Intercalation of Alkylamines into Layered Copper Phosphonates

Yiping Zhang, Karen J. Scott, and Abraham Clearfield*

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received October 27, 1992. Revised Manuscript Received February 1, 1993

Dehydration of layered copper phosphonates $Cu(O_3PR)\cdot H_2O$ (R = CH_3, C_6H_5, $CH_2C_6H_5$) yields layered anhydrous salts $Cu(O_3PR)$ which show an increase of more than 1 Å in interlayer spacing compared to its monohydrate. Primary amines $C_nH_{2n+1}NH_2$ (n = 3–8) were intercalated into anhydrous $Cu(O_3PCH_3)$ and $Cu(O_3PC_6H_5)$. The copper methylphosphonate takes up 1 mol of amine forming $Cu(O_3PCH_3)\cdot(RNH_2)$, while 2 mol of amines were absorbed by copper phenylphosphonate. A plot of the interlayer distances of the intercalates vs the number of carbon atoms in the alkyl chain gives a straight line with a slope of 2.01 Å, which indicates that the alkyl chains of amine are packed as double layers with a tilt angle of 53° with respect to the mean plane of the layer. The behavior of copper phosphonates was compared to those of Mn, Co, and Zn phosphonates.

Introduction

Layered metal phosphonate chemistry is rapidly becoming a well-developed branch of inorganic chemistry. Early work was centered on the zirconium compounds,[1,2] but it has now been shown that a variety of metals will form layered phosphonates.[3] One area of interest is the intercalation behavior of these compounds. In the case of zirconium phosphonates the metal atom is octahedrally coordinated by phosphonate oxygens[4] so that coordinative intercalation of Lewis bases is not possible. However, if the organic portion is functionalized, acid–base type intercalation may take place.[5] Several of the divalent phenyl- and methylphosphonates are also six coordinate,[6,7] but the metal coordination sphere contains a water molecule. These compounds can be dehydrated leaving a metal coordination site available for coordinative intercalation.[8] An example of this type of reaction was demonstrated by Johnson et al.[9] for vanadyl phosphonates. The host compounds were prepared by thermal removal of benzyl alcohol from $VO(O_3PR)\cdot H_2O\cdot C_6H_5CH_2OH$. This loss of alcohol leaves a vacant site on the V(IV) atoms of the layer and allows a variety of primary alcohols to bind at these sites, while the secondary alcohols are excluded. This site selectivity is a consequence of the steric constraints imposed by the R group. For example, Cao and Mallouk found that primary amines with branching in the α-position were excluded from both anhydrous zinc and cobalt methylphosphonates, while those without α-branching were sorbed. In a similar study it was found that only NH_3 was sorbed from the gas phase into zinc phenylphosphonate.[10] Alkylamines were excluded presumably due to the packing of the bulky phenyl rings. However, alkylamines were taken up from the liquid state.[11]

Recently we reported[12] the synthesis and crystal structures of two copper phosphonates. These compounds have copper in an unusual five-coodinate environment in which a water molecule is bonded in the equatorial position of a distorted square pyramidal arrangement. On dehydration these metal phosphonates have been shown to sorb amines, the details of which are reported here.

Experimental Section

Materials and Methods. Copper phosphonates were synthesized by the same methods described in our previous paper.[12] All other chemicals were from commercial sources and used without further purification. X-ray powder diffraction (XRD) patterns were obtained with a Seifert-Scintag PAD-V instrument using Cu Kα radiation. XRD patterns of dehydrated $Cu(O_3PR)$ were carried out in a special air-sensitive sample holder. Thermogravimetric analyses were performed on a Du Pont Thermal Analyst 2000 system under N_2 flow with a typical heating rate 10 °C/min. Infrared spectra were taken on a Bio-Rad FTS-40 by the KBr disk method.

