

Inorganic Coordination Polymers. XV. Dioctylphosphinates of Chromium(II), Manganese(II), Iron(II), Nickel(II), and Copper(II)^{1,2}

H. D. GILLMAN

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The dioctylphosphinates $\text{Cr}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$, $\text{Mn}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$, $\text{Fe}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$, $\text{Ni}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$, and $\text{Cu}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$ have been prepared and characterized. In the solid state all appear to have octahedral or square-planar coordination around the metal. The nickel derivative converts to a tetrahedral form above its melting point, whereas the copper and manganese derivatives change geometry upon dissolution. The infrared spectra of these materials in the PO_2 stretching region suggest that several different types of metal phosphinate coordinate linkages are present.

Introduction

In a recent report from our laboratories³ a novel form of cobalt(II) dioctylphosphinate, $(\text{Co}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2)\text{-II}$, which most probably contains octahedral cobalt(II) centers, was discussed. All of the previously known cobalt(II) phosphinates⁴⁻¹³ were reported to contain tetrahedral cobalt(II) and symmetrical bridging O, O' -phosphinate groups. The other first-row transition metal(II) phosphinates of general type $\text{M}(\text{OPRR}'\text{O})_2$ which have been studied include those of chromium(II),¹⁴ manganese(II),^{11,15} nickel(II),¹⁶ and copper(II).^{5,17} The reports on the chromium(II) and copper(II) bis(phosphinates) were not extensive and no structural or molecular weight data have been given. The several nickel(II) bis(phosphinates) studied were assigned tetrahedral nickel(II) centers on the basis of their magnetic susceptibilities and visible spectra, and manganese(II) bis(diphenylphosphinate) was assigned tetrahedral manganese(II) centers on the basis of its elemental analyses and infrared spectrum. However, the data for these metal(II) phosphinates can also be interpreted in terms of octahedral metal centers for some of the compounds.

In most of the metal phosphinates reported the phosphinate group has been assigned a bridging O, O' structure,¹⁸ and in order to determine the extent of this phenomenon it was of interest to study a series of phosphinates of different metals. Thus this report presents the preparation and characterization of chromium(II), manganese(II), iron(II), nickel(II), and copper(II) dioctylphosphinates and compares them to the previously reported first-row transition metal phosphinates.

Experimental Section

Dioctylphosphinic acid (Hynes Chemical Research, Durham, N. C.) was purified by recrystallization from ethanol. Chromium pellets 99.999% pure were purchased from United Mineral and Chemical Corp. (New York, N. Y.). Other chemicals were reagent grade and were used without further purification.

$\text{Cr}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$. This compound, which oxidizes readily in air, was prepared by a method similar to that described for other chromium(II) phosphinates.¹⁹ An aqueous CrCl_2 solution was prepared by adding 20 ml of 2.5 M HCl to a large excess of chromium shot. After the reaction was complete, the resulting chromium(II) chloride solution was filtered into another nitrogen-filled flask and then treated dropwise with 0.045 mol of $\text{KOP}(\text{C}_8\text{H}_{17})_2\text{O}$ in a solution which had been prepared by neutralizing 13.07 g of $(\text{C}_8\text{H}_{17})_2\text{-P}(\text{O})\text{OH}$ with 3.110 g of K_2CO_3 in 100 ml of deaerated methanol and boiling the solution for 15 min. The blue precipitate which formed was filtered off, washed three times with 100-ml portions of methanol, and dried for 5 hr at 70° under vacuum; yield 9.0 g. *Anal.* Calcd for $\text{C}_{32}\text{H}_{68}\text{CrO}_4\text{P}_2$: C, 60.93; H, 10.87; Cr, 8.24; P, 9.82. Found: C, 60.25; H, 10.44; Cr, 8.28; P, 10.08.

$\text{Mn}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$. This material was prepared by combining 0.02 mol of $\text{KOP}(\text{C}_8\text{H}_{17})_2\text{O}$ (5.81 g of $(\text{C}_8\text{H}_{17})_2\text{-P}(\text{O})\text{OH}$ neutralized with 1.38 g of K_2CO_3) in 50 ml of 50% methanol with 1.9 g (0.01 mol) of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 50 ml of H_2O . The resulting precipitate (either pink or white) was filtered off, washed with water, and then dried for 8 hr under vacuum at 70-100°. It was then recrystallized in carbon tetrachloride; yield 6.0 g. *Anal.* Calcd for $\text{C}_{32}\text{H}_{68}\text{MnO}_4\text{-P}_2$: C, 60.64; H, 10.81; Mn, 8.67; P, 9.77. Found: C, 60.24; H, 10.35; Mn, 8.36; P, 9.77. The same procedure utilizing $\text{Mn}(\text{C}_2\text{H}_5\text{-O})_2 \cdot 4\text{H}_2\text{O}$ and $(\text{C}_8\text{H}_{17})_2\text{-P}(\text{O})\text{OH}$ as the starting materials gave a product with an infrared spectrum identical with and a dsc curve similar to those of the product from above.

