with interdigitated monolayer and double-layer alkyl chains.

For $Zn(O_3PCH_3)(n\text{-}C_nH_{2n+1}NH_2)$, the interlayer distance does not increase with $n$ monotonically, as shown in Figure 6. Close inspection of the data points reveals that all the compounds with an even number of carbon atoms in the amine molecule have interlayer distances that fall on one straight line in the plot, with a slope of 1.4762 Å/$CH_2$ and an intercept at $n = 0$ of 7.49 Å; those with an odd number of carbon atoms fall on another straight line with a slope of 1.1635 Å/$CH_2$ and an intercept of 7.52 Å at $n = 0$. From these results the packing of alkyl chains can be rationalized as follows: the alkyl chains must be packed as double layers for even values of $n$ and as interdigitated monolayers for odd values of $n$ within the interlamellar region, because the slope of 1.4762 Å/$CH_2$ for compounds with even $n$ is greater than 1.27 Å/$CH_2$ (vide supra), the slope of 1.1635 Å/$CH_2$ is smaller than 1.27 Å/$CH_2$ for compounds with odd $n$, and the $n$, $n + 5$ contact mentioned previously obviously does not exist for compounds with $n = 3$ or 5. Therefore the tilt angles for these compounds, calculated accordingly, are 35.5° for compounds with even $n$ and 66.4° for those with odd $n$. It is interesting to note that the two intercepts differ slightly (7.49 and 7.52 Å), implying that very little change in the basal structure ($Zn{-}O{-}PCH_3$ network) is involved when the alkyl chains of the amine molecule go from double-layer to single-layer arrangements. In addition, since the two intercepts are significantly smaller than those of $Co(O_3PCH_3)(n\text{-}C_nH_{2n+1}NH_2)$ (8.10 Å), the $M{-}O{-}PCH_3$ networks for M = Co and Zn change in considerably different ways upon intercalation with alkylamines.

The odd/even dependence of the single- or double-layer arrangement for $Zn(O_3PCH_3)(n\text{-}C_nH_{2n+1}NH_2)$ is not at present understood. It must involve some subtle steric factors that make the more efficient interdigitated monolayer packing of alkyl chains impossible for the intercalation compounds with even $n$ values. To elucidate these factors, more structural work is needed, and model building may prove useful. These studies are currently in progress.

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# Intercalation of Ammonia into Zinc and Cobalt Phenylphosphonates

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$Zn(O_3PC_6H_5)\cdot H_2O$ and $Co(O_3PC_6H_5)\cdot H_2O$ can be easily dehydrated to yield structures that are isomorphous with the corresponding monohydrate. The dehydration is reversible since both derivatives quickly reabsorb moisture from the atmosphere. The dehydration reaction leaves an open coordination site on the metal allowing both anhydrous zinc and cobalt phenylphosphonates to intercalate ammonia upon exposure to a flow of ammonia gas, as evidenced by FTIR, elemental analysis, and TGA data. Carbon dioxide, carbon monoxide, oxygen, propylamine, and ethylene were not similarly intercalated. Computer-simulated calculations indicate that intercalation of molecules larger than $NH_3$ result in significant overlap of van der Waals surfaces between the intercalate and the phenyl rings.

## Introduction

Pillared clays are a new class of porous compounds with potential for many future applications in that they are amenable to incorporation of specific and selective structural features and properties such as acidity, surface area, pore size, redox behavior, and ion exchange.[1,2] Layered metal phosphonates in one sense may be considered to be pillared since the metal-oxygen portion of the layers may be separated from each other by predicted amounts.[3-6] The spacing of the organic groups on the layer surface depends upon the bite or bridging reach of the phosphonate groups. Generally, this is of the order of 4-5 Å, which is insufficient to allow access to the interlamellar space by reactant molecules. However, the divalent and some trivalent metal phosphonates contain metal-coordinated water molecules that are readily removed thermally.[7] This procedure leaves a vacant metal coordination site which may be accessible to other species and serve as reaction sites. This report together with that of Cao and Mallouk[10] presents some details on this feature of the divalent metal phosphonates.

