

## Photochemical Behavior of Metal Complexes Intercalated in Zirconium Phosphate

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Intercalation compounds of  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O ( $\alpha$ -ZrP) with Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Cr(en)<sub>3</sub><sup>3+</sup> (en = ethylenediamine), Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Co(en)<sub>3</sub><sup>3+</sup>, and Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup> have been prepared by aqueous ion exchange with the *n*-butylamine derivative of  $\alpha$ -ZrP, (C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub>)<sub>2</sub>Zr(PO<sub>4</sub>)<sub>2</sub>. X-ray powder diffraction was used to determine interlayer spacings. Irradiation of intercalated Cr(en)<sub>3</sub><sup>3+</sup> with a Hg-vapor lamp ( $\lambda_{\text{max}} = 254$  nm) resulted in a red shift of the ligand field absorption maximum from 457 to 560 nm, suggesting loss of all coordinated ethylenediamine and substitution by lattice water and phosphate. Irradiation of Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> results in a smaller red shift, suggesting kinetic stabilization of the ammine complex by inclusion in the phosphate host. The iron and cobalt complexes do not react under similar photolysis conditions, in contrast to their behavior in aqueous solution, where reduced complexes result. The potential for use of host lattices in stabilization of unstable species is discussed. © 1991 Academic Press, Inc.

### Introduction

The chemical properties of inclusion compounds have gained increasing attention in recent years. New catalysts and synthetic reagents have resulted from the study of zeolites (1, 2) and their ability to include molecular species within rigid chambers in the lattice. More recently, molecular host compounds, including cyclodextrins (3), which can include small molecules and be manipulated in solution, have shown some promise as homogeneous catalysts.

Intercalation reactions of many layered solids have long been known, but only recently have the products been exploited for their chemical, rather than electronic, properties. In particular, the potential of clay

minerals (4), layered double hydroxides (5), and layered phosphates (6) is expanding as researchers have discovered a wide variety of ionic and neutral species which can diffuse into interlayer "galleries." By introducing rigid "pillars" into the interlayer regions in the form of alkyl chains or polyoxo ions, zeolitic media can be constructed with channel and pore sizes rivalling natural zeolites.

$\alpha$ -Zirconium phosphate, Zr(HPO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O ( $\alpha$ -ZrP), has proven to be a versatile and robust host lamellar solid. Its structure, determined by Clearfield et al. (7), consists of polymeric [Zr(PO<sub>4</sub>)<sub>2</sub>]<sub>n</sub><sup>2n-</sup> layers with exchangeable protons residing in the hydrated interlamellar region. The interlayer separation of 7.6 Å can be easily expanded to 18.6 Å by interaction of  $\alpha$ -ZrP with an aqueous *n*-C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub> solution (8), which results in in-

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tercalation of a bilayer of butylammonium cations with their carbon chains oriented at an angle of 55–60° to the layers. Once the kinetic barrier to layer separation has been removed, butylammonium ions can be subsequently exchanged with large transition metal complexes (9). Alkyl phosphonates,  $Zr(RPO_3)_2 \cdot xH_2O$  include permanent pillars (10) to allow inclusion of neutral solvent species and larger molecules.

In this work, we examine the intercalation behavior of several prototypical complexes of chromium, iron, and cobalt with the zirconium phosphate lattice and the photochemical behavior of the intercalated complexes. Both photochemical ligand exchange reactions and photoreductions requiring excited state electron transfer were studied. The results highlight the potential of the two-dimensional vise-like framework as a "solid solvent," a rigid, sterically demanding environment in which to study metal–ligand interactions.

### Experimental

$\alpha$ -Zirconium phosphate was prepared in powder form by the method of Clearfield (11) and refluxed in 85%  $H_3PO_4$  for 13 days. Butylammonium zirconium phosphate (BAZrP) was prepared by suspending 2.0 g of  $\alpha$ -ZrP in 200 ml of an aqueous solution that was 0.25 M in  $n-C_4H_9NH_2$  and 0.25 M in  $n-C_4H_9NH_3Cl$  for 24 hr.

