. Welch Foundation, Houston, TX, Grant No. Y-749.

---

(15) Brown, K. L.; Hakimi, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 496–503.
(16) Bonnett, R.; Redman, D. G. *Proc. R. Soc. London, A* **1965**, *288*, 342–343.
(17) Hill, H. A. O; Mann, B. E.; Pratt, J. M.; Williams, R. J. P. *J. Chem. Soc. A.* **1968**, 564–567.
(18) Bonnett, R.; Cannon, J. R.; Clark, V. M.; Johnson, A. W.; Parker, L. F. J.; Smith, E. L.; Todd, A. *J. Chem. Soc.* **1957**, 1158–1168.
(19) Dolphin, D.; Johnson, A. W.; Shaw, N. *Nature (London)* **1963**, *199*, 170–171.
(20) Wagner, F. *Proc. R. Soc. London, A.* **1965**, *288*, 344–347.
(21) Reference 12; p 281.
(22) Tamao, Y.; Morikawa, Y.; Shimizu, S.; Fukui, S. *Biochim. Biophys. Acta* **1968**, *151*, 260–266.
(23) Barker, H. A. In *The Enzymes*, 3rd ed.; P. D. Boyer, Ed.; Academic: New York, 1979; Vol. 6 Chapter 14.

Department of Chemistry
The University of Texas at Arlington
Box 19065
Arlington, Texas 76019

Kenneth L. Brown*
Sherri Peck

Received August 13, 1987

Synthesis and Coordination Chemistry of Poly(4-vinyl-4'-methyl-2,2'-bipyridine) Films on Electrode Surfaces

Sir:

Reductive electrochemical polymerization of vinyl-containing transition metal complexes has provided a convenient preparative route to redox-active, thin polymeric films on metallic and semiconductor electrodes.[1] However, the absence of a variety of preparative strategies, along with redox instabilities during the electropolymerization, limits the generality of this approach.[2] Here we describe a significant advance in the underlying preparative chemistry of chemically modified electrodes that is based on octahedral $Zn(vbpy)_3^{2+}$ and the square-planar complexes $[M(vbpy)(COD)]^+$ (vbpy is 4-vinyl-4'-methyl-2,2'-bipyridine; COD is 1,5-cyclooctadiene; M is Rh(I) or Ir(I)).[3] In both cases the metal ions are relatively labile and can be removed to give metal ion free films that have *different* coordination chemistries. Alternatively, the metal ions can be displaced by using suitable metal precursors to give redox-active films containing different metal ions. Our approach differs from those of previous studies in that it emphasizes preparative chemistry at the polymer electrode/solution interface.

The preparations of $Zn(vbpy)_3^{2+}$ and $[M(vbpy)(COD)]^+$ are straightforward or follow from literature procedures.[4a-c] The complexes have been characterized by elemental analyses and ^1H NMR spectroscopy.[4d]

Thin polymeric films of poly-$[Zn(vbpy)_3]^{2+}$ are prepared from the monomer by reductive electropolymerization by using potential scans from −0.8 to −1.5 V (vs the NaCl saturated calomel electrode, SSCE) in 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)/CH_3CN on Pt-button, glassy-carbon-button, or planar Au/polyester electrodes. Under similar scanning conditions in fresh electrolyte, poly-$[Zn(vbpy)_3]^{2+}$ exhibits sequential bpy-based reductions at $E_{p,c}$ = −1.48 and −1.61 V, with the corresponding oxidations being at $E_{p,a}$ = −1.40 and −1.57 V. Typical surface coverages, which were estimated by the integrated peak areas, are ca. 10^{-8}–10^{-7} mol/cm^2 for ca. 0.12-cm^2 Pt-disk electrodes.[5] Reductive cycling past −1.75 V results in rapid