Dehydration of $Cu(O_3PR)\cdot H_2O$ (R = CH_3, C_6H_5, $CH_2C_6H_5$) and Intercalation of Amines into $Cu(O_3PCH_3)$ and $Cu(O_3PC_6H_5)$. The $Cu(O_3PR)\cdot H_2O$ samples were dehydrated by heating in vacuo at approximately 180 °C overnight. As the samples dehydrated, the color changed from bright blue to light green/blue. A slight decrease in volume was observed as $Cu(O_3PCH_3)\cdot H_2O$ was dehydrated, whereas dehydration of $Cu(O_3PC_6H_5)\cdot H_2O$ showed a slight volume increase. The dehydrated samples were stored in a drybox prior to use.

Intercalation of amines was carried out using two different methods. Method A involves a solid–liquid reaction in which the dehydrated samples were immersed in the appropriate liquid amine at room temperature. The color of the solids turned from light blue to a dark brilliant blue immediately upon contact of the liquid amine and the apparent volume of the solids increased

---

* To whom all correspondence should be addressed.

[1] Alberti, G.; Costantino, U.; Allulli, S.; Tomassini, J. *J. Inorg. Nucl. Chem.* 1978, *40*, 1113.

[2] Yamanaka, S. *Inorg. Chem.* 1976, *15*, 2811.

[3] For a relatively complete listing of metal phosphonate references see: Cao, G.; Mallouk, T. E. *Inorg. Chem.* 1991, *30*, 1434.

[4] Poojary, D.; Clearfield, A. *Acta Crystallogr.*, submitted. This paper describes the crystal structure of zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$.

[5] Környei, J.; Szirtes, L.; Costantino, U. *J. Radioanal. Nucl. Chem.* 1985, *89*, 331.

[6] Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* 1988, *27*, 2781.

[7] Martin, K.; Squattrito, P. J.; Clearfield, A. *Inorg. Chim. Acta* 1989, *155*, 7.

[8] Cao, G.; Mallouk, T. E. *Inorg. Chem.* 1991, *30*, 1434.

[9] Johnson, L. W.; Jacobson, A. J.; Butler, W. M.; Rosenthal, S. E.; Brody, J. F.; Lewandowski, J. T. *J. Am. Chem. Soc.* 1989, *111*, 381.

[10] Frink, K. J.; Wang, R-C.; Colon, J. L.; Clearfield, A. *Inorg. Chem.* 1991, *30*, 1438.

[11] Zhang, Y.-P.; Clearfield, A., paper in preparation.

[12] Zhang, Y.-P.; Clearfield, A. *Inorg. Chem.* 1992, *31*, 2821.

0897-4756/93/2805-0495$04.00/0

Table I. Reaction Times of $Cu(O_3PR)$ with Gas-Phase *n*-Alkylamines

n-alkylamine	$Cu(O_3PCH_3)$	$Cu(O_3PC_6H_5)$
propylamine		1 week
butylamine	3 days	10 days
amylamine	1 week	10 days
hexylamine	1 week	3 weeks
heptylamine	>6 weeks[a]	>6 weeks[a]
octylamine	>6 weeks[a]	>6 weeks[a]

[a] Reaction not complete after 6 weeks.

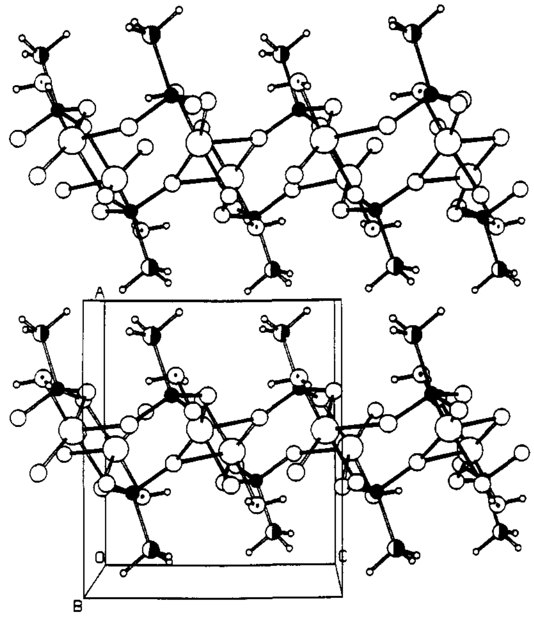

Figure 1. Layered structure of $Cu(O_3PCH_3){\cdot}H_2O$. The largest circles represent Cu atoms, the smallest ones hydrogen atoms, full-filled circles P atoms, half-filled circles C atoms, dotted circles water molecules.