$Cr(NH_3)_6(NO_3)_3$  (12),  $Cr(en)_3Cl_3$  (13),  $Fe(C_5H_5)_2$  (14),  $Co(NH_3)_6Cl_3$  (15), and  $Co(en)_3Cl_3$  (15) were all prepared by literature methods. Intercalations of the chromium and cobalt complexes were performed by suspending 500 mg of BAZrP in 30 ml of 0.3 M aqueous solutions of the appropriate complexes. Solid products were gravity filtered and washed with water.  $Fe(C_5H_5)_2^+$  was intercalated by oxidizing ferrocene with sulfuric acid (14), then following the procedure for the other ionic complexes. Neutral ferrocene in benzene solution was not ob-

TABLE I  
STOICHIOMETRIES AND INTERLAYER SPACINGS  
OF ZIRCONIUM PHOSPHATE DERIVATIVES,  
 $[Com]_xZr(PO_4)_2$

Complex	<i>x</i>	Interlayer spacing (Å) <sup>a</sup>
$\alpha$ -ZrP		7.6
BAZrP		18.6
$Cr(NH_3)_6^{+3}$	0.28	10.8
$Cr(en)_3^{+3}$	0.24	11.3
$Fe(C_5H_5)_2^+$	0.18	11.6
$Co(NH_3)_6^{+3}$	0.50	15.0
$Co(en)_3^{+3}$	0.27	14.8

<sup>a</sup> Interlayer spacings were determined from X-ray powder diffraction. 00L lines ( $L = 1$  to 4) were used to index the spacing.

served to intercalate after 72 hr at room temperature (16).

Photolyses were carried out by suspending 50 mg of solid phosphate in 20 ml of water while irradiating with a water-cooled low-pressure mercury vapor lamp ( $\lambda_{max} = 254$  nm). Solid products were filtered and analyzed as pressed KBr pellets by infrared and UV–visible spectroscopy.

Ultraviolet–visible spectra were obtained on a Perkin–Elmer Lambda 4 system using quartz cuvettes for solutions and silicone grease mulls (17) for solid samples. Infrared spectra were obtained on a Nicolet Series 6000 FTIR. X-ray powder diffraction was performed on an Enraf-Nonius FR590 Guinier system, using an internal silicon standard with all samples. Interlayer spacings for the zirconium phosphate derivatives are summarized in Table I.

Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGS-2 thermogravimetric analyzer interfaced to a System 7/4 analysis console. Results of TGA under dry nitrogen showed between two and three water molecules per formula unit for the chromium and cobalt compounds and six waters for the ferricenium derivative.

Elemental analyses (intercalating metal,

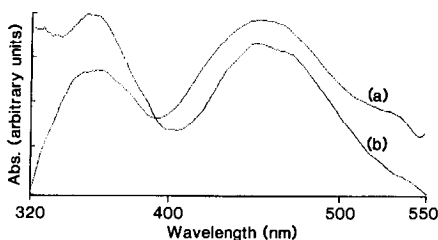


FIG. 1. UV-visible spectra of solid  $\text{Cr}(\text{en})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$  (a) and  $[\text{Cr}(\text{en})_3]_{0.24}\text{Zr}(\text{PO}_4)_2$  (b), as silicone grease mulls.

Zr, N) of the zirconium phosphate derivatives were performed by Schwartzkopf Microanalytical Laboratory and Galbraith Laboratories and were consistent with the stoichiometries summarized in Table I. They also indicated that a small amount ( $<0.05$  moles excess N/mole Zr) of  $\text{C}_4\text{H}_9\text{NH}_3^+$  remained in the lattice after the exchange reactions.

## Results and Discussion

When  $\alpha$ -ZrP was suspended in a 0.30 M solution of  $\text{Cr}(\text{en})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$  for 6 hr, no reaction was observed. The solid product remained colorless and the X-ray powder diffraction pattern matched that of  $\alpha$ -ZrP. (The same result was achieved under more forcing conditions, a 0.50 M solution heated to  $70^\circ\text{C}$ .) The difficulty of this and many aqueous exchange reactions stems from the strong kinetic barrier to disrupting the interlayer attractions of  $\alpha$ -ZrP and expanding the gallery. For this reason, all intercalations were performed using BAZrP as the starting material.