The synthesis of a series of layered divalent metal phenylphosphonates of general formula $M(O_3PR)\cdot H_2O$ was first carried out by Cunningham et al.[7] They correctly surmised that the metal was octahedrally coordinated but did not provide further structural detail. In several crystal structure studies[8,9] it was found that these compounds form zigzag layers in which two phosphonate oxygens chelate the metal and at the same time bridge to other metals. The third oxygen is only two-coordinate, being involved in bridging a metal center. The sixth metal coordination site is occupied by the water molecule.

Cunningham[7] also reported that the coordinated water can be removed upon heating to leave a vacant coordination site. Cao and Mallouk[10] show that the resulting dehydrated phosphonates remain crystalline and in some cases retain the same space group

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(1) Pillared Clays. Special issue of *Catal. Today* **1988**, *2*, 185 ff.

(2) Clearfield, A. In *Surface Organometallic Chemistry, Molecular Approaches to Surface Catalysis*; Basset, J. M., Gates, B. C., Candy, J. P., Chaplin, A., Laconte, M., Quignard, F., Santini, C., Eds.; Klower Academic Publishers: Norwell, MA, 1988.

(3) Alberti, G.; Costantino, U.; Alluli, S.; Tomassini, J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113.

(4) Dines, M. B.; Di Giacomo, P. *Inorg. Chem.* **1981**, *20*, 92.

(5) Johnson, J. W.; Jacobsen, A. J.; Brody, J. F.; Lewandowski, J. T. *Inorg. Chem.* **1984**, *23*, 3844.

(6) Clearfield, A. In *Design of New Materials*; Cocke, A., Clearfield, A., Eds.; Plenum: New York, 1986.

(7) Cunningham, D.; Hennelly, P. J. D.; Deeney, T. *Inorg. Chim. Acta* **1979**, *37*, 95.

(8) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781.

(9) Martin, K. J.; Squattrito, P. J.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *155*, 79.

(10) Cao, G.; Mallouk, T. E. Previous article in this issue.

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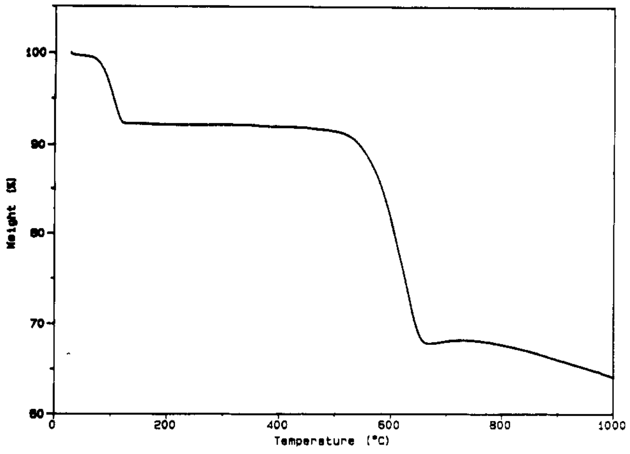

**Figure 1.** Thermogravimetric analysis curve of zinc phenylphosphonate.

symmetry with similar unit cell dimensions as the initial starting material. Furthermore, they report that the dehydrated metal phosphonates show shape and chemical selectivity in intercalating amines. They demonstrated in studying compounds of the type $M^{II}(O_3PR)\cdot H_2O$, where R is an alkyl group but primarily a methyl group, that only primary amines are intercalated.

In keeping with our studies of divalent metal phenylphosphonates, $M^{II}(O_3PC_6H_5)\cdot H_2O$, we have found that a large number of the divalent metals are isomorphous with the zinc phenylphosphonate. Herein, we report on the dehydration and interacalation behavior for both zinc and cobalt phenylphosphonates, as opposed to the methyl phosphonate behavior described in the preceding paper.

## Experimental Section

**Materials and Methods.** Zinc and cobalt phenylphosphonates were synthesized by the same methods reported in the literature.[7-9] Typically, 1 g of zinc chloride was dissolved in 20 mL of deionized water. An equal number of moles of phenylphosphonic acid dissolved in 20 mL of deionized water was added to the stirred metal salt solution. Aqueous NaOH (1 M) was added to make the pH 5–6. A white precipitate begins to form when the pH reaches about 3. All other chemicals were purchased from commercial sources and used without further purification. Deionized water used in all the experiments was purified with a Barnstead Nanopure-II system to a resistivity of 17.6 MΩ cm. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. X-ray powder diffraction patterns were obtained with a Seifert-Scintag PAD II instrument using Cu K$\alpha$ radiation. Thermogravimetric analyses were performed with a Du Pont Thermal Analyst 2000 system. The heating rate was 10°/min. Infrared spectra of samples in the form of a KBr disk or a Nujol mull were taken on a Bio-Rad FTS-40.