noticeably. To ensure complete reaction, the dehydrated copper methylphosphonates were usually immersed in amines for at least 10 h and the dehydrated copper phenylphosphonates for 3 days or more. Complete intercalation of the copper phenylphosphonates usually occurred within 3 days. The dark blue solids were recovered by simple filtration. As the solid air-dried, the color usually turned to light blue, similar to that of the hydrated sample. The drying process was monitored by XRD. The second method (B) involves a solid–gas reaction in which the dehydrated $Cu(O_3PR)$ is exposed to the amine vapors in a reaction system similar to that described in the literature.[8,10] In the case of amylamine and longer chain *n*-alkylamines, the vessel containing amine was heated to a temperature just below the boiling point of the amine to ensure a sufficient amount of amine in the gas phase. The gas-phase reactions were kept in progress for at least several days (Table I). The resulting blue solids were stored in a drybox prior to characterization.

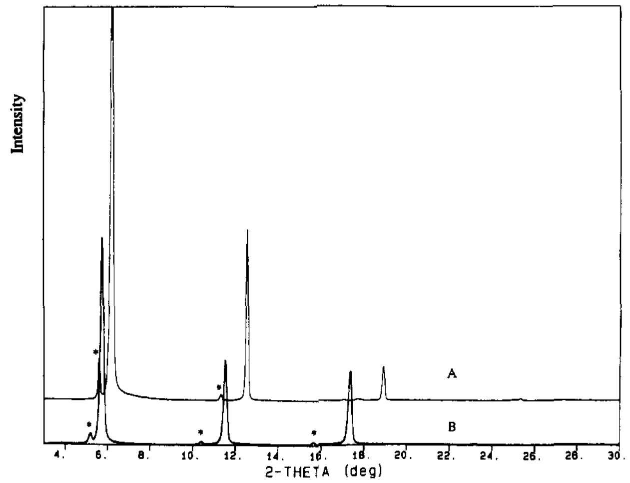

Figure 2. XRD powder patterns of (A) $Cu(O_3PC_6H_5){\cdot}H_2O$ and (B) $Cu(O_3PC_6H_5)$. Asterisks donate reflections due to Kβ radiation.

Table II. TGA, Elemental Analysis, and Interlayer Distance of Hydrated, Dehydrated, and Intercalated Copper Phosphonates

compound	TGA (%RNH_2) calcd	TGA (%RNH_2) obsd	interlayer dist (Å)
$Cu(O_3PCH_3)$			9.7
$Cu(O_3PCH_3){\cdot}H_2O$			8.5
$Cu(O_3PC_6H_5)$			15.4
$Cu(O_3PC_6H_5){\cdot}H_2O$			14.0
$Cu(O_3PCH_2C_6H_5)$			17.3
$Cu(O_3PCH_2C_6H_5){\cdot}H_2O$			15.8
$Cu(O_3PCH_3){\cdot}(C_3H_7NH_2)$	27.3	25.2	
$Cu(O_3PCH_3){\cdot}(C_4H_9NH_2)$	31.7	30.5	
$Cu(O_3PCH_3){\cdot}(C_5H_{11}NH_2)$	35.6	35.8	
$Cu(O_3PCH_3){\cdot}(C_6H_{13}NH_2)$	39.1	39.8	
$Cu(O_3PCH_3){\cdot}(C_7H_{15}NH_2)$	42.2	39.2	
$Cu(O_3PCH_3){\cdot}(C_8H_{17}NH_2)$	45.0	37.6	
$Cu(O_3PC_6H_5){\cdot}(C_3H_7NH_2)_2$	35.0	36.3	14.1
$Cu(O_3PC_6H_5){\cdot}(C_4H_9NH_2)_2$	40.0	42.5	14.8
$Cu(O_3PC_6H_5){\cdot}(C_5H_{11}NH_2)_2$	44.3	44.4	17.1
$Cu(O_3PC_6H_5){\cdot}(C_6H_{13}NH_2)_2$	48.0	49.4	19.2
$Cu(O_3PC_6H_5){\cdot}(C_7H_{15}NH_2)_2$	51.2	50.7	20.9