---

(1) (a) Abruña, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (b) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1984; Vol. 13, and references therein.
(2) (a) Calvert, J. A.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151. (b) Abruña, H. D., Calvert, J. M.; Denisevich, P.; Ellis, C. D.; Meyer, T. J.; Murphy, W. R., Jr.; Murray, R. W.; Sullivan, B. P.; Walsh, J. L. In *Chemically Modified Surfaces in Catalysis and Electrocatalysis*; Miller, J. S., Ed.; ACS Symposium Series 192; American Chemical Society: Washington, DC, 1984; p 132. (c) Calvert, J. M.; Sullivan, B. P.; Meyer, T. J. *Ibid.*, p 159. (d) Leidner, C. R.; Sullivan, B. P.; Reed, R. A.; White, B. A.; Crimmins, M. T.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 882.
(3) Note, for example, for relevant catalytic applications, the following references on hydrogenation and transfer hydrogenation: (a) Mestroni, G.; Zassinovich, G.; Camus, A. *J. Organomet. Chem.* **1977**, *140*, 63. (b) Camus, A.; Mestroni, G.; Zassinovich, G. *J. Mol. Catal.* **1979**, *6*, 231. (c) Mestroni, G.; Zassinovich, G.; Camus, A.; Martinelli, F. *J. Organomet. Chem.* **1980**, *198*, 87. (d) Martinelli, F.; Mestroni, G.; Camus, A.; Zassinovich, G. *Ibid.* **1981**, *220*, 383.
(4) (a) Cocevar, C.; Mestroni, G.; Camus, A. *J. Organomet. Chem.* **1972**, *35*, 389. Mestroni, G.; Camus, A.; Zassinovich, G. *Ibid.* **1974**, *73*, 119. (b) Preparation of $[Zn(vbpy)_3][PF_6]_2$: On a ca. 0.5 mM scale the Zn complex was prepared by heating at reflux a 3:1 ratio mixture of vbpy and $ZnCl_2$ in a convenient volume of reagent grade MeOH for 30 min. After this time the reaction mixture was cooled and a solution of NH_4PF_6 in MeOH was added to precipitate the white $[Zn(vbpy)_3][PF_6]_2$ product. Purification was achieved by precipitation from CH_3CN with Et_2O. (c) The vbpy ligand can now be prepared in large quantities (10–20 g) by a slight modification of the published procedure, i.e.: Abruña, H. D.; Breikss, A. I.; Collum, D. B. *Inorg. Chem.* **1985**, *24*, 988. (d) For example, in the ^1H NMR spectrum of $[Rh(vbpy)(COD)][PF_6]$ in CD_3CN the vbpy ring and vinylic proton resonances (δ) are found at 8.21 (d, 1), 7.73 (m 2), 7.55 (d, 1), 7.42 (d, 1), 6.86 (d of d, 1), 6.33 (d, 1), and 5.79 (d, 1); the Me group is found at 2.48 (s, 3), and the COD protons are found at 4.54 (br s, 4), 2.58 (br s, 4), 2.13 (m, 4). Anal. Calcd for $Zn(vbpy)_3(PF_6)$: C, 49.63; H, 3.82; N, 8.91. Found: C, 49.22; H, 3.73; N, 8.75.

0020-1669/87/1326-4145$01.50/0

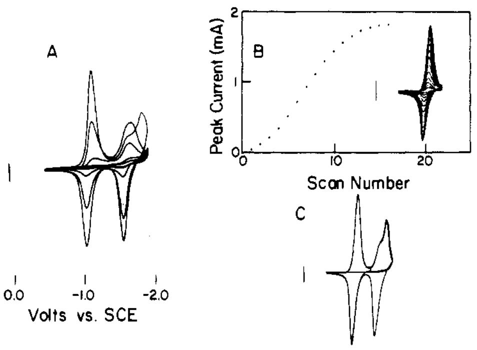


Figure 1. Removal and reincorporation of Rh^I from poly-[Rh(vbpy)(COD)]$^+$ films on a Pt-button electrode (0.13 cm^2) in 0.2 M (TEA)Br/CH_3CN: (A) successive reductive electrochemical scans of a poly-[Rh(vbpy)(COD)]$^+$ film in the presence of PPh_3 over the scan range −0.45 to −1.95 V at a scan rate of 50 mV/s (the electrode was cycled for six more times before the reincorporation of Rh^I ions as shown in Figure 1B); (B) growth curve for reincorporation of Rh^I by using $[Rh(COD)Cl]_2$ in the external solution; (C) cyclic voltammogram of the reconstituted poly-[Rh(vbpy)(COD)]$^+$ electrode (two reductive scans).

degradation of the films accompanied by the deposition of zinc metal.

