grateful to Professors F. A. Cotton and J. San Fillipo, Jr., for the valuable exchange of information prior to publication.

Registry No. $Re_2Cl_6(dppm)_2$, 58312-74-6; $Re_2Cl_4(PEt_3)_2(dppm)$, 58298-38-7; $Re_2Cl_4(dppm)_2$, 58298-10-5; $Re_2Br_5(dppm)_2$, 58396-14-8; $[ReBr_2(dppm)]_n$, 58312-72-4; $Re_2Cl_4(dppe)_2$, 58298-35-4; $[ReCl_3(dppe)_{1.5}]_n$, 58298-36-5; $ReCl_3(dppe)\cdot CH_3CN$, 58298-37-6; $Re_2Cl_4(arphos)_2$, 58396-16-0; $Re_2Br_6(arphos)_2$, 58298-34-3; $ReBr_4(arphos)$, 58342-99-7; $Re_2Br_4(arphos)_2$, 58396-15-9; $Re_2Cl_6(dpae)_2$, 58312-73-5; $(Bu_4N)_2Re_2Cl_8$, 14023-10-0; $Re_2Cl_4(PEt_3)_4$, 55400-06-1; $Re_2Cl_4[(P(n\text{-}Pr)_3]_4$, 55400-08-3; $(Bu_4N)_2Re_2Br_8$, 14049-60-6; $Re_2Br_4[P(n\text{-}Pr)_3]_4$, 58298-33-2; $Re_2Cl_6(dppe)_2$, 53139-98-3; $Re_2Cl_5(PEtPh_2)_3$, 55450-45-8; CBr_4, 558-13-4.

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Inorganic Coordination Polymers. XIX. Steric Effects of Hydrocarbon Side Groups on the Structure and Properties of Zinc(II), Cobalt(II), Manganese(II), Nickel(II), and Copper(II) Bis(phosphinates)[1]

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The metal(II) dialkylphosphinates $M[OPR_2O]_2$ (M = Mn, Co, Ni, Cu, Zn; R = $C(CH_3)_3$, $CH_2CH_2CH_2CH_3$, $CH(CH_3)CH_2CH_2CH_3$) have been investigated. The structures of the complexes with straight-chain R substituents vary for the different metals and include polymers with both octahedrally and tetrahedrally coordinated metal centers. On the other hand, the metal(II) phosphinates which contain bulky alkyl R substituents all appear to have the same structure which contains tetrahedrally coordinated metal centers and symmetrically bridging O,O' phosphinate groups.

Metal(II) bis(phosphinates) have received attention in a number of laboratories because of their polymeric structures.[2] Ripamonti, et al., have made a number of single-crystal x-ray studies of beryllium(II), zinc(II), and cobalt(II) bis(phosphinates) and reported that the structures contain chains of tetrahedrally coordinated metal atoms linked by symmetrical O,O' phosphinate bridges.[3] Other workers have assigned similar polymeric structures to other metal(II) bis(phosphinates) including those of nickel(II)[4] and manganese(II).[5] Recently our investigations have shown that a variety of structures occur for these materials, including octahedrally coordinated metal atoms linked by unsymmetrical phosphinate bridges.[6] In order to extend our understanding of these systems further, we have investigated the properties and structural changes that occur with some of these metal centers upon changing the bulkiness and chain lengths of hydrocarbon substituents on the phosphorus.