	%C (found)	%N (found)	%H (found)
$Cu(O_3PC_6H_5){\cdot}(C_4H_9NH_2)_2$	45.96 (45.57)	7.44 (7.99)	7.65 (8.20)
$Cu(O_3PC_6H_5){\cdot}(C_5H_{11}NH_2)_2$	48.74 (46.19)	7.93 (7.96)	7.11 (6.52)

Results

Figure 1 provides a view of the layered structure looking down the *b* axis of $Cu(O_3PCH_3){\cdot}H_2O$. In contrast to the octahedral coordination previously reported for divalent metal phosphonates,[6,7] each copper atom was found to have square-pyramidal coordination with a water molecule occupying one of the four equatorial sites. Because removal of the coordinated water molecule would result in a rare and unfavorable coordination of the Cu atom, high dehydration temperatures are to be expected for these compounds. Indeed, $Cu(O_3PCH_3){\cdot}H_2O$ and $(Cu(O_3PC_6H_5){\cdot}H_2O$ lose their water of coordination at 190 and 160 °C, respectively. In comparison, the corresponding zinc phenylphosphonate dehydrates at 80 °C.[10] Dehydrated copper phosphonates begin to lose organic components around 370 °C, a temperature more than 100 °C lower than the Co and Zn derivatives, which is indicative of the relative instability of the dehydrated copper phosphonates. The anhydrous copper phosphonates are less crystalline than their monohydrates as evidenced by the XRD powder pattern. Figure 2 shows the XRD powder patterns of hydrated and dehydrated copper phenylphosphonates emphasizing the increase in the interlayer spacing upon dehydration. On an expanded intensity scale the non 00*l* reflections appear and those for the dehydrated phase are much broader than those of the hydrate. We were unable to index the pattern of the dehydrated form due to unresolved *hkl* reflections. However, their layered nature is apparent and is shown by the first, second, and third order reflections of the interlayer distance. These reflections are enhanced due to preferred orientation which is characteristic of layered compounds. A most surprising feature of these copper phosphonates is that the interlayer spacing increases by more than 1 Å upon dehydration as

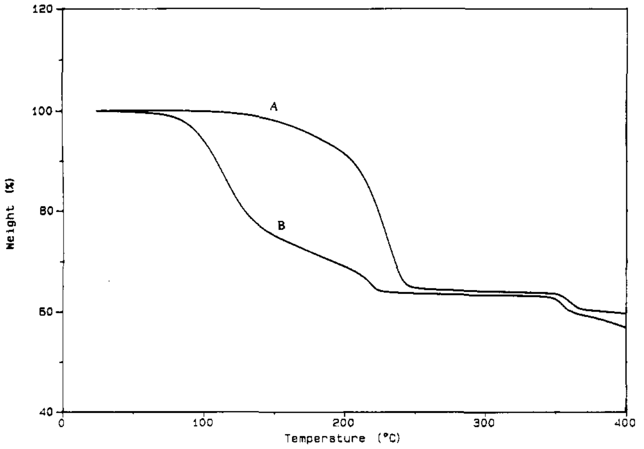

Figure 3. TGA curve of (A) $Cu(O_3PCH_3)\cdot(C_5H_{11}NH_2)$ and (B) $Cu(O_3PC_6H_5)\cdot(C_3H_7NH_2)_2$. The large weight loss represents amine removal and the smaller one decomposition of the phosphonate group.