$\text{Fe}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$. Because this compound oxidizes readily in air, its preparation was carried out in a nitrogen atmosphere with deaerated solvents. The white precipitate formed when 0.02 mol of $\text{KOP}(\text{C}_8\text{H}_{17})_2\text{O}$ in 50% methanol was slowly added to 2.78 g (0.01 mol) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water. It was filtered off and washed with 100-ml portions of water until the washings no longer indicated the presence of sulfate ions. It was then washed with 100 ml of methanol and dried for 6 hr at 70-100° under vacuum; yield 6.0 g. *Anal.* Calcd for $\text{C}_{32}\text{H}_{68}\text{FeO}_4\text{P}_2$: C, 60.56; H, 10.80; Fe, 8.80; P, 9.76. Found: C, 60.76; H, 10.79; Fe, 8.98; P, 10.40.

$\text{Ni}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2$. This yellow compound precipitated after 0.02 mol of $\text{KOP}(\text{C}_8\text{H}_{17})_2\text{O}$ in a water-methanol solution was added to 2.38 g (0.01 mol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in water. It was filtered off,

(1) Presented, in part, at the 164th National Meeting of the American Chemical Society, Aug 29, 1972.

(2) Part XIV: P. Nannelli and H. D. Gillman, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 221 (1974). In the previous papers from our laboratories the formula $\text{M}[\text{OPRR}'\text{O}]_2$ has been used to represent metal phosphinates with bridging phosphinate groups. It is used in this report as a matter of convenience and no structural implication is intended.

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washed thoroughly with 100 ml of hot water, and then dried for 8 hr at 120° under vacuum; yield 6.2 g. *Anal.* Calcd for $C_{32}H_{68}NiO_4P_2$: C, 60.29; H, 10.75; Ni, 9.21; P, 9.72. Found: C, 60.29; H, 10.82; Ni, 8.78; P, 9.82. The reaction of $Ni(C_2H_5O_2)_2 \cdot 4H_2O$ with $(C_8H_{17})_2P(O)OH$ gave a compound having spectra and properties identical with those of the above material.

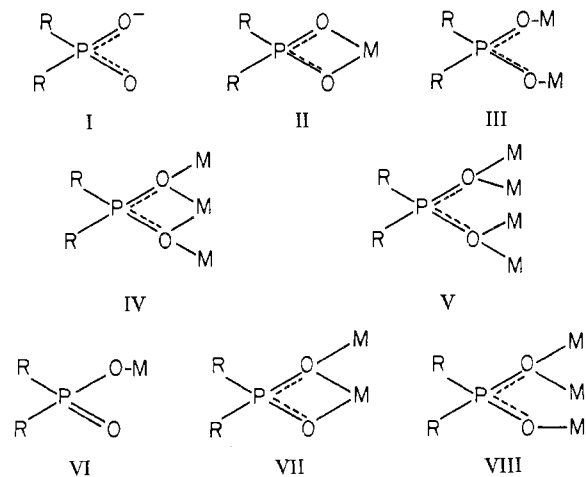
$Cu[OP(C_8H_{17})_2O]_2$. A solution containing 0.02 mol of $KOP(C_8H_{17})_2O$ in 100 ml of 50% methanol was added dropwise to 1.596 g (0.01 mol) of $CuSO_4$ in water. The resulting blue precipitate was filtered off, washed with water and methanol, and finally dried for several hours at 70° under vacuum; yield 6.2 g. *Anal.* Calcd for $C_{32}H_{68}CuO_4P_2$: C, 59.83; H, 10.67; Cu, 9.89; P, 9.64. Found: C, 59.67; H, 10.35; Cu, 10.26; P, 9.36.