Experimental Section

The dibutyl- and bis(1-methylbutyl)phosphinic acids were prepared by the procedure of Kosolapoff.[7] The dibutyl acid was purified by recrystallization from hexane. The bis(1-methylbutyl)phosphinic acid was found to be very impure after distillation at 178 °C and 2.2 mmHg. Further purification was accomplished through the preparation, purification, and hydrolysis of its acid chloride. To 11.5 ml of crude compound was added 22.5 ml of thionyl chloride in five increments, and after the initial exothermic reaction subsided, the

Table I. Summary of Analytical Data for $M[OPR_2O]_2$

		Anal., %							
		C		H		P		M	
M	R	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Co	$CH(CH_3)$-$CH_2CH_2CH_3$	51.2	51.0	9.46	9.07	13.2	13.4	12.6	12.5
Co	$C(CH_3)_3$	46.5	46.2	8.78	8.78	15.0	14.8	14.3	15.0
Mn	$CH(CH_3)$-$CH_2CH_2CH_3$	51.6	51.8	9.53	9.55	13.3	13.2		
Mn	$C(CH_3)_3$	47.0	47.0	8.86	8.91	15.1	15.0	13.4	13.0
Ni	$C(CH_3)_3$	46.5	46.3	8.78	8.65	15.0	14.3	14.2	13.2
Ni	$CH_2CH_2CH_2CH_3$	46.5	46.9	8.78	8.95	15.0	15.1	14.2	13.8
Cu	$C(CH_3)_3$	46.0	46.0	8.68	8.71	14.8	15.1	15.2	14.9
Zn	$C(CH_3)_3$	45.8	46.1	8.64	8.80	14.8	15.1	15.6	15.2

Table II. PO_2 Stretching Frequencies of Various $M[OPR_2O]_2$

M	R	PO_2 str freq,[a] cm^{-1}		Sepn, cm^{-1}
Zn	$CH_2CH_2CH_2CH_3$	1135	1055 (1035)	80
Zn	$CH(CH_3)CH_2CH_2CH_3$	1135	1065 (1035)	70
Zn	$C(CH_3)_3$	1138	1040	98
Co	$CH_2CH_2CH_2CH_3$	1128	1055 (1032)	73
Co	$CH(CH_3)CH_2CH_2CH_3$	1132	1062 (1035)	70
Co	$C(CH_3)_3$	1112	1028	84
Cu	$CH_2CH_2CH_2CH_3$	1110	1050 (1085, 1032)	60
Cu	$C(CH_3)_3$	1135	1040 (1055)	95
Mn	$CH_2CH_2CH_2CH_3$	1140	1065 1010 (1040, 1092)	
Mn	$CH(CH_3)CH_2CH_2CH_3$	1135	1065	70
Mn	$C(CH_3)_3$	1128	1035	93
Ni	$CH_2CH_2CH_2CH_3$	1110	990 (1050)	120
Ni	$C(CH_3)_3$	1130	1035	95

[a] The bands which appear in parentheses are very weak and may be either overtones, combination bands, or PO_2 stretching frequencies caused by phosphinate structures not predominant in the bulk polymer.

mixture was refluxed for 30 min. The excess thionyl chloride was removed at reduced pressure, and $[CH_3CH_2CH_2C(CH_3)H]_2P(O)Cl$ was distilled at 88–90 °C and 0.1 mmHg; yield 8.2 g. The chloride was then hydrolyzed by stirring it with 35 ml of H_2O for 5 h at room temperature. This solution was extracted with hexane, the hexane was evaporated, and the product was vacuum dried; yield 4.5 g. Anal. Calcd for $C_{10}H_{23}O_2P$: C, 58.2; H, 11.2. Found: C, 57.8; H, 10.8.

Di-*tert*-butylphosphinic acid was prepared by the hydrolytic oxidation of di-*tert*-butylphosphinous chloride with basic potassium permanganate. Other chemicals and solvents were reagent grade and were used without further purification.

