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Synthesis and Reactivity of a New Microporous Lewis Base

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Synthesis and reactivity of two new zirconium phosphonates with the α-layered structure are reported. $Zr(O_3P(CH_2)_3NH_3^+)_2(Cl^-)_2$ (abbreviated $ZrP(PA)_2$) has an interlayer spacing of 15.3 Å and a highly crowded interlayer region, which limits reactions with potential guest species. $Zr(O_3P(CH_2)_3NH_2)_{0.2}(O_3PCH_3)_{1.8}\cdot 2H_2O$ (abbreviated $ZrP(PA)_{0.2}(Me)_{1.8}$) has an interlayer spacing of 10.4 Å and a relatively porous interlayer gallery, which allows facile protonation of the amine and inclusion and subsequent exchange of anions. $ZrP(PA)_{0.2}(Me)_{1.8}$ also reacts with Cu(II) in solution to produce intercalation compounds, in which Cu(II) is coordinated to the interlayer amine and counterions are also included. The potential for exploitation of such microporous materials with "built-in" metal centers is discussed.

Introduction

Due to its layered structure and ion-exchange capability,[1] α-zirconium phosphate, $Zr(HPO_4)_2\cdot H_2O$ has proven to be a versatile solid host compound.[2] It can mimic reactions of zeolites and other microporous solids, with the advantage of expandable pore size, in one dimension, due to weak interlayer interactions.[3]

More recently, layered phosphonates, such as $Zr(O_3PR)_2\cdot xH_2O$ ($R = OC_2H_5, CH_2CHCH_2, C_6H_5$, etc.), have excited some interest due to their microporous nature.[4,5] While such phosphonates generally lack ion-exchange properties, the solids can be synthesized using a wide variety of organic pendant groups and porous products can result from reaction mixtures containing combinations of two or more organophosphonic acids which are mismatched in size.[6] This synthetic aspect can potentially be exploited to tailor the pore dimensions of the resulting materials in an effort to design new heterogeneous catalysts and ion-exchange materials.

In a further effort to design new materials, chemistry can also be performed on the solid layer surfaces through reactive functional groups on the organic moieties. Thompson et al. have recently shown that a pendant acyl chloride group displays reactivity in the interlayer medium similar to its solution reactivity.[7] This synthetic advantage results in solids with distinct pore sizes and new resident reactive sites.

In this work, we have begun to explore a new group of reactive phosphonates with a basic functional group, $Zr(O_3P(CH_2)_3NH_2)_x(O_3PCH_3)_{2-x}\cdot yH_2O$, and have examined the reactivity of the organic amine within the interlayer medium. In particular, we are interested in its ability to coordinate metals to produce microporous materials with "built-in" active centers for controlled catalysis. Continuing research focuses upon the solid phosphates and phosphonates as "solid solvents" for unique chemical reactions.

Experimental Section

Materials. $ZrOCl_2\cdot 8H_2O$, $CuCl_2\cdot 2H_2O$, $CuSO_4\cdot 5H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, and methylphosphonic acid (Aldrich), as well as (3-aminopropyl)phosphonic acid (Sigma), were used as received.

Preparation of Zirconium Phosphonates. $Zr(O_3P(CH_2)_3NH_3^+)_2(Cl^-)_2$ (abbreviated $ZrP(PA)_2$) was prepared by dropwise addition of 2 mL of a 0.7 M aqueous solution of $ZrOCl_2\cdot 8H_2O$ to 8 mL of a 0.4 M aqueous solution of $H_2N(CH_2)_3PO_3H_2$. This mixture was refluxed under N_2 for 4 d; then 0.7 mL of 2 M HF was added and reflux continued for 3 d. The colorless solid was isolated by gravity filtration, washed with water, acetone, and diethyl ether, and air-dried: yield 95%; IR (KBr) 3450 (w, br), 2950 (m, br), 2047 (m, br), 1591 (s), 1462 (m), 1244 (s), 1047 (s, br), 789 (m), 726 (s) cm^{-1}.

$Zr(O_3P(CH_2)_3NH_2)_{0.2}(O_3PCH_3)_{1.8}$ (abbreviated $ZrP(PA)_{0.2}(Me)_{1.8}$) was prepared as the hydrochloride salt by dropwise addition of 18 mL of a 0.65 M aqueous solution of $ZrOCl_2\cdot 8H_2O$ to 21 mL of solution which was 0.14 M in $H_2N(CH_2)_3PO_3H_2$ and 1.0 M in $H_3CPO_3H_2$. After 1 h of stirring, 250 mL of concentrated HCl was added to the resulting colorless gel and the mixture was refluxed under N_2 for 12 d. The colorless solid was filtered off, washed, and dried as indicated above: yield 85%; IR (KBr) 3400 (m, vbr), 2975 (m), 2914 (m), 2081 (w, br), 1620 (m), 1410 (m), 1302 (s), 1030 (s, br), 773 (m) cm^{-1}. The free base was isolated by stirring 0.25 g (0.8 mmol) of the salt in 20 mL of 0.1 M NaOH solution for 12 h at 20 °C, filtered off, washed, and dried as indicated above. Greater excesses of base resulted in noncrystalline products. IR (KBr): 3440 (s, br), 2975 (m), 2914 (m), 2082 (w, br), 1630 (m), 1410 (m), 1310 (s), 1050 (s, br), 778 (m) cm^{-1}.