Elemental analyses were run by standard methods in the Pennwalt Analytical Department. Infrared spectra were recorded with a Perkin-Elmer 337 grating spectrophotometer on both Nujol and hexachlorobutadiene mulls between KBr disks, as solutions in CCl_4 and as the pure molten compounds between KBr plates. The molecular weight of $Cu[OP(C_8H_{17})_2O]_2$ was obtained with a Mechrolab Model 301A vapor pressure osmometer.

Near-infrared and visible spectra were recorded with a Perkin-Elmer 450 spectrophotometer on Nujol mulls, melts (using glass plates), and CCl_4 solutions. The dsc curves were obtained with a Du Pont dsc cell module and the Du Pont 990 thermal analyzer. The X-ray diffraction unit was a vertical tube mount and standard General Electric 14.32-cm diameter cameras. The magnetic susceptibilities for the powders were determined with a Faraday balance, whereas the magnetic susceptibility of $Cu[OP(C_8H_{17})_2O]_2$ in CCl_4 was determined with a Varian HR-60 nmr spectrometer.

Results and Discussion

The phosphinate groups in the metal phosphinates can assume a variety of possible bonding modes, such as I-VIII.



The mode of coordination of the phosphinate group in each metal phosphinate is in part determined by the coordination number and geometry of the metal centers, and knowledge of these will aid in determining the possible coordination modes in each compound. Additional information on the coordination modes of the phosphinate group can be obtained from their infrared spectra in the PO_2 stretching region by using the same reasoning as is used for the CO_2 stretching frequencies of the metal carboxylates. The separation and position of the symmetric and antisymmetric CO_2 stretching frequencies in the infrared spectra of metal carboxylates has been used extensively²⁰ to differentiate between symmetrical and unsymmetrical carboxylate groups. The reason for this is that a decrease in the equality of the carbonyl groups will result in an increase in the frequency separation of the two carboxyl bands. Similarly the unsymmetrical types of phosphinate groups VI-VIII would be expected to have a larger difference between their PO_2 sym-

metric and antisymmetric absorption frequencies than the symmetric types I-V.

All of the compounds prepared for this study were crystalline and all had unique X-ray powder patterns, except for those of $Mn[OP(C_8H_{17})_2O]_2$ and $Fe[OP(C_8H_{17})_2O]_2$, which are isomorphous with one another as well as with $Co[OP(C_8H_{17})_2O]_2$ -II.³ None of these materials are isomorphous with $Co[OP(C_8H_{17})_2O]_2$ -I which has been shown to contain tetrahedral metal centers as well as symmetrical bridging O, O' -phosphinate groups.³ The anhydrous nature of these compounds was confirmed by the absence of any OH bands in their infrared spectra.

$Cr[OP(C_8H_{17})_2O]_2$. Chromium(II) dioctylphosphinate is a light blue powder readily oxidized by air in the presence of moisture to the chromium(III) polymer $\{Cr(H_2O)_n(OH)[OP(C_8H_{17})_2O]_2\}_x \cdot pH_2O$.²¹ The visible spectrum of $Cr[OP(C_8H_{17})_2O]_2$, presented in Table I, is consistent with six-coordinate chromium(II). The infrared spectrum in the PO_2 stretching region, presented in Table II, contains two broad bands which are similar to those found at 1105 and 1045 cm^{-1} in the spectrum of the oxidation product of $Cr[OP(C_8H_{17})_2O]_2$. The phosphinate groups in the chromium(III) polymers are known to be of the symmetrical bridging type²¹ (type III) so it is reasonable to conclude that the phosphinate groups in $Cr[OP(C_8H_{17})_2O]_2$ are also symmetrical. The broadness of the PO_2 stretching frequencies suggests that several different types of phosphinate groups are occurring, which include the symmetrical types III and IV in order to satisfy a coordination number of 6.

A reversible blue to pink color change is observed upon heating $Cr[OP(C_8H_{17})_2O]_2$ above 185°. It is interesting to note that $Cr[OP(C_6H_5)_2O]_2$ is pink,¹⁹ but it does not change color on either heating to 200° or cooling to -196°.