$M[OPR_2O]_2$. All of the metal(II) bis(phosphinates) except $Ni[OP(C_4H_9)_2O]_2$[8] were prepared by the same general procedure. The phosphinic acid was first neutralized in an aqueous solution by treating it with 0.5 mol of K_2CO_3/mol of acid. An excess of K_2CO_3 was avoided, so that metal(II) hydroxyphosphinates would not be formed in the next step. The potassium phosphinate was then added slowly with stirring to an aqueous solution of metal(II) sulfate (0.5 mol of metal(II) salt/mol of potassium phosphinate) except that the nitrate was used for the cobalt polymers. In most cases a precipitate of metal(II) phosphinate formed either immediately or after boiling for 0.5–1.0 h. The exception was $Ni\{OP[C(CH_3)_3]_2O\}_2$ which slowly crystallized as beautiful green needles of the hydrate. The products were filtered, washed with water, and dried under vacuum at 100 °C. These drying conditions are sufficient to dehydrate even $Ni\{OP[C(CH_3)_3]_2O\}_2$, which turns from green to purple during this process. All of the phosphinates were reasonably pure at this point except $Cu\{OP[C(CH_3)_3]_2O\}_2$, which exhibited a strong sharp OH band in its infrared spectrum. Heating this copper phosphinate to 235 °C caused hydroxyl-containing material to sublime, leaving a residue of pure copper bis(phosphinate). The analytical results appear in Table I except for $Zn[OP(C_4H_9)_2O]_2$,[9] $Zn\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$,[10] $Co[OP(C_4H_9)_2O]_2$,[11] $Mn[OP(C_4H_9)_2O]_2$,[12] and $Cu\{OP[OP(C_4H_9)_2O]_2$,[13] which have all been reported previously.

$Ni[OP(C_4H_9)_2O]_2$. This material was prepared by the reaction of $NiCl_2 \cdot 6H_2O$ with $Na[OP(C_4H_9)_2O]$ (0.5 mol of nickel(II) chloride/mol of sodium dibutylphosphinate) in absolute ethanol. The reaction mixture was refluxed for several hours to give a yellow precipitate corresponding to a 40% yield of $Ni[OP(C_4H_9)_2O]_2$. It was dried at 100 °C under vacuum.

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. Near-infrared and visible spectra were recorded with a Perkin-Elmer 450 spectrophotometer on Nujol mulls between glass plates. 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 with standard General Electric 14.32-cm diameter cameras. The magnetic susceptibilities for the powders were determined with a Faraday balance. The mass spectrum of $Zn\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$ was obtained on a Perkin-Elmer RMV-6M mass spectrometer. The molecular weight of $Mn\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$ was obtained with a Mechrolab Model 301A vapor pressure osmometer.

Results and Discussion

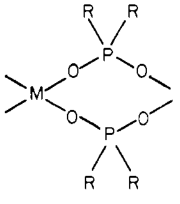
A previous investigation indicated that the PO_2 stretching region of the infrared spectra of the metal(II) bis(dioctylphosphinates) was sensitive to the mode of coordination of the phosphinate groups.[6] The separation of the symmetric and antisymmetric PO_2 stretching bands for unsymmetrical phosphinate groups was considerably greater than for symmetrical phosphinate groups. This information, as well as the coordination geometry as obtained from visible spectra and magnetic measurements, can aid in assigning possible structures for other metal(II) bis(phosphinates). The PO_2 stretching bands for the metal(II) bis(phosphinates) prepared for this study are given in Table II; their visible absorption bands and magnetic moments are given in Table III.

$Co[OPR_2O]_2$ and $Zn[OPR_2O]_2$. The x-ray powder patterns of cobalt and zinc di-*tert*-butylphosphinates show these materials to be crystalline and isomorphous with one another, whereas the cobalt and zinc bis(1-methylbutyl)phosphinates are amorphous. All of the previously studied zinc and cobalt phosphinates were assigned polymeric structures with tetrahedrally coordinated metal centers and symmetrical bridging O,O' phosphinate groups, except for one metastable isomer of $Co[OP(C_8H_{17})_2O]_2$ which probably contains six-coordinate metal centers.[14] The visible spectra of the cobalt phosphinates in this study are similar to those of the previously reported stable cobalt phosphinates and are characteristic of tetrahedrally coordinated cobalt(II). The infrared spectra in the PO_2 stretching region are also similar to the previously studied tetrahedral cobalt and zinc phosphinates suggesting that the phosphinate groups in all of these polymers are coordinating in the same fashion. There are three general types of polymeric structures for the bis(phosphinates) $M[OPR_2O]_2$ with O,O' symmetrically bridging phosphinate groups and tetrahedrally coordinated metal atoms. Polymers with structures I and II are linear and would be expected to be soluble in noncoordinating solvents, although if the molecular weight is very high only swelling would be observed. On the other hand, polymers