Reactions of Zirconium Phosphonates. Exchange of NO_3^- for Cl^- in $ZrP(PA)_{0.2}(Me)_{1.8}\cdot 0.2HCl$ was performed by stirring a suspension of the hydrochloride in a 0.1 M solution of HNO_3 for 12 h. The product was filtered off, washed, and dried as indicated above: IR (KBr) 3425 (s, vbr), 2975 (m), 2914 (m), 2081 (w, br), 1622 (m), 1368 (s), 1300 (s), 1048 (s, br), 770 (m) cm^{-1}.

$ZrP(PA)_{0.2}(Me)_{1.8}$ was converted back to the hydrochloride salt or to the hydronitrate salt by stirring a suspension of the free base in a 0.1 M solution of the appropriate acid for 1–3 d. The products were filtered off, washed, and dried as indicated above.

Intercalation of Cu(II) salts was accomplished by stirring a suspension of $ZrP(PA)_{0.2}(Me)_{1.8}$ in a large excess of 0.14 M $CuCl_2$, $Cu(NO_3)_2$, or $CuSO_4$ solution for 8–11 d at 70 °C. The pale blue-green products were filtered off, washed, and dried as indicated above. $CuCl_2$ derivative: IR (KBr) 3438 (s), 3352 (s), 3303 (s), 2987 (m), 2926 (m), 2085 (w, br), 1622 (m), 1302 (s), 1027 (s, br), 773 (m) cm^{-1}. $Cu(NO_3)_2$ derivative: IR (KBr) 3426 (s), 2987 (m), 2922 (m), 2081 (w, br), 1622 (m), 1376 (s), 1305 (s), 1048 (s, br), 773 (m) cm^{-1}. $CuSO_4$ derivative: IR (KBr) 3570 (s), 3488 (s), 2995 (m), 2955 (m), 2085 (w, br), 1622 (m), 1410 (m), 1306 (s), 1063 (s, br), 773 (m) cm^{-1}.

Characterization. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGS-2 thermogravimetric analyzer interfaced to a System 7/4 analysis console. Ultraviolet visible spectra were obtained on a Perkin-Elmer Lambda 4 system using quartz cuvettes for solutions and silicone grease mulls[8] for solid samples. Infrared (IR) spectra were obtained on a Nicolet Series 6000 FTIR instrument. Electron spin resonance (ESR) spectra were obtained on powder samples at 78 K on

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(1) Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 117.

(2) Clearfield, A. *Comments Inorg. Chem.* **1990**, *10*, 89.

(3) Tindwa, R. M.; Ellis, D. K.; Peng, G.-Z.; Clearfield, A. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 545.

(4) Alberti, G.; Costantino, U.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113.

(5) Dines, M. B.; DiGiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92.

(6) Dines, M. B.; Cooksey, R. E.; Griffith, P. C.; Lane, R. H. *Inorg. Chem.* **1983**, *22*, 1003.

(7) Burwell, D. A.; Thompson, M. E. *Chem. Mater.* **1991**, *3*, 730.

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

0020-1669/92/1331-3104$03.00/0

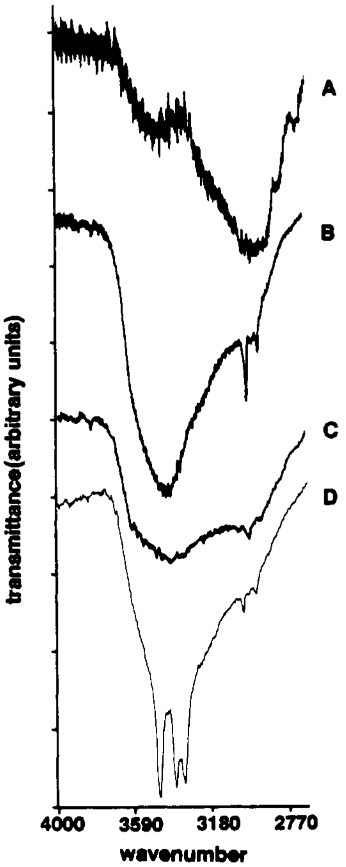

Figure 1. N–H stretching region of IR spectra of phosphonates: (A) $ZrP(PA)_2$; (B) $ZrP(PA)_{0.2}(Me)_{1.8}$; (C) $ZrP(PA)_{0.2}(Me)_{1.8}\cdot 0.2HCl$; (D) $ZrP(PA)_{0.2}(Me)_{1.8}\cdot 0.2CuCl_2$.

a Varian E-4 system, field-calibrated with DPPH ($g = 2.0036$). X-ray powder diffraction was performed on an Enraf-Nonius FR590 Guinier system, using an internal silicon standard with all samples. Interlayer spacings were determined from 00*l* (l = 1–3) reflections. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory.