**Dehydration of $M(O_3PC_6H_5)\cdot H_2O$ (M = Zn, Co) and Intercalation of Ammonia into the Resulting Layered Product.** Both zinc and cobalt phenylphosphonates were dehydrated by heating in vacuo at approximately 400 °C for nearly 4 h. Dehydrated samples were stored in a drybox prior to use.

The intercalation of ammonia was effected by exposing the dehydrated metal phosphonate to a flow of ammonia gas (prior to reaction, gaseous ammonia was condensed and dried by adding small pieces of sodium metal). For dehydrated cobalt phenylphosphonate, the reaction appeared to be complete in under 3 min, as evidenced by a color change from blue (dehydrated) to pink and by heat loss (the reaction vessel, which consisted of a simple tube with a stopcock at both ends, became warm to the touch). The vessel containing dehydrated zinc phenylphosphonate also became warm to the touch in under 3 min. To ensure complete reaction, the metal phenylphosphonates were usually exposed to ammonia for approximately 2 h, and the ammoniated metal phosphonates were then stored in an inert atmosphere. Longer exposure to the flow of ammonia did not produce different results.

## Results and Discussion

**Preliminary Structure of Dehydrated $M(O_3PC_6H_5)\cdot H_2O$ (M = Zn, Co).** The reaction of divalent metals with alkyl- and arylphosphonic acids to form layered compounds appears to be a general one. Derivatives in which the metals are Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, and Cd have been described.[7-9] X-ray data show that the monohydrates are isomorphous, and in the case of the phenyl derivatives the interlayer spacings are 14.34 (1) Å for the zinc compound and 14.30 (1) Å (uncorrected) for the cobalt compound. These spacings are 5.6 Å larger than the corresponding methyl compounds and reflect the fact that the phenyl rings are 2.8 Å from carbon end to carbon end.

Figure 1 shows the thermogravimetric curve for $Zn(O_3PC_6H_5)\cdot H_2O$. The first weight loss is due to the coordinated water molecule and begins to occur at about 80 °C for zinc (Figure 1) and at about 120 °C for the cobalt derivative (Figure 4). The dehydration temperatures that Mallouk[10] reported for $Zn(O_3PCH_3)\cdot H_2O$ and $Co(O_3PCH_3)\cdot H_2O$, which are 70 and 155 °C respectively, correspond well with our findings. For $Zn(O_3PC_6H_5)\cdot H_2O$ the loss of coordinated water amounts to 7.82%, as compared to a calculated value of 7.53%. The second weight loss results from removal of the aromatic ring, which, should be noted, does not begin until about 500 °C. This is a remarkable stability for organically constituted layers. The weight loss calculated by assuming a $C_6H_4$ group is lost is 32.65%, as compared to an observed value by 31.7%. The sample at this stage is black, being covered with a carbon residue. This residue burns off slowly but at higher temperatures, reducing some of the phosphate groups to phosphorus. This is indicated by the positive slope of the curve above 700 °C.

Upon dehydration, zinc phenylphosphonate and the cobalt derivative retain their crystallinity and appear to be isomorphous with their corresponding monohydrate based on XRD powder patterns. Indeed, Mallouk[10] has indexed the XRD powder pattern of dehydrated $M(O_3PCH_3)$, where M = Zn, Co, Mg, and has shown that the anhydrous phase exists in the same space group as the monohydrate with similar unit cell dimensions. Furthermore, both dehydrated cobalt and zinc phenylphosphonates retain almost the same interlayer distance as the hydrated analogue. For zinc, this interlayer distance is 14.34 Å for the hydrated form and 14.30 Å for the dehydrated state, as determined by the XRD powder pattern (no internal standard was used).