Table III. Spectral and Magnetic Properties of $M[OPR_2O]_2$

M	R	Color	Electronic spectra,[a] $\bar{\gamma}$, cm^{-1}	μ_{eff}, BM
Co	$CH(CH_3)CH_2CH_2CH_3$	Dark blue	5 800	*b*
			6 400	
			7 300	
			16 000	
			17 200	
			18 200	
Co	$C(CH_3)_3$	Dark blue	5 700	4.6
			6 300	
			7 200	
			15 800	
			17 100	
			18 200	
Ni	$C(CH_3)_3$	Purple	8 700 vw	3.3
			13 200 vw	
			15 800	
			17 500	
Ni	$CH_2CH_2CH_2CH_3$	Yellow	7 300 w	3.2
			12 300 w	
			14 500 vw	
			17 000 w, sh	
			21 700 vw, sh	
			23 000	
			27 600 br, sh	
Cu	$C(CH_3)_3$	Blue	10 500	1.8
Cu	$CH_2CH_2CH_2CH_3$	Blue	11 000	
Mn	$C(CH_3)_3$	White		5.4
Mn	$CH(CH_3)CH_2CH_2CH_3$	White		5.5
Mn	C_8H_{17}	White		5.6

[a] Key: sh, shoulder; w, weak; vw, very weak; br, broad. [b] Not measured.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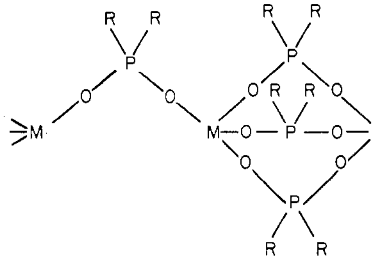
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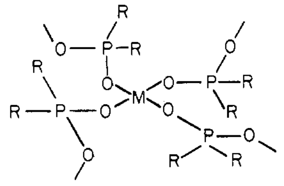

III

with structure III are completely cross-linked and should be insoluble.

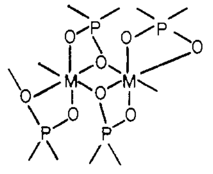
It is also possible that an insoluble polymer can contain linear units of type I or II with some interchain cross-links. A polymer that is cross-linked in this fashion should have low crystallinity and would probably only gel or swell in noncoordinating solvents.

A number of soluble zinc and cobalt phosphinates have been studied by single-crystal x-ray techniques, and all have been found to have alternating single–triple bridges[3] as in structure II. On the other hand, it has been suggested[10] that placing bulky side groups on the phosphorus makes structure I more likely because of the steric hindrance that would be present in structure II. Thus, the x-ray photographs of oriented fibers of $Zn\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$ have been interpreted in terms of structure I.[10]

We found both $Zn\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$ and $Co\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$ to be soluble polymers and concluded that they have either structure I or II. On the other hand, $Zn\{OP[C(CH_3)_2]_2O\}_2$ and $Co\{OP[C(CH_3)_3]_2O\}_2$ are completely insoluble and do not swell or gel in all solvents tested, suggesting a polymeric structure of type III. It is probable that other similar insoluble phosphinates such as $Co[OP(C_6H_5)_2O]_2$ and $Zn[OP(C_6H_5)_2O]_2$[15] also have structure III. For the zinc and cobalt bis(phosphinates) the bulkiness or chain length of the hydrocarbon side groups has little if any effect on the coordination geometry about the metal center or the mode of coordination of the phosphinate groups, but the overall polymer structure may be affected.