$Mn[OP(C_8H_{17})_2O]_2$ and $Fe[OP(C_8H_{17})_2O]_2$. The infrared spectrum of solid manganese(II) dioctylphosphinate is almost identical with the spectra of $Fe[OP(C_8H_{17})_2O]_2$ and $Co[OP(C_8H_{17})_2O]_2$ -II, the only difference being in the position of the absorption maxima. Because these materials are all isomorphous, the similarity of the infrared spectra is expected and the coordination symmetry should be the same for all the metals. The white or pink color of $Mn[OP(C_8H_{17})_2O]_2$ and the near-infrared spectrum of $Fe[OP(C_8H_{17})_2O]_2$ (Table I) indicate octahedral coordination,²² which supports the previous assignment to $Co[OP(C_8H_{17})_2O]_2$ -II of six-coordinate metal centers.³ Korshak, *et al.*,¹⁵ prepared the white $Mn[OP(C_6H_5)_2O]_2$ and assigned it a tetrahedral structure with double phosphinate bridges without any structural evidence to support this. It is more likely that this material is also octahedral since tetrahedral manganese(II) compounds are usually yellow-green and octahedral manganese(II) compounds are pink or white.²²

There are three strong bands in the PO_2 stretching region of the infrared spectrum of solid $Mn[OP(C_8H_{17})_2O]_2$; however, in the molten state ($>112^\circ$) or in solution there are just two strong bands, quite similar to those found in the spectra of $Co[OP(C_8H_{17})_2O]_2$ -I³ and $Zn[OP(C_8H_{17})_2O]_2$.⁷ This suggests symmetrical phosphinate groups for $Mn[OP(C_8H_{17})_2O]_2$ in the melt and in solution. This structural transformation is similar to the conversion of $Co[OP(C_8H_{17})_2O]_2$ -II to $Co[OP(C_8H_{17})_2O]_2$ -I except that in the co-

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Table I. Spectral and Magnetic Properties of $M[OP(C_8H_{17})_2O]_2^a$

M	Color	Electronic spectra, $\bar{\nu}$, cm^{-1}	Medium	μ_{eff} , BM
Cr ^b	Blue	15,400	Nujol mull	4.8
		18,500 sh		
Fe ^b	White	8,400	Nujol mull	
		5,750		
Co-I ^c	Blue	6,500	Nujol mull	
		7,500		
		15,800		
		17,000		
		18,200		
		9,100		
		16,300		
Co-II ^d	Blue	17,000	Nujol mull	4.9
		18,200		
		18,200		
		18,200		
Ni	Yellow	7,250 vw	Nujol mull	3.04
		12,500 vw		
		17,300 vw		
		18,700 vw		
		23,200		
Ni	Purple	8,500 vw	Melt (>200°)	2.01
		15,900		
		17,700		
		20,000 br, sh		
Cu	Blue-green	8,250	Solidified melt	
		10,000		
Cu	Blue	11,100	CCl ₄	
		13,300		

^a Key: sh, shoulder; vw, very weak; br, broad. No visible absorptions were observed for $Mn[OP(C_8H_{17})_2O]_2$ as a mull or in solution. ^b No meaningful magnetic measurements or solution spectra could be made on these materials due to their oxidative instability. ^c Tetrahedral form. ^d Octahedral form.³

Table II. PO₂ Stretching Frequencies of Various Dioctylphosphinates

Dioctylphosphinate	Medium	PO ₂ str Freq, cm^{-1}	Septn
NaOP(C ₈ H ₁₇) ₂ O	Nujol mull	1144, 1047	97
KOP(C ₈ H ₁₇) ₂ O	Nujol mull	1142, 1041	101
Cr[OP(C ₈ H ₁₇) ₂ O] ₂	Nujol mull	1133 br, 1055 br	78
Mn[OP(C ₈ H ₁₇) ₂ O] ₂	Nujol mull	1140, 1067, 1015	70
	CCl ₄	1135, 1065	
	Melt (>120°)	1130 br, 1050 br	
Fe[OP(C ₈ H ₁₇) ₂ O] ₂	Nujol mull	1139, 1072, 1020	80
Co[OP(C ₈ H ₁₇) ₂ O] ₂ -I ^a	Nujol mull	1128, 1050	78
Co[OP(C ₈ H ₁₇) ₂ O] ₂ -II ^a	Nujol mull	1135, 1065, 1012	78
Ni[OP(C ₈ H ₁₇) ₂ O] ₂	Nujol mull	1109, 994	115
	Melt (>196°)	1120 br, 1045 br	
	Nujol mull	1109, 1045	
Cu[OP(C ₈ H ₁₇) ₂ O] ₂	Nujol mull	1109, 1045	64
	CCl ₄	1160, 1040	
	Melt (>150°)	1115 br, 1045 br	

^a Reference 3.

balt system the transformation is not reversible whereas in the manganese system it is.