Both cobalt and zinc are in an octahedral environment in the monohydrate state with a water molecule occupying the sixth coordination site. A coordination number change upon dehydration is evidenced by the cobalt derivative, which undergoes a color change from a red-violet to a brilliant blue. Cunningham[7] was the first to report this color change when he measured the magnetic moments of both the hydrated and dehydrated cobalt phenylphosphonate. $Co(O_3PC_6H_5)\cdot H_2O$ was reported to have magnetic moment of 5.11 $\mu_B$, which was consistent with an octahedral arrangement of the metal center. The magnetic moment of dehydrated cobalt phenylphosphonate decreased to 4.73 $\mu_B$, which indicated a decrease in coordination number.

Although it is more common for zinc than cobalt to exist in a five-coordinate geometry,[11] both divalent metal phosphonates absorb moisture from the atmosphere quickly, as indicated by a color change for the cobalt derivative and the evolution of heat from both zinc and cobalt phenylphosphonates, during the sorption process.

The infrared spectra of both the monohydrate and the dehydrated zinc and cobalt phenylphosphonates show striking similarities. The spectra for the monohydrates are virtually superimposable as are those for the dehydrated derivatives. These consistencies give additional support that cobalt phenylphosphonate and its dehydrated form are isostructural with its zinc analogues. The IR spectrum for $Zn(O_3PC_6H_5)\cdot H_2O$ is given in Figure 2A and that for the dehydrated phase in Figure 2B. Note that in the dehydrated compound the OH stretching mode at 3400 cm$^{-1}$ and the OH bending mode at 1600 cm$^{-1}$ are not present.

**Intercalation of Ammonia into $M(O_3PC_6H_5)$ (M = Co, Zn).** The empty coordination site of anhydrous divalent metal phosphonates may be exploited by reaction with ammonia and primary amines to form intercalation compounds. As mentioned above, we report that $Co(O_3PC_6H_5)(NH_3)$ and $Zn(O_3PC_6H_5)(NH_3)$ are synthesized by exposing the dehydrated species to a flow of am-

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(11) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1980; pp 600–601, 766–783.

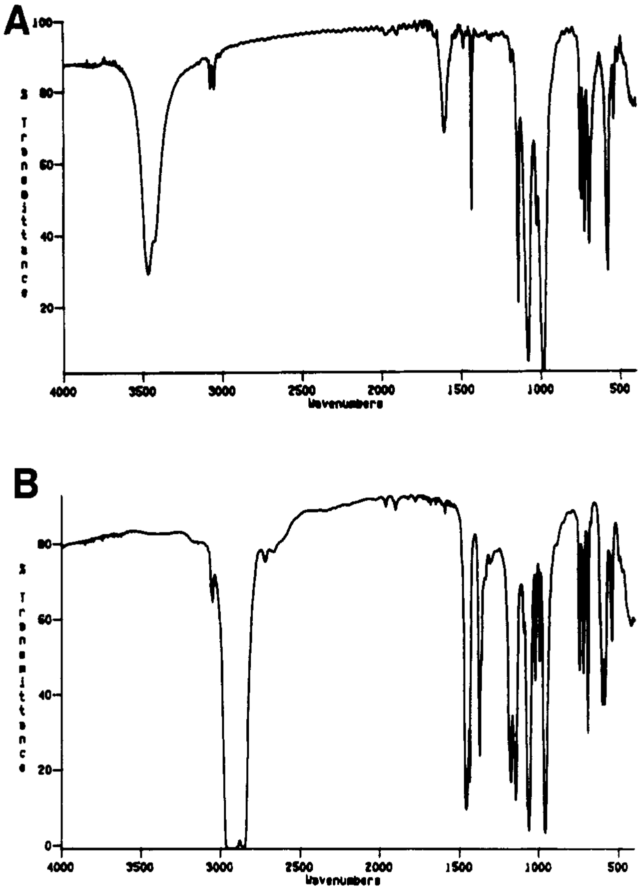

Figure 2. Infrared spectra of (A) hydrated and (B) dehydrated zinc phenylphosphonate.