UV-visible absorption spectra of  $\text{Cr}(\text{en})_3\text{Cl}_3$  and  $[\text{Cr}(\text{en})_3]_{0.24}\text{H}_{1.3}\text{Zr}(\text{PO}_4)_2$ , both taken as solid state spectra in silicone grease mulls, are shown in Fig. 1. While the absorption maxima of the intercalated complex do not appear to shift significantly from the values for the unintercalated salt, the low-energy ligand-field transition is split

into at least two absorptions. This result can be attributed to the nonuniform microenvironment within the zirconium phosphate galleries and minor perturbations on the ligand field due to interactions with the lattice. The infrared spectrum of the intercalated product is dominated by the very strong and broad phosphate  $\nu_3$  stretch around  $1000\text{ cm}^{-1}$  (18), but shows the  $\text{Cr}(\text{en})_3^{+3}$  metal ligand stretch (19) at  $550\text{ cm}^{-1}$  as a broadening of the phosphate  $\nu_4$  stretch toward higher frequency (Fig. 2).

Table II summarizes the results of photolysis for several time periods. All photolyses were performed upon separate samples. Within minutes after photolysis began, a noticeable color change occurred from yellow to red. The red shift in UV-visible absorption maxima corresponds to the replacement of ethylenediamine with water molecules in the Cr coordination sphere. Elemental analysis of the photoproducts showed that, in all cases, a slight ( $<10\%$ ) loss of Cr was observed, probably due to desorption of aquated complexes from surfaces. However, the Cr : N ratio of the solid product remained constant throughout photolysis. Based upon this evidence that ethylenediamine remains in the lattice after photolysis, the conversion involves a rearrangement of molecules within the interlayer gallery, and not a high degree of diffusion of small molecules in and out of the lattice over the course of the reaction.

The photolysis reaction reached a limit after approximately 4 hr, with no further reaction apparent after 24 hr. The infrared and UV-visible spectra of the violet solid produced at the photolysis limit are shown in Figs. 2 and 3. The UV-visible absorption maxima are very near those of fully aquated  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  (20) and of intercalated aqueous Cr(III) ions (Fig. 3). The IR spectrum shows a splitting in the  $\nu_4$  phosphate stretch centered at  $525\text{ cm}^{-1}$ . The presence of the absorption at  $515\text{ cm}^{-1}$  can be attributed to coordination of phosphate oxygen to the

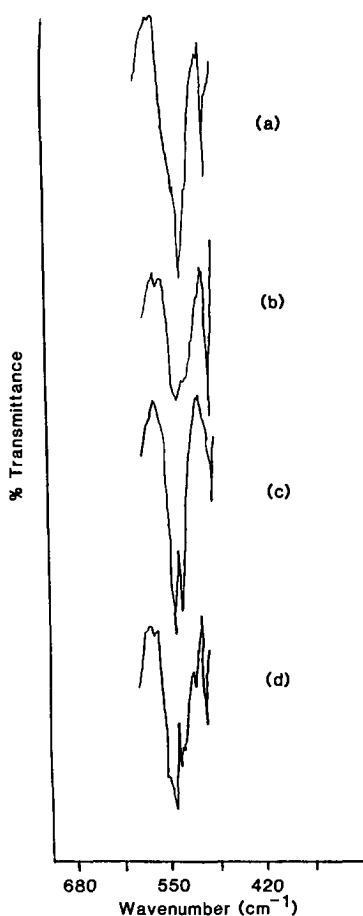


FIG. 2. Infrared spectra in the region of the phosphate  $\nu_4$  absorption for solid  $[\text{Cr}(\text{en})_3]_{0.24}\text{H}_{1.3}\text{Zr}(\text{PO}_4)_2$  before photolysis (a), and after 2 hr (b), 4 hr (c), and 24 hr (d) of irradiation.

metal center (21). The sharp absorptions at approximately  $3500$  and  $3600\text{ cm}^{-1}$  have disappeared entirely, indicating the absence of water molecules coordinated to phosphate in the photolyzed product (11). While X-ray powder diffraction patterns taken of the products at shorter periods of photolysis were extremely faint and diffuse, the X-ray pattern of the final product was relatively sharp and indicated an interlayer separation of  $10.9\text{ \AA}$ . The interlayer spacing of the photoproduct is consistent with an intercalated

chromium complex of dimensions similar to those of  $\text{Cr}(\text{en})_3^{+3}$ .