The zinc and cobalt polymers in this study were all found to sublime under vacuum; however, all of the sublimates obtained were partially decomposed. Decomposition is indicated by low C and H analyses of the sublimates as well as the presence of alkyl and alkene groups in the sublimation gases (as observed by mass spectral analysis). In some cases the sublimate also gave off a phosphine type odor. The infrared spectra of the majority of these sublimates were similar to those of the starting phosphinate, but in a few cases some changes in the PO_2 stretching bands were observed. The sublimation of $Zn\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$ was followed by mass spectrometry out to a mass of 1361. A very complicated spectrum of over 150 peaks was obtained, but a number of these peaks can be assigned to partially decomposed, zinc-containing monomers, dimers, and trimers. The peaks which were observed at very high mass numbers may be due to higher oligomers, but because they were very weak, they could not be assigned with certainty.

$Ni[OPR_2O]_2$. The spectroscopic and magnetic properties of $Ni[OP(C_4H_9)_2O]_2$ are similar to those of the analogous dioctyl derivative[6] and suggest octahedrally coordinated nickel(II) centers and unsymmetrical phosphinate bridges. Thus the bulk polymer probably contains units of type IV and V. The dibutyl derivative converts to a purple form upon melting at 218 °C, whereas the dioctyl derivative first melts to a paracrystalline form at 180 °C and subsequently converts to a purple isomer at 196 °C. The total ΔH as determined from DSC for the conversion from the yellow form to the purple paracrystalline form for the dioctylphosphinate is 25.1 cal/g and for the dibutyl derivative it is 39.2 cal/g. The spectroscopic properties of the purple form of both $Ni[OP(C_8H_{17})_2O]_2$ and $Ni[OP(C_4H_9)_2O]_2$ indicate that the phosphinate groups are symmetrical and the metal atoms are tetrahedrally coordinated. A structure with monomer units of type III is consistent with the insolubility of the purple isomers in nonpolar solvents. This structure is also the most probable one for $Ni\{OP[C(CH_3)_3]_2O\}_2$, which is insoluble in noncoordinating solvents and has spectroscopic properties similar to the purple isomers of the nickel(II) phosphinates with linear alkyl side groups.[6] On the other hand, the magnetic moment of $Ni\{OP[C(CH_3)_3]_2O\}_2$ suggests that the nickel(II) centers are in a distorted tetrahedral environment. Cooling this material down to liquid-nitrogen temperatures does not produce a yellow form, and heating to 350 °C does not cause any melting. Thus, the bulkiness of the side groups has a substantial effect on the structure of the nickel(II) bis(phosphinates), including the mode of coordination of the phosphinate groups and the coordination geometry of the nickel(II) atoms.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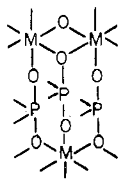
V

$Mn[OPR_2O]_2$. All of the manganese(II) phosphinates in this study are pure white with subnormal magnetic moments. The properties of $Mn[OP(C_4H_9)_2O]_2$ are almost identical with those of $Mn[OP(C_8H_{17})_2O]_2$, including the presence of three strong PO_2 stretching bands in its infrared spectrum.[6] In contrast, there are only two strong PO_2 stretching bands in the spectra of both $Mn\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$ and $Mn\{OP[C(CH_3)_3]_2O\}_2$, and the separation of these bands is consistent with symmetrical phosphinate groups. The molecular weight of $Mn\{OP[CH(CH_3)CH_2CH_2CH_3]_2O\}_2$ in carbon tetrachloride is greater than 35000, whereas $Mn\{OP[C(CH_3)_3]_2O\}_2$ is insoluble in all solvents tested. Its x-ray powder pattern shows $Mn\{OP[C(CH_3)_3]O\}_2$ to be isomorphous with the *tert*-butylphosphinates of cobalt(II), zinc(II), and nickel(II), and therefore it should also have a distorted tetrahedral structure. It is generally believed that tetrahedrally coordinated manganese(II) compounds are yellow or green and those with octahedral symmetry are white. The white appearance of $Mn\{OP[C(CH_3)_3]_2O\}$ must then be rationalized on the basis that it does not have pure tetrahedral symmetry and therefore p–d orbital mixing cannot occur.