Table I. Infrared Frequencies (cm$^{-1}$) of $[Co(NH_3)_6]Cl_2$ vs $Co(O_3PC_6H_5)\cdot NH_3$

| | $\nu_a(NH_3)$ | $\nu_s(NH_3)$ | $\delta_a(HNH)$ | $\delta_s(HNH)$ | $\rho_r(NH_3)$ |
|---|---|---|---|---|---|
| $[Co(NH_3)_6]Cl_2$ | 3330 | 3250 | 1602 | 1163 | 654 |
| $Co(O_3PC_6H_5)\cdot NH_3$ | 3334 | 3263 | 1603 | 1259, 1223 | 627 |

monia gas. Uptake of the ammonia occurs most readily, as seen by a color change from brilliant blue to violet-pink for the cobalt compound and by a detectable heat evolution for cobalt and zinc phenylphosphonates. However, uptake of carbon dioxide, carbon monoxide, oxygen, propylamine, and ethylene did not occur under similar reaction conditions, as evidenced by FTIR analyses. Furthermore, the color change expected for cobalt when expanding its coordination number upon intercalation was not observed. The IR spectra were all consistent with dehydrated cobalt or zinc phenylphosphonate.

IR data provide strong evidence that $NH_3$ occupies the empty coordination site created upon dehydration. According to Nakamoto,[12] antisymmetric and symmetric $NH_3$ stretching occurs in the 3400–3000-cm$^{-1}$ region. $NH_3$ deformation is observed in the 1650–1550-cm$^{-1}$ region with symmetric deformation taking place at 1370–1000 cm$^{-1}$. Finally, rocking vibrations occur between 950–590 cm$^{-1}$. Table I shows that many of these bands are found for $[Co(NH_3)_6]Cl_2$ and also coincide with those observed for $Co(O_PC_6H_5)(NH_3)$. The spectrum for $Zn(O_3PC_6H_5)(NH_3)$ is virtually superimposable with that of the cobalt derivative.

It can be visually seen that the spectra of $Co(O_3PC_6H_5)\cdot H_2O$ and $Co(O_3PC_6H_5)(NH_3)$, shown in Figure 3A,B, have many bands in common, lending significant support that the layered phenylphosphonate remains virtually unchanged aside from replacement of $H_2O$ by $NH_3$. It is clear that $Co^{2+}$ and $Zn^{2+}$ both show a stronger affinity for $H_2O$ than $NH_3$. When the exposure

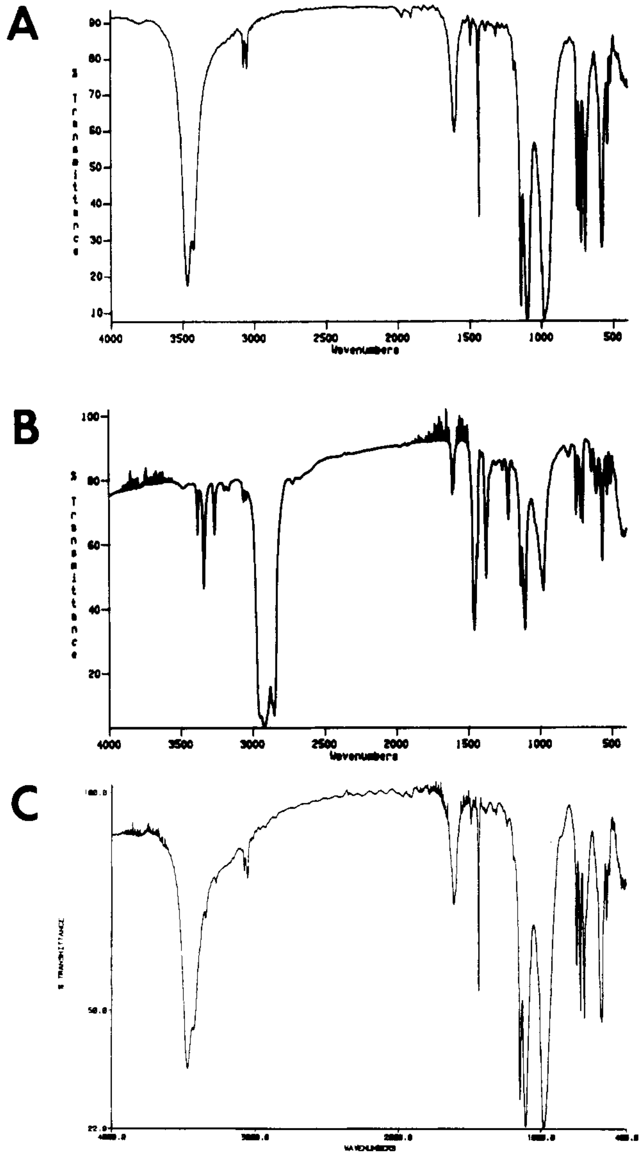

Figure 3. Infrared spectra of (A) hydrated and (B) ammoniated $Co(O_3PC_6H_5)$ and (C) $Co(O_3PC_6H_5)(NH_3)$ after 3 weeks exposure in the atmosphere.