shown in Table II. The increase in the interlayer distance may be caused by a reversible structural rearrangement after dehydration. However, it should be mentioned that a structural transformation was not detected by differential thermal analysis (DTA). The consistent increase in the interlayer distance of all three copper derivatives indicates that a reversible structural rearrangement may be unique to copper and involves a change in the coordination environment around Cu after dehydration. An increase in the interlayer distance following dehydration has also been reported[8] for $Ni(O_3PCH_3)\cdot H_2O$ which undergoes a change from 8.68 to 9.96 Å. However, dehydration of the Ni^{2+} derivative was not found to be reversible and the loss of the coordinated water occurs at much higher temperature (260 °C). The irreversible nature of $Ni(O_3PCH_3)\cdot H_2O$ has been attributed to a structural rearrangement resulting in octahedral coordination around Ni atom following dehydration.[8] The copper phosphonates do not show this irreversible behavior. Anhydrous $Cu(O_3PCH_3)$ absorbs water from the air rapidly to form the original $Cu(O_3PCH_3)\cdot H_2O$ as indicated by XRD. The $Cu(O_3PC_6H_5)$ and $Cu(O_3PCH_2C_6H_5)$ also reabsorb water but very slowly because of the bulky organic groups. However, they quickly return to the original monohydrated forms when added to water.

Intercalation Reactions of $Cu(O_3PCH_3)$. Like Co and Zn methylphosphonates, anhydrous copper methylphosphonate is quite reactive with primary amines forming $Cu(O_3PCH_3)\cdot(RNH_2)$ (R = n-C_3H_7 to n-C_8H_{17}) through both solid–liquid (method A) and solid–gas (method B) reactions. Using method A, the reaction begins instantaneously and reaches completion within a few hours as evidenced by the immediate color change of the solid from light blue to dark blue and the XRD powder patterns. Thermogravimetric analyses (TGA) confirm the $Cu(O_3PCH_3)\cdot(RNH_2)$ stoichiometry (Table II). All of the observed results agree with the expected results except those for octylamine which may not have reached equilibrium due to incomplete occupation of the empty coordination sites as a result of the larger size of the alkyl chain. A representative TGA curve is shown in Figure 3. The $Cu(O_3PCH_3)\cdot(C_5H_{11}NH_2)$ begins to lose amine at 120 °C which is complete around 250 °C. The second weight loss at 350 °C results from loss of the methyl group.

Another interesting feature of the solid–liquid amine intercalation reactions of copper phosphonates is that the amine intercalates undergo a phase change while drying in air. As the sample dries, the crystalline intercalated phase or phases converts to a final stable crystalline layered phase. Typical XRD patterns accompanying this phase change of $Cu(O_3PCH_3)\cdot(C_7H_{15}NH_2)$ during drying are shown in Figure 4. As the sample dries, the intensity of the reflections of the phase with an interlayer distance of 24.3 Å decreases (to complete disappearance) as the intensities of the reflections of the final phase increases. The XRD powder pattern of the final phase shows it to be layered with at least 3 orders of $00l$ reflections which do not change further. The composition and interlayer distance of the final dried phase agreed very well with that of the solid–gas intercalation product (method B) in each case. For example, $Cu(O_3PCH_3)\cdot(C_5H_{11}NH_2)$ synthesized by method A has an interlayer spacing of 17.1 Å and an interlayer spacing of 16.9 Å when synthesized by method B. The time required to complete the phase transformation during drying is directly related to the size of the primary amines. The larger the amine, the longer the time required, ranging from 3 h for propylamine to 3 days for heptylamine. It is apparent that excess amine is trapped between the layers (when the sample is most wet) perhaps solvating the layered compound in an orderly fashion. As the excess amine volatilizes, the sample goes to the final unsolvated phase where only 1 mol of amine is present occupying the coordination site created upon dehydration. Sorption of excess amine does not occur in the gas–solid reaction. The final product always contains just 1 mol of amine per formula weight or slightly less in the case of long chain amines.

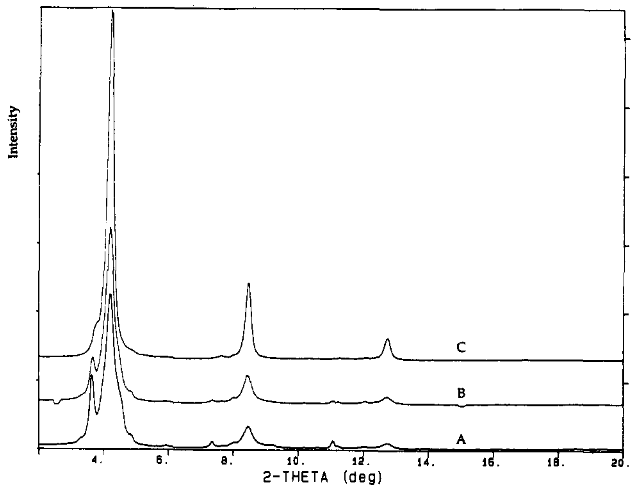

Figure 4. XRD powder patterns of $Cu(O_3PCH_3)\cdot(C_7H_{15}NH_2)$ after filtration and drying in air at room temperature for (A) 29, (B) 48, and (C) 72 h.