The most effective procedure for growing films of poly-[Rh^I(vbpy)(COD)]$^+$ involves using reductive scans from −0.45 to −1.45 V in 0.1–0.2 M tetraethylammonium bromide ((TEA)Br)/CH_3CN. In the films, waves appear at $E_{p,c} = -1.22$ V ($E_{p,a} = -1.05$ V) and $E_{p,c} = -1.85$ V ($E_{p,a} = -1.57$ V) at 50 mV/s in fresh 0.2 M (TEA)Br/CH_3CN. The potentials of the surface couples are in close correspondence with those for the model complex [$Rh^I(Me_2bpy)$(COD)]$^+$ ($E_{1/2}(1) = -1.24$ V and $E_{1/2}(2) = -1.74$ V). The energy of the Rh(I) → bpy charge-transfer transition[6a] in the model ($\lambda_{max} = 456$ nm) also corresponds closely to that obtained for a DMF-soluble fraction of the polymer extracted from a Au/polyester electrode surface ($\lambda_{max} = 451$ nm). For films of poly-[Ir(vbpy)(COD)]$^+$ prepared under identidal conditions but with a potential sweep from −0.45 to −1.25 V, the bpy-based reductions appear at $E_{p,c} = -1.09$ V ($E_{p,a} = -0.95$ V) and $E_{p,c} = -1.80$ V ($E_{p,a} = -1.41$ V).[6b] One element of the synthetic versatility of the square-planar complexes is illustrated by the copolymerization of [Ir(vbpy)(COD)]$^+$ and $[Ru(vbpy)_3]^{2+}$ on Pt by scanning between −0.5 and −1.15 V. Since $Ru(vbpy)_3^{2+}$ is not electropolymerized at these potentials, the Ir complex must *initiate* the formation of the copolymeric film. This observation is significant because it demonstrates that radical anion based polymerization occurs for the Ir complexes instead of physical deposition (e.g., stacking) of the square-planar metal complexes. When the complex concentrations are varied in the external solution, the Ir:Ru ratio of the films can be varied from 5:1 to ~1:1.

When the chelating agent $NaS_2CN(CH_2Ph)_2$ (Na(dbdtc)) or monodentate phosphines such as PPh_3 or PPh_2Me are added to the external solution, the metal ions can be totally removed to give electrochemically inactive, metal-free poly-[vbpy] films (Figure 1). The metal ion content of the films can be reconstituted by cycling electrochemically in the presence of $[M(COD)Cl]_2$ (Figure 1B). A series of experiments demonstrates that complete metal ion removal from the film occurs and that loss of redox activity is not simply due to a deactivation in the electrochemical response. For example, the Rh^I and Ir^I ions in a 1:1 copolymeric film can be removed with Na(dbdtc) to give an electrochemically inactive poly-[vbpy] film. If the film is then reconstituted with $[Rh(COD)Cl]_2$, *only* the characteristic surface waves of poly-[Rh(vbpy)(COD)]$^+$ appear.

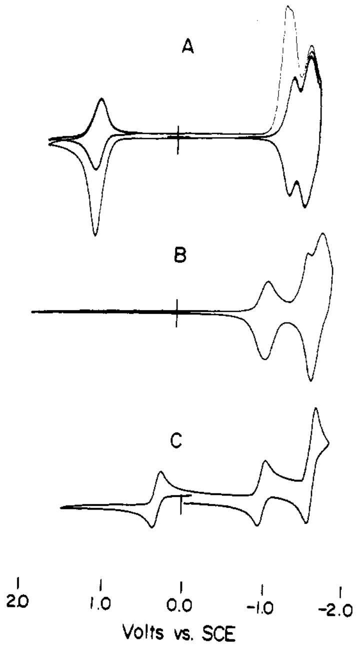


Figure 2. (A) Cyclic voltammogram of poly-$[Fe(vbpy)_3]^{2+}$ produced by metal ion exchange between poly-$[Zn(vbpy)_3]^{2+}$ and $FeCl_2$ in CH_3CN. The data were collected in 0.2 M TEAP/CH_3CN at a scan rate of 50 mV/s. (B) Cyclic voltammogram of poly-$[Co(vbpy)_3]^{2+}$ produced by metal ion exchange between poly-$[Zn(vbpy)_3]^{2+}$ and $CoCl_2$. The data were collected in 0.2 M TEAP/CH_3CN at a scan rate of 50 mV/s. (C) Solution cyclic voltammogram of $[Co(bpy)_3][PF_6]_3$ in 0.2 M TEAP/CH_3CN. Note the absence of the $Co^{III/II}$ wave process in the above surface-immobilized poly-$[Co(vbpy)_3]^{2+}$ complex.

Na(dbdtc) also can be used to remove Zn^{2+} from poly-$[Zn(vbpy)_3]^{2+}$ and the resulting film reconstituted with $ZnCl_2$ or converted into poly-$[Fe(vbpy)_3]^{2+}$ by exposure to a fresh solution containing $FeCl_2$.[7] However, a more convenient procedure for the latter involves direct metal ion exchange between poly-$[Zn(vbpy)_3]^{2+}$ and $FeCl_2$. In a similar manner, the use of $CoCl_2 \cdot 6H_2O$ in 0.2 M tetraethylammonium perchlorate (TEAP)/CH_3CN (Figure 2A) gives poly-$[Co(vbpy)_3]^{2+}$. The incorporation of Co^{II} sites is notable since previous attempts to obtain poly-$[Co(vbpy)_3]^{2+}$ electrodes via direct electropolymerization of $[Co(vbpy)_3]^{3+}$ have failed.[8]

Both the Fe^{II}- and Co^{II}-containing films exhibit "memory effects" in that an initial electrochemical cycling period of 10–20 min is required to fully develop the redox response of the couples. Apparently, the internal film structure must be reorganized before facile electron transfer can occur.