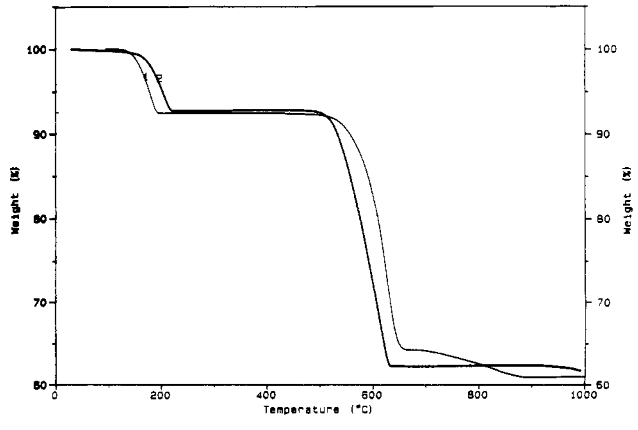

Figure 4. Thermogravimetric analysis curves of (1) hydrated and (2) ammoniated cobalt phenylphosphonate.

of $Co(O_3PC_6H_5)(NH_3)$ to moisture in the air over a period of days is monitored by using FTIR spectroscopy, appearance of the OH stretching peak gradually occurs over time. Figure 3C shows that, after a period of 3 weeks exposure to the atmosphere, a large OH stretching band occurs with shoulders corresponding to the three NH stretching bands. Thus, slow replacement of $NH_3$ by water

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(12) Nakamoto, K. *Infrared and Raman Spectra*; John Wiley and Sons Inc.: New York, 1986, pp 191–192.

**Table II.** Elemental Analysis of $Co(O_3PC_6H_5)(NH_3)$

| | % C | % H | % N |
|---|---|---|---|
| actual | 31.11 | 3.40 | 5.80 |
| theoret | 31.05 | 3.48 | 6.05 |

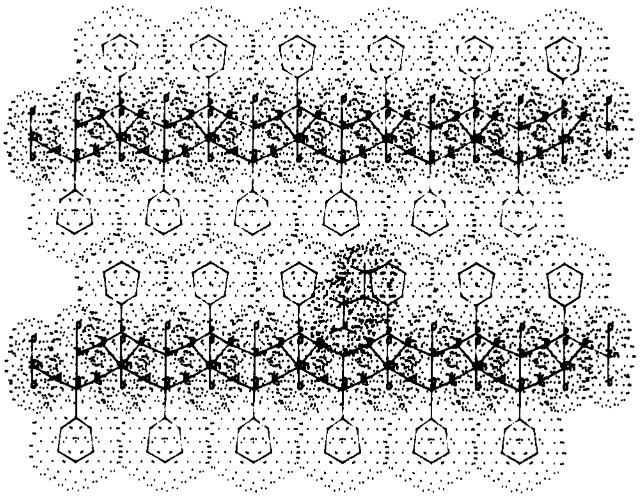

**Figure 5.** Computer simulation of zinc phenylphosphonate with intercalated propylamine generated with an E&S PS-390 graphics system. Dots indicate extent of van der Waals interactions.

vapor has taken place. This same behavior was observed with $Zn(O_3PC_6H_5)(NH_3)$.

Further evidence for the formation of $Co(O_3PC_6H_5)(NH_3)$ can be revealed through thermogravimetric analysis, elemental analysis, and X-ray powder diffraction. Examination of Figure 4 reveals that loss of $NH_3$ begins at approximately 110 °C, slightly higher than the onset of water loss in the hydrated cobalt phenylphosphonate. The loss of mass between 110–300 °C constitutes 7.27% of the total mass. The theoretical value calculated by assuming the formula $Co(O_3PC_6H_5)(NH_3)$ is 7.34%, indicating an excellent agreement with the expected value. Further support of successful occupation of the empty coordination site of dehydrated cobalt phenylphosphonate by ammonia is the elemental analysis of $Co(O_3PC_6H_5)(NH_3)$. Table II shows good agreement between the theoretical and actual values. The slight decrease in the percent N found relative to the theoretical value may be due to the incomplete occupation of all the empty coordination sites. Furthermore, the powder pattern of $Co(O_3PC_6H_5)(NH_3)$ shows an interlayer (010) spacing of 14.2 Å, which is consistent with the value observed for the hydrated compound.