Photolysis of  $\text{Cr}(\text{en})_3^{+3}$  in aqueous solution under similar conditions yields  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ , comparable in color to that of the intercalated photolysis product. After 2 hr of photolysis, a  $6 \times 10^{-3}\text{ M}$  solution of  $\text{Cr}(\text{en})_3^{+3}$  turns from yellow to violet, with absorption maxima at  $405$  and  $556\text{ nm}$  (Fig. 3). Ion exchange of aqueous  $\text{Cr}^{+3}$  for  $\text{H}^+$  in  $\alpha\text{-ZrP}$  results in an intercalation compound ( $[\text{Cr}(\text{H}_2\text{O})_x]\text{ZrP}$ ,  $x \approx 6$ ) of the same color with UV-visible absorption maxima at  $398$  and  $566\text{ nm}$  (Fig. 3).

Photolysis of the intercalated hexammine complex for 12 hr resulted in a shift of  $\lambda_{\text{max}}$  from  $475\text{ nm}$  to  $491\text{ nm}$  for the ligand-field absorption band, suggesting a loss of two  $\text{NH}_3$  ligands (22). After 48 hr of photolysis, the reaction reached completion at room temperature with  $\lambda_{\text{max}}$  shifting to  $526\text{ nm}$ . This result indicates that the fully aquated  $\text{Cr}^{+3}$  complex is not produced under these conditions, since  $\lambda_{\text{max}}$  for the ligand-field absorption band occurs at  $526\text{ nm}$  in aqueous  $\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{+3}$  (22) and  $575\text{ nm}$  in  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ .

Attempts to perform photochemical reductions of intercalated ferricenium and of the intercalated cobalt ammine complexes

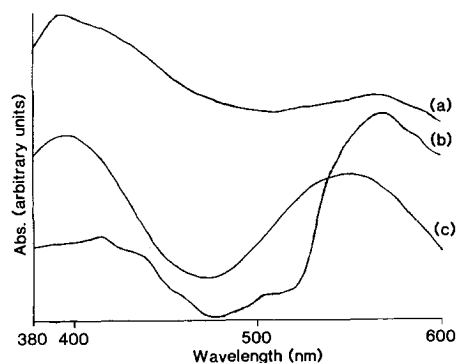


FIG. 3. UV-visible spectra of solid  $[\text{Cr}(\text{en})_3]_{0.24}\text{H}_{1.3}\text{Zr}(\text{PO}_4)_2$  after 24 hr photolysis at  $25^\circ\text{C}$  (a), solid  $[\text{Cr}(\text{H}_2\text{O})_x]\text{ZrP}$  (b), and aqueous  $\text{CrCl}_3$  (c).

TABLE II

RESULTS OF PHOTOLYSIS REACTIONS OF  $[\text{Cr}(\text{en})_3]_{0.24}\text{H}_{1.3}\text{Zr}(\text{PO}_4)_2$  SUSPENDED IN WATER AT ROOM TEMPERATURE

Time (hr)	$\lambda_1$ (nm)	$\lambda_2$ (nm)
0	457	351
1.0	535	375
2.5	560	385
3.5	560	400
4.0	550	405
24.0	560	410

were unsuccessful. While aqueous ferricenium is readily reduced to ferrocene under photolytic conditions (23), neither the mechanism nor even the identity of oxidized products has been clearly established. In the included case, since the separation between intercalated ions within a gallery is close to 15 Å, assuming an even distribution of ferricenium ions, the excited complex is denied contact with potential electron donors other than the phosphate lattice itself and intercalated water molecules, thereby precluding any disproportionation or ion pairing mechanisms.

Similarly, photolysis of intercalated cobalt ammine complexes  $\text{Co}(\text{NH}_3)_6^{+3}$  and  $\text{Co}(\text{en})_3^{+3}$  produced no reaction, which was confirmed by infrared and UV-visible spectra and X-ray diffraction. Since the mechanism of the redox decomposition is thought to involve an intramolecular metal-ligand interaction (24), the reason for this stability may simply be the lack of absorption by the cobalt ammine complexes in the mercury lamp emission region. The phosphate lattice filters out much of this radiation, which is absorbed only at the tail of the broad absorption band of the complexes.