Examination of the cyclic voltammetry of poly-$[Co(vbpy)_3]^{2+}$ in fresh 0.2 M TEAP/CH_3CN (Figure 2B,C) shows that the $Co^{III/II}$ couple is absent at slow to moderate scan rates (10–100 mV/s). The appearance of an $Fe^{III/II}$ couple but the absence of a $Co^{III/II}$ couple is consistent with slow, rate-determining electron hopping between adjacent redox centers as the dominant mechanism for electron transfer,[8,9] given the self-exchange rate constants for the $Co(bpy)_3^{3+/2+}$ (10 M^{-1} s^{-1}) and $M(bpy)_3^{3+/2+}$ (M = Fe, Ru) couples (>10^8 M^{-1} s^{-1}).

---

(5) The surface coverage applies to electrodes that were prepared by using (5–6) × 10^{-4} M solutions of $Zn(vbpy)_3^{2+}$ and 10–20 scans in the potential range −0.8 to −1.5 V.

(6) (a) Fordyce, W. A.; Crosby, G. A. *Inorg. Chem.* **1982**, *21*, 1023. Fordyce, W. A.; Pool, K. H.; Crosby, G. A. *Ibid.* **1982**, *21*, 1027. (b) Makrlik, E.; Hanzlik, J.; Camus, A.; Mestroni, G.; Zassinovich, G. *J. Organomet. Chem.* **1977**, *142*, 95.

(7) Some examples of the degree of reincorporation of Rh^I into a demetalated film are (1) with PPh_3 as the demetalating reagent −102% and (2) with Na(dbdtc) −88%. For $Zn(vbpy)_3^{2+}$, metal removal resulted in ~60% Fe incorporation for several experiments (these depend critically on the exposure of the film to Na(dbdtc)) but >95% for direct metal exchange. These experiments were accomplished by comparing the area of the vbpy waves before and after metal reincorporation.

(8) (a) Facci, J. S.; Schmehl, R. H.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 4959. (b) Ikeda, T.; Leidner, C. R.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *138*, 343. (c) Pickup, P. G.; Murray, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 4510.

(9) For a similar effect for $Co(bpy)_3^{2+}$ that is electrostatically bound in a Nafion film, see: Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685.

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.

Acknowledgment. We wish to thank Dr. Nigel Surridge and Dr. Alison Downard for help during the early phases of this work. We also wish to acknowledge the support of the Army Research Office—Durham under Grant No. DAAG29-85-K-0121 and the Gas Research Institute under Grant No. 5083-260-0827.

Department of Chemistry
The University of North Carolina at Chapel Hill
Chapel Hill, North Carolina 27514
Thomas J. Meyer
B. Patrick Sullivan*

Central Research and Development Department
Experimental Station E328
E. I. du Pont de Nemours and Company, Inc.
Wilmington, Delaware 19898
Jonathan V. Caspar*

Received July 30, 1987

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.

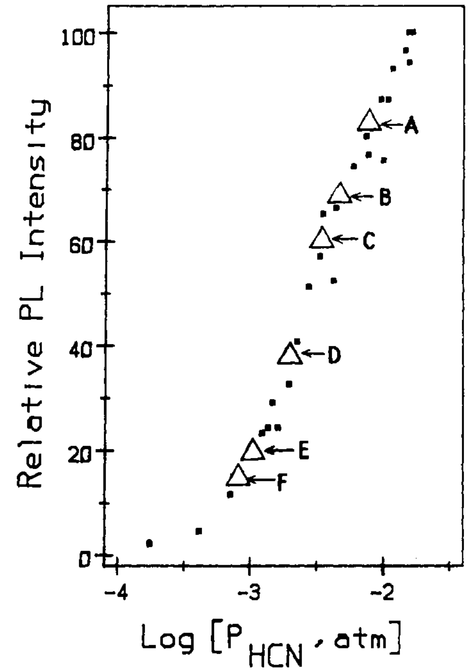


Figure 1. PL intensity at 525 nm of a sample of silica-dispersed $AgUO_2PO_4$ as a function of the partial pressure of HCN gas. Data, represented by the squares, were obtained in random order and are plotted relative to the maximum PL value observed at high P_{HCN}. Points labeled A-F are "doped" samples 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

---

[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.

0020-1669/87/1326-4147$01.50/0