In conclusion, the phenylphosphonates were able to readily intercalate ammonia but not larger molecules as does the methyl derivative. Neither two nor three atom molecules such as ethylene, oxygen, or carbon dioxide were intercalated. While it may be argued that these molecules are much less basic than ammonia, they also appear to be restricted by the positioning of the phenyl groups. Computer-simulated structures indicate that the phenyl ring protons provide a barrier to positioning of small molecules at the open coordination site. This is graphically illustrated by the positioning of propylamine at the vacant coordination site of zinc phenylphosphonate (Figure 5). It can be seen that there is significant overlap of the van der Waals surfaces. Even when the rings on alternate sites are turned 90° to each other, the same interference occurs. This is also the case when CO is substituted for propylamine. Therefore, additional synthetic procedures are in progress to alter structures to allow accessibility to the metal site.

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# Inclusion of a Small Molecule in a Big Cage: Preparation and Structure of *catena*-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]–Toluene(1/1)

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The preparation and crystal structure of the title compound are described. This compound, $Cd[NH_2(CH_2)_8NH_2]Ni(CN)_4 \cdot C_6H_5CH_3$, crystallizes in the monoclinic space group $P2/m$ with $a$ = 11.348 (3) Å, $b$ = 7.652 (2) Å, $c$ = 7.042 (1) Å, $\alpha$ = 90.00°, $\beta$ = 106.07 (2)°, $\gamma$ = 90.00°, and $Z$ = 1. The structure determination indicated the inclusion of a toluene molecule, which is orientationally disordered within a rigid host cage. The distribution of orientations was modeled by analyzing the occupancies of the toluene guest atoms.

## Introduction

Crystal inclusion chemistry has recently attracted interest in a variety of fields.[1,2] Since K. A. Hofmann reported the synthesis of $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$,[3] several compounds of this type have been investigated extensively and can be categorized as classical clathrates.[4–6] After Iwamoto replaced a pair of ammine groups by ethylenediamine,[7] both the Iwamoto group[8] and the Davies group[9] have subsequently reported that a long α,ω-diaminoalkane can replace a pair of ammine groups in the clathrate series to give a novel three-dimensional lattice-structure compound (Hofmann-diam-type): $Cd[NH_2(CH_2)_nNH_2]Ni(CN)_4 \cdot Guest$.[10–14] In the case where $n$ is even, the typical structure consists of ridged cyanometal sheets bridged by all-*trans*-diaminoalkanes. The cage formed by this lattice can contain aromatic guest molecules. We

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(1) Atwood, J. L.; Davies, J. E. D.; MacNicol, K. K., Eds. *Inclusion Compounds*; Academic Press: London, 1984; Vol. 1.
(2) For example: Miki, K.; Masui, A.; Miyata, M.; Shibakami, N.; Takemoto, K. *J. Am. Chem. Soc.* **1988**, *90*, 6594 and references therein.
(3) Hofmann, K. A.; Kuspert, Z. *Z. Anorg. Chem.* **1897**, *15*, 204.
(4) Iwamoto, T. The Hofmann-Type and Related Inclusion Compounds. In ref 1, pp 29–57.
(5) Sharpe, A. G. *The Chemistry of Cyanocomplexes of the Transition Metals*; Academic Press: London, 1976.
(6) Cernak, J.; Dunaj-Jurco, M.; Melnik, M.; Chomic, J.; Skorsepa, J. *Rev. Inorg. Chem.* **1988**, *9*, 259.
(7) Iwamoto, T. *Inorg. Chim. Acta* **1968**, *2*, 269.
(8) Hasegawa, T.; Nishikiori, S.; Iwamoto, T. *J. Inclusion Phenom.* **1984**, *1*, 365.
(9) Davies, J. E. D.; Marer, A. M. *J. Mol. Struct.* **1983**, *102*, 203.