Manganous dioctylphosphinate is soluble only in hot CCl₄ and even dilute solutions gel upon cooling suggesting a polymeric structure for the solid. It was not possible to determine the molecular weight of $Mn[OP(C_8H_{17})_2O]_2$ in these solutions by vapor-phase osmometry because of the high temperatures necessary to keep the solutions from gelling. The very small boiling point elevations observed for these solutions did not allow an accurate molecular weight determination. However, they do indicate a polymeric structure for $Mn[OP(C_8H_{17})_2O]_2$ in solution.

Ni[OP(C₈H₁₇)₂O]₂. The magnetic moment and visible spectrum of the yellow $Ni[OP(C_8H_{17})_2O]_2$ are characteristic of octahedral nickel(II) (see Figure 1 and Table I). Its room-temperature infrared spectrum in the PO₂ stretching region contains two sharp bands with a much greater separation than the corresponding bands in the spectra of sodium, potassium, and cobalt(II) dioctylphosphinates which have

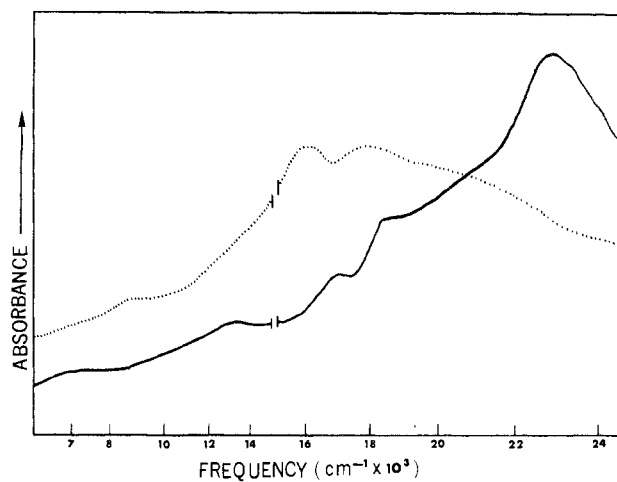


Figure 1. Visible and near-infrared spectra of $Ni[OP(C_8H_{17})_2O]_2$ at room temperature (solid line) and above 200° (dotted line). The symbol || indicates a change in the frequency scale.

symmetrical phosphinate coordination modes. This suggests an unsymmetrical phosphinate mode of coordination for $Ni[OP(C_8H_{17})_2O]_2$ and types VII and VIII satisfy this requirement as well as the octahedral symmetry of nickel(II) centers. Nickel dioctylphosphinate is insoluble in most organic solvents but gels in various aromatic solvents, such as toluene and chlorobenzene, a behavior which is characteristic of cross-linked polymers. Thus, the yellow form of $Ni[OP(C_8H_{17})_2O]_2$ probably consists of a cross-linked polymeric structure involving octahedral nickel(II) centers and unsymmetrical phosphinate bridges of type VII or type VIII or both.

A reversible transformation to a purple form of $Ni[OP(C_8H_{17})_2O]_2$ was observed when it was heated above 196°. The infrared spectrum in the PO₂ stretching region for this form contains two bands which are broadened and shifted from the corresponding bands of the yellow form. The separation and position of the PO₂ stretching frequencies in the infrared spectrum of the purple form are indicative of a symmetrical phosphinate group, and the visible spectrum is characteristic of tetrahedral nickel(II). On this basis the most likely structure is either a double- or alternating single- and triple-bridged polymer as described for other tetrahedral phosphinates with symmetrical phosphinate groups. This however does not rule out the possibility of chelating phosphinate groups because it has not been possible to establish whether the purple form is polymeric. Pitts, Robinson, and Troitz¹⁶ prepared and studied the purple $Ni[OP(C_6H_5)_2O]_2$ and yellow $Ni[OP(H)(C_6H_5)O]_2$ and assigned tetrahedral symmetries to the nickel atoms in both compounds on the basis of their visible spectra and magnetic moments. The tetrahedral assignment for $Ni[OP(C_6H_5)_2O]_2$ is in agreement with the present assignment of the purple form of $Ni[OP(C_8H_{17})_2O]_2$; however their data for $Ni[OP(H)(C_6H_5)O]_2$ are more consistent with octahedral nickel(II) atoms as in the yellow form of $Ni[OP(C_8H_{17})_2O]_2$. It appears then that the nickel atoms in various nickel phosphinates can have either octahedral or tetrahedral symmetry depending upon the substituents on the phosphorus.