Results and Discussion

The fully derivatized (aminopropyl)phosphonate hydrochloride, $ZrP(PA)_2$, possesses a highly crowded interlayer gallery (interlayer spacing = 15.26 Å) which is unable to accommodate would-be guest species, except at the surfaces of microcrystals. The N–H stretching region of the IR spectrum (Figure 1) shows a broad absorption at 2950 cm^{-1} ($-NH_3^+$) and a weaker one at 3450 cm^{-1} ($-NH_2$), indicating that the interlayer amine is substantially protonated. Due to the steric constraints within the galleries, reaction conditions which attempted to utilize the anion-exchange potential of the solid resulted in no reaction in the bulk of the solid samples. Attempts at deprotonation with NaOH solutions resulted in amorphous materials.

Of the mixed phosphonates, $Zr(O_3P(CH_2)_3NH_2)_x(O_3PCH_3)_{2-x}$, the compound with $x = 0.2$, $ZrP(PA)_{0.2}(Me)_{1.8}$, was most closely studied. The solid was obtained in microcrystalline form only after reflux in HCl solution; thus the hydrochloride salt was first isolated with an interlayer spacing of 11.30 Å. This salt acts as an anion-exchange material in reaction with HNO_3, resulting in a new derivative with an interlayer spacing of 11.14 Å.

When the hydrochloride salt was stirred in NaOH solution, the free base, $Zr(O_3P(CH_2)_3NH_2)_{0.2}(O_3PCH_3)_{1.8}\cdot 2H_2O$, was obtained with an interlayer spacing of 10.40 Å. This spacing suggests that the gross structure of the mixed phosphonate is that of Figure 2A, rather than a "staged" structure (Figure 2B) in which methyl groups are segregated from aminopropyl groups.

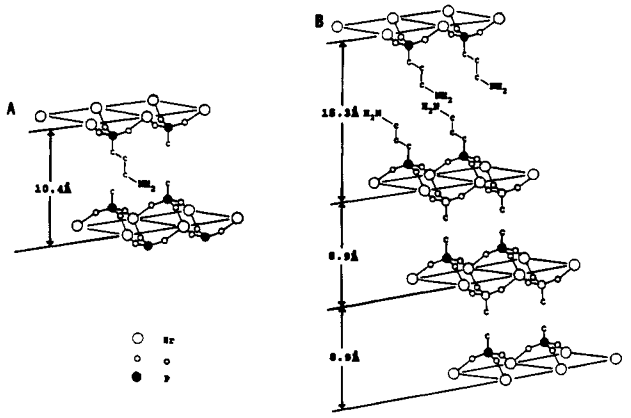

Figure 2. (A) Proposed gross structure of $Zr(PA)_{0.2}(Me)_{1.8}$. (B) Alternative staged structure of $Zr(PA)_{0.2}(Me)_{1.8}$, showing segregation of methyl and aminopropyl groups.

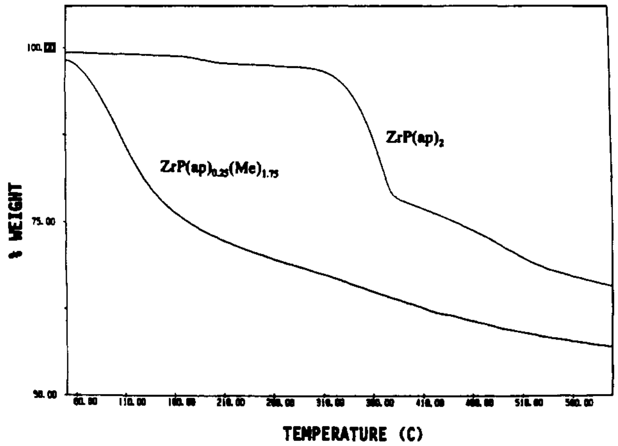

Figure 3. TGA traces for $Zr(PA)_2$ and $Zr(PA)_{0.2}(Me)_{1.8}$. Plots begin at 50 °C, at which a small amount of weight has been lost.