$Cu[OPR_2O]_2$. The properties of $Cu[OP(C_4H_9)_2O]_2$ are similar to those of $Cu[OP(C_8H_{17})_2O]_2$, suggesting that the same type of structure occurs in both materials.[6] On the other hand, $Cu\{OP[C(CH_3)_3]_2O\}_2$ is insoluble in all solvents tested and isomorphous with all of the other *tert*-butylphosphinates in this study. Thus, $Cu\{OP[C(CH_3)_3]_2O\}_2$ should also have distorted tetrahedrally coordinated metal centers and symmetrical bridging phosphinate groups.

Conclusions

It is evident from this study that the first-row transition metal(II) bis(phosphinates) with bulky side groups prefer a configuration with tetrahedrally coordinated metal centers and bridging phosphinate groups, whereas for those with linear-chain alkyl side groups other configurations readily occur. Although the length of the alkyl chain side groups has little effect on the structure of the bis(phosphinates), some physical property differences are observed for different chain lengths. The magnetic behavior of these and other phosphinate polymers is presently being investigated,[16] but to date it has not been possible to correlate the structural parameters with the magnetic properties in these simple metal(II) systems.

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Registry No. $Zn[OP(C_4H_9)_2O]_2$, 29469-35-0; $Zn[OP(CH(CH_3)CH_2CH_2CH_3)_2O]_2$, 58281-30-4; $Zn[OP(C(CH_3)_3)_2O]_2$, 58281-32-6; $Co[OP(C_4H_9)_2O]_2$, 36788-28-0; $Co[OP(CH(CH_3)CH_2CH_2CH_3)_2O]_2$, 58281-34-8; $Co[OP(C(CH_3)_3)_2O]_2$, 56698-21-6; $Cu[OP(C_4H_9)_2O]_2$, 58281-36-0; $Cu[OP(C(CH_3)_3)_2O]_2$, 58281-38-2; $Mn[OP(C_4H_9)_2O]_2$, 52664-86-5; $Mn[OP(CH(CH_3)CH_2CH_2CH_3)_2O]_2$, 58281-40-6; $Mn[OP(C(CH_3)_3)_2O]_2$, 56698-23-8; $Ni[OP(C_4H_9)_2O]_2$, 58281-42-8; $Ni[OP(C(CH_3)_3)_2O]_2$, 58281-44-0.

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trans-Dihydridotetrafluorophosphate(V) Anion, *trans*-$H_2PF_4^-$

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The novel $H_2PF_4^-$ anion was synthesized in the form of its K^+ and Cs^+ salts. Both compounds are white stable solids decomposing at 266 and 284 °C, respectively. Vibrational and ^{19}F NMR spectroscopy show that the anion has a pseudooctahedral structure with the hydrogen ligands in trans position. All ten active fundamentals expected for symmetry D_{4h} were observed and assigned. A normal-coordinate analysis was carried out and shows that $H_2PF_4^-$ contains highly polar PF bonds.

Introduction

During the synthesis of H_2PF_3 according to the method[1] of Holmes and Storey we observed that the NaF, used for the removal of the HF impurity, formed a labile adduct with H_2PF_3. Whereas numerous alkyl- or aryl-substituted fluorophosphates are known,[2,3] to our knowledge no reports have been published on the existence of the corresponding parent compounds, the hydridofluorophosphates. In view of this and the general interest in fluorine-substituted phosphorus compounds, it seemed interesting to synthesize stable hydridofluorophosphates. For $H_2PF_4^-$ further interest was added by the question of whether the two hydrogen ligands are in cis or in trans position.

Experimental Section

Apparatus and Materials. The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 4251 F4Y). Pressures were measured with a Heise Bourdon tube type gauge (0–1500 mm ±0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were