Table III. List of Interlayer Distances (Å) for $M(O_3PCH_3)(RNH_2)$ (M = Co,[a] Zn,[a] Cu)

R	Co	Zn	Cu
n-C_3H_7	11.61	10.97	12.8
n-C_4H_9	12.63	13.64	14.8
n-C_5H_{11}	13.92	13.41	17.1
n-C_6H_{13}	16.06	16.23	19.2
n-C_7H_{15}	17.36	15.62	21.0
n-C_8H_{17}	18.71		22.7
$CH_2{=}CHCH_2$			12.5

[a] Data are from ref 8.

Table III lists the interlayer distances of the air-dried n-alkylamine intercalated intercalates of copper methylphosphonate. For comparison purposes similar values

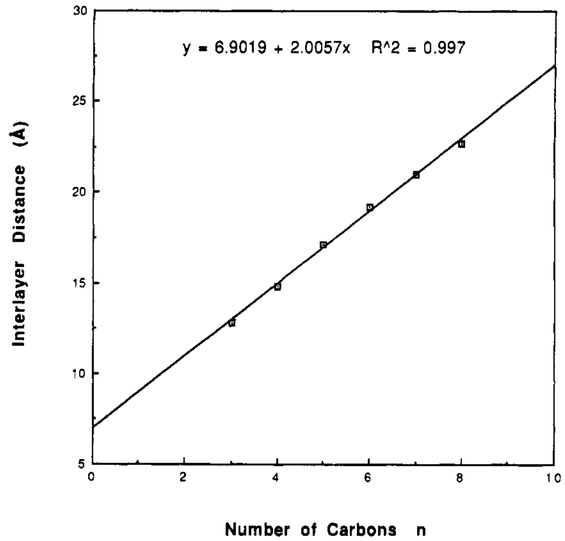

Figure 5. Plot of interlayer distance vs number of carbon atoms in the *n*-alkyl chain for $Cu(O_3PCH_3)\cdot(n\text{-}C_nH_{2n+1}NH_2)$.

for the cobalt and zinc derivatives are also listed. While these latter amine intercalates do not give rise to a regular increase in the interlayer spacing with the number of carbon atoms in the chain,[8] the copper compounds do so. This feature is illustrated in Figure 5. The slope of the straight line is 2.01 Å/carbon atom. Since the slope is much greater than 1.27 Å/CH_2 which is the maximum possible increase in interlayer distance per carbon atom for a interdigitated monolayer arrangement of fully extended all-trans alkyl chains, the alkyl chains in the interlayer region of copper compounds must be packed in a bilayer with a tilt angle of about 53° with respect to the mean plane of the layer.

Infrared spectra also provide strong evidence that the amine occupies the empty coordination site created upon dehydration. The O–H stretching band (3242 cm^{-1}) of coordinated water in $Cu(O_3PCH_3)\cdot H_2O$ (Figure 6) is replaced by three sharper bands around 3244, 3206, and 3123 cm^{-1} which are due to N–H stretching of the amine coordinated to the copper atom in $Cu(O_3PCH_3)\cdot(RNH_2)$. The four bands between 2990 and 2850 cm^{-1} are attributed to the C-H stretch of methyl and methylene groups. Four bands between 1200 and 930 cm^{-1} representing PO_3 vibrations, which remain virtually unchanged, may indicate that the basic structure is retained after amine intercalation. The IR spectra of the $Cu(O_3PCH_3)\cdot(RNH_2)$ series are virtually superimposable (as seen for two such members in Figure 6) indicating the similarity of their basic structures. The only difference is found in the intensities of a few bands. For example, the intensities of the two stretching bands of methylene at 2850 and 2918 cm^{-1} increase significantly as the size of the alkyl chain increases.