## Conclusions

The photochemical reactivity of the intercalated  $\text{Cr}(\text{en})_3^{+3}$  ion provides a baseline for

comparison of reactivity between species in familiar surroundings and the "solid solvent" environment of the layered phosphate. Although it proceeds slowly, the ligand substitution reaction takes place to the same extent in the solid and in liquid solution. While ligand substitution also takes place in the  $\text{Cr}(\text{NH}_3)_6^{+3}$  ion, the  $\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{+3}$  ion exhibits stability to substitution in the solid that does not exist in solution. In the cases of ferricenium and the cobalt ammine complexes, the anticipated photoreductions are thwarted by inclusion in the solid lattice, showing that species in the included state can display stability under conditions which would ordinarily result in reaction or decomposition.

The potential advantages of layered materials over zeolitic media in designing systems with novel chemical properties are twofold. First, the ability of interlayer galleries to expand permits the accommodation of large species and can allow significant two-dimensional movement within the galleries. Second, the vise-like nature of the layers ensures that intercalated molecules will remain in contact with the "solid solvent" and exhibit the steric effects of that contact. The steric limitations of the solid lattice may be utilized in the future to control reaction rates without eliminating all activity, and to stabilize species which are unstable in ordinary solution.

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## References

1. T. P. NEWCOMB, P. G. GOPAL, AND K. L. WATERS, *Inorg. Chem.* **26**, 809 (1987).
2. M. SANO, T. MARUO, H. YAMATERA, M. SUZUKI, AND Y. SAITO, *J. Am. Chem. Soc.* **109**, 52 (1987).
3. K. S. HALL, R. S. NISSAN, R. L. QUINTANA, AND R. A. HOLLINS, *J. Catal.* **112**, 464 (1988).

4. T. J. PINNAVAIA, *Science*, **220**, 365 (1980).
5. T. KWON, G. A. TSIGDINOS, AND T. J. PINNAVAIA, *J. Am. Chem. Soc.* **110**, 3653 (1988).
6. A. CLEARFIELD AND D. J. THAKUR, *J. Catal.* **65**, 185 (1980).
7. A. CLEARFIELD AND G. D. SMITH, *Inorg. Chem.* **8**, 431 (1969).
8. A. CLEARFIELD AND R. M. TINDWA, *J. Inorg. Nucl. Chem.* **41**, 871 (1979).
9. A. CLEARFIELD AND R. M. TINDWA, *Inorg. Nucl. Chem. Lett.* **15**, 250 (1979).
10. M. B. DINES AND P. M. GIACOMO, *Inorg. Chem.* **20**, 92 (1981).
11. A. CLEARFIELD AND J. A. STYNES, *J. Inorg. Nucl. Chem.* **26**, 117 (1964).
12. A. L. OPPEGARD AND J. C. BAILAR, *Inorg. Syn.* **3**, 153 (1950).
13. R. D. GILLARD AND P. R. MITCHELL, *Inorg. Syn.* **13**, 184 (1972).
14. W. L. JOLLY, "The Synthesis and Characterization of Inorganic Compounds," p. 484, Prentice-Hall, Englewood Cliffs (1970).
15. J. BJERRUM AND J. P. McREYNOLDS, *Inorg. Syn.* **2**, 216 (1946).
16. J. JOHNSON, *J. C. S. Chem. Commun.*, 263 (1980). Cobaltocene was found to intercalate via oxidation of Co(II) to Co(III) and production of H<sub>2</sub>.
17. M. M. OLKEN, R. N. BIAGIONI, AND A. B. ELLIS, *Inorg. Chem.* **22**, 4128 (1983).
18. S. E. HORSLEY, D. V. HOWELL, AND D. T. STEWART, *Spectrochim. Acta Part A* **30**, 535 (1974).
19. J. GOUTERON-VAISSERMAN, *Compt. Rend.* **275B**, 149 (1972).
20. C. K. JORGENSEN, *Adv. Chem. Phys.* **5**, 33 (1963).
21. S. F. LINCOLN AND D. R. SHANKS, *Aust. J. Chem.* **21**, 37 (1968).
22. R. I. COLMAR AND F. W. SCHWARTZ, *J. Am. Chem. Soc.* **54**, 3204 (1932).
23. P. BORRELL AND E. HENDERSON, *Inorg. Chim. Acta* **12**, 215 (1975), and reproduced in our laboratory.
24. V. BALZANI AND V. CARASSITI, "Photochemistry of Coordination Compounds," Ch. 11, Academic Press, New York, 1970.