Cu[OP(C₈H₁₇)₂O]₂. The absorptions in the visible spectrum of $Cu[OP(C_8H_{17})_2O]_2$ in the solid state are somewhat shifted from those observed in the spectrum of its carbon tetrachloride solutions, but both are consistent with a variety of structures including square planar, distorted octahedral,

Table III. Dsc Transitions for Various Dioctylphosphinates, $M[OP(C_8H_{17})_2O]_2$

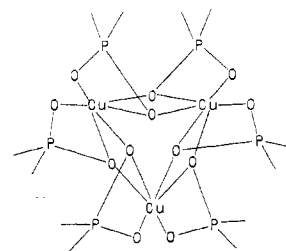
M	Approx transition Temp, °C	ΔH , cal/g	Assignments and comments
Cr	90	15.2	Reversible change in metal symmetry (color change from blue to pink)
	185	[5.9] ^a	
Mn	112	20.5	Melting
Fe	104	19.2	Melting
Ni	180	7.0	Reversible transition from crystalline form to paracrystalline form.
	196	18.1	Reversible change in metal symmetry (color change from yellow to purple)
Cu-I	120	22.9	Melting; transition from form I to form II
Cu-II	81	15.3	Melting

^a This value may be very low due to the partial oxidation of $Cr[OP(C_8H_{17})_2O]_2$. At high temperatures this material is extremely air sensitive, and it is difficult to deaerate the apparatus used in this measurement enough to overcome this problem.

and eight-coordinate.²³⁻²⁵ This is in agreement with the magnetic susceptibility measurements which also indicate that there is no quenching of the spin moment as found in some copper carboxylates. The infrared spectra confirm the existence of different structures in the solid state and in solution because the separation of the PO_2 stretching frequencies of $Cu[OP(C_8H_{17})_2O]_2$ in solution is almost twice the value found in its solid-state spectrum. In the solid form of $Cu[OP(C_8H_{17})_2O]_2$ the phosphinate group probably has a symmetrical mode of coordination (types I-V) as indicated by the relatively small separation of the PO_2 symmetric and antisymmetric stretching frequencies.

Copper(II) dioctylphosphinate has a molecular weight in carbon tetrachloride of ca. 2000 which corresponds to that of the trimer $\{Cu[OP(C_8H_{17})_2O]_2\}_3$. It also appears that the phosphinate group is unsymmetrical since the separation of the PO_2 stretching bands is considerably greater than the separations found for symmetrical phosphinate groups. In addition the sharpness of these bands indicates only one coordination mode for the phosphinate group. A probable structure for this trimer is drawn in Figure 2 in which the phosphinate groups are bridging in a manner similar to that of the acetate groups in $CaCu[OOCCH_3]_4 \cdot 6H_2O$.²⁵

Dsc Studies. These materials were studied by differential scanning calorimetry, and the results are listed in Table III. A light-polarizing microscope was also used to study the air-stable materials in order to determine which convert to a paracrystalline form.^{3,12} The ΔH values obtained for true melting were considerably higher than those values obtained for a transition to a paracrystalline form. The ΔH values of 5.7 and 5.8 cal/g previously obtained for $Zn[OP(C_8H_{17})_2O]_2$ ²⁶ and $Co[OP(C_8H_{17})_2O]_2$ ³, respectively, are consistent

**Figure 2.** Proposed structure for $\{Cu[OP(C_8H_{17})_2O]_2\}_3$.

with the value obtained for $Ni[OP(C_8H_{17})_2O]_2$ for conversion to a paracrystalline form.

Copper dioctylphosphinate had an initial melting point of 120° , but upon cooling and reheating the melting point was lowered to 81° . Although the infrared spectra of the sample before and after heating above 120° were identical, the X-ray powder patterns were considerably different. This transformation to a new crystalline form probably does not involve any change in the backbone because there is no change in the infrared spectrum. A similar polymorphism has been observed for various cobalt and zinc phosphinates, and in these cases the phenomenon has been attributed to changes in the orientation of the side groups.¹²

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Registry No. $Cr[OP(C_8H_{17})_2O]_2$, 51540-17-1; $Mn[OP(C_8H_{17})_2O]_2$, 51540-19-3; $Fe[OP(C_8H_{17})_2O]_2$, 51540-20-6; $Ni[OP(C_8H_{17})_2O]_2$, 51540-21-7; $Cu[OP(C_8H_{17})_2O]_2$, 51540-15-9; $\{Cu[OP(C_8H_{17})_2O]_2\}_3$, 51540-16-0.

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