$Cu(O_3PCH_3)$ is not reactive toward alcohols at both room temperature and elevated temperatures under similar conditions and prolonged reaction time. The failure of alcohol to intercalate was also observed for Co and Mn phosphonates[8] and is most likely due to the weaker basicity of alcohol relative to amines.

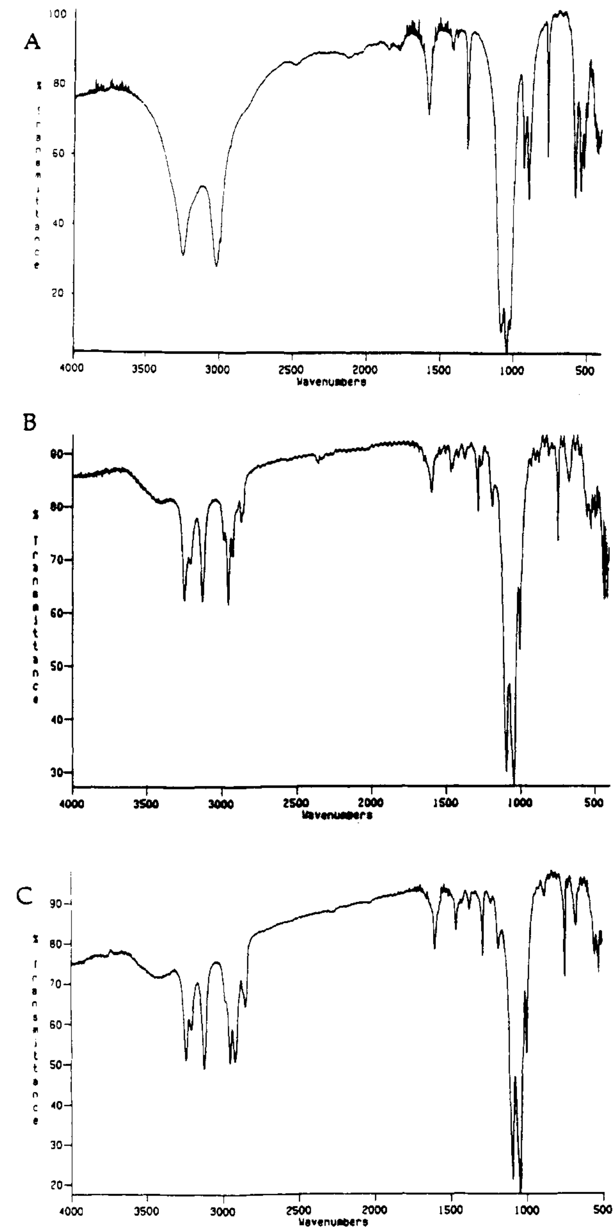

Figure 6. FTIR spectra of (A) $Cu(O_3PCH_3)\cdot H_2O$, (B) $Cu(O_3PCH_3)\cdot(C_4H_9NH_2)$, and (C) $Cu(O_3PCH_3)\cdot(C_6H_{13}NH_2)$.

Intercalation of Primary Amines into $Cu(O_3PC_6H_5)$. Using the solid–gas reaction method, dehydrated zinc or cobalt phenylphosphonate was unable to intercalate larger amines than ammonia after several days of reaction.[10] In contrast, dehydrated copper phenylphosphonate is reactive towards *n*-alkylamines under these conditions. However, the gas–solid intercalation reaction of the copper phenyl derivative was found to be much slower than the copper methyl derivatives (Table I). Zinc and cobalt phenylphosphonate may also require an extended period of time to effect intercalation and this point is under investigation. As expected, reaction of dehydrated copper phenylphosphonate with liquid *n*-alkylamines is much faster and generally complete within 3 days. The reactions were easily followed by XRD as with the methyl derivatives. As the reaction proceeds, the intensities of the 00*l* reflections of the intercalated phase increase at the expense of the intensities attributed to the dehydrated phase $Cu(O_3PC_6H_5)$. The interlayer distances of the intercalates are listed in Table II, along with elemental analyses and weight loss data. The interlayer distances are consistent with those of the intercalated methyl derivatives. However, C,H,N elemental analyses and TGA indicate that the dehydrated $Cu(O_3PC_6H_5)$ intercalates approximately two moles of amine. TGA shows that the loss of amine begins at lower temperature (around 70 °C, compared to

120 °C for intercalated copper methyl phosphonates) and completes below 220 °C (Figure 3). The second weight loss at 350 °C results from decomposition of the phenyl group. It can be seen in Figure 3 that the amine loss is not a single step as in the case of $Cu(O_3PCH_3)\cdot(RNH_2)$, but it is a two-step process.