The significant positive deviation from Vegard's law,[9] which predicts that a solid solution of this composition would have an interlayer spacing closer to that of $Zr(CH_3PO_3)_2$ (8.9 Å[10]), is manifested in a relatively porous interlayer region with unusually weak interlayer attractions. The inclusion of water molecules within the structure is largely a consequence of its porous nature.

TGA of $ZrP(PA)_2$ (Figure 3) indicates not only the lack of included water but also the stability of the structure up to (about 300 °C), a characteristic which also pertains to layered phosphates. The mixed phosphonate loses water of hydration from about 80 to 200 °C, after which the organic groups slowly fragment as heating continues past 500 °C.

Included water in the mixed phosphonate also eases transport of species from solution into the interlayer medium and vice versa. The two-step anion-exchange reaction of the ammonium salt involving deprotonation (and removal of anions) followed by acidification (with a different acid), without apparent loss of crystallinity, indicates that this medium is highly amenable to exploitation as a "solid solvent" to facilitate small-molecule reactions.

Of particular interest is the ability of materials of this type to incorporate metal ions and complexes. The resulting solids would not only be size- and shape-selective in their interaction with species in solution but also provide a known chemical environment for included species and allow for more predictability in designing catalytic systems. To this end, the porous mixed phosphonate appeared well suited to the task of coordinating transition metals from solution.

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[9] Pearson, W. B. *The Crystal Chemistry and Physics of Metal Alloys*; Wiley: New York, 1972.

[10] Dines, M. B.; Griffith, P. C. *J. Phys. Chem.* **1982**, *86*, 571.

Table I. Interlayer Spacings and Visible Absorption Maxima of Cu(II) Derivatives of $Zr(PA)_{0.2}(Me)_{1.8}$

anion	spacing (Å)	λ_{max} (nm)
Cl^-	11.22	690
NO_3^-	11.22	648
SO_4^{-2}	11.56	712

Reactions of the fully-functionalized material with aqueous solutions of Cu^{2+} and Pd^{2+} were unsuccessful, presumably due to the highly crowded interlayer region and the strong interaction between layers. The mixed phosphonate, however, was successful in incorporating Cu^{2+} ions from solution. Reactions of aqueous $CuCl_2$ with $ZrP(PA)_{0.2}(Me)_{1.8}$ resulted in a solid with interlayer spacing of 11.22 Å, indicating incorporation of Cu(II) into the bulk of the solid. The visible absorption maximum was also shifted, from 781 nm in solid $CuCl_2{\cdot}2H_2O$ to 690 nm in the intercalated form. The pores in the structure of the mixed phosphonate allow cations from solution to diffuse into the bulk of the material, as well as their accompanying anions. Elemental analysis (5.34% Cu, 37.88% Zr, 5.90% Cl) indicated a ratio of 0.2 $CuCl_2$ unit per formula unit. The ESR spectrum of the powder showed a singlet as expected, at $g = 2.12$.

Larger anions, such as NO_3^- and SO_4^{2-}, also accompanied Cu^{2+} into the interlayer region. The interlayer spacing of these derivatives is similar to that of the $CuCl_2$ derivative, and the absorption maxima (Table I) are also shifted to higher energy by coordination to the interlayer amine.

IR spectra were used chiefly to examine the environment around the amine nitrogen and to identify nitrate as an intercalating counterion. Vibrations in the aliphatic carbon chain[11] and the very strong P–O stretch[12] near 1040 cm^{-1} were common to all samples. In general, the N–H stretching region was broadened and shifted to slightly lower energy for the protonated amine solids (Figure 1). For the material in which chloride was exchanged for nitrate, the IR spectrum of the solid showed a strong new NO_3^- signature band[11] near 1370 cm^{-1}. The N–H stretches sharpened markedly in Cu-intercalated derivatives, presumbly due to limiting of vibrational freedom within the more organized galleries.

Conclusions

The porous solid $ZrP(PA)_{0.2}(Me)_{1.8}$ displays a unique ability to coordinate cations to basic sites in its interlayer galleries while also including counterions. Its chemistry shows promise for exploitation in catalysts, chemical energy storage, and ion exchange. Related compounds are expected to vary in size and shape selectivity.

The rational design of microporous solids represents a significant new branch of solid-state chemistry. Synthesis of solids with reactive moieties on internal surfaces and inclusion of active metal centers into pores of such solids in a predictable manner will eventually aid in designing solids to perform specific tasks. We and others have shown that such inclusions are relatively straightforward and can be performed with a variety of synthetic strategies.

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Supplementary Material Available: A table of elemental analyses for zirconium phosphonates (1 page). Ordering information is given on any current masthead page.

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(11) Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic Press: New York, 1963.

(12) Thomas, L. C. *The Identification of Functional Groups in Organophosphorus Compounds*; Academic Press: New York, 1974.