Discussion

n-Alkylamines can be intercalated into dehydrated $Cu(O_3PR)$ by way of solid–gas or solid–liquid reactions. Results show that the direct reaction of dehydrated $Cu(O_3PR)$ with neat liquid amines occurs more rapidly and efficiently than the analogous solid–gas reaction producing the same resulting end product on air drying.

The copper phosphonates used as host lattices for the amines have layered structures in which the copper atoms exhibit distorted tetragonal pyramidal coordination.[12] Reference to Figure 1 shows this coordination as well as the layer structure of the methylphosphonate compound. Unit cell dimensions for this compound are a = 8.495 Å, b = 7.580(4) Å, c = 7.289(4) Å, β = 90.08(4)° with a representing the interlayer distance. Copper phenylphosphonate crystallizes in the orthorhombic system with an interlayer distance of 13.99 Å which is half of the c axis. The a and b axes are 7.5547(4) and 7.4478(6) Å, respectively. The water molecule in both compounds lies in the equatorial plane and points into the interlayer space in a slightly slanted direction to that of the methyl or phenyl group. Upon dehydration, all the methyl-, phenyl-, and the benzylphosphonates show an increase of more than 1 Å in the interlayer distance. The dehydration step creates not only an open coordination site on the metal but also the lattice expansion which allows for greater accessibility to this site. In the case of the methylphosphonate, it is the intercalated amine which determines the new interlayer distance. For example, in the *n*-propylamine intercalate the new interlayer distance is 12.8 Å as compared to 8.5 Å for the unintercalated parent host. In contrast, the *n*-propylamine intercalate of the phenylphosphonate is determined by the spacing requirement of the phenyl rings. Only when the alkyl chain contained four or more carbon atoms did the interlayer spacings match those of the copper methylphosphonate.

It is important to note that 2 mol of amine was intercalated by the phenylphosphonate as opposed to 1 mol for the methylphosphonate. This means that the second mole of amine is most likely coordinated to the copper in the open axial position of the tetragonal pyramid. This position has its orbital direction only slightly tilted from the mean plane of the layer. Thus, the presence of this additional mole of amine does not further increase the interlayer distance. Why the additional amine does not coordinate to copper in the methylphosphonate we cannot say, but it is likely a steric effect.

It is instructive to compare the behavior of the copper phosphonates with those of Mn, Co, and Zn. X-ray structure determinations of the Mn and Zn phenylphosphonate, $M(O_3PC_6H_5)\cdot H_2O$, show that each metal is in a distorted octahedral coordination in which a water molecule occupies one of the six sites. The metal water bond is directed parallel to the phenyl rings and is roughly perpendicular to the layer direction. In the case of methyl phosphonates, the interlayer distances decrease by ~1.8 Å upon dehydration[8] in contrast to copper compounds which show an increase in this value. However, the phenylphosphonates of Mn, Co, and Zn do not exhibit a similar decrease in interlayer spacing upon dehydration but retain the same value as the monohydrate. This undoubtedly stems from the bulkiness of the phenyl groups which do not permit closer approach of the layers. It is this bulkiness which sterically prevents amines from being sorbed from the gas phase.[10] However, in contact with amine solutions some swelling must occur to allow the amines access to the vacant coordination site. Even though the alkyl chains would then be directed into the interlayer space, they do not exhibit a regular increase in the interlayer spacing. A full report on the amine intercalation by zinc phenylphosphonate will be presented in a subsequent publication.

Acknowledgment. We acknowledge with thanks the financial support of the Robert A. Welch Foundation under Grant No. A673.