AD-A041 511   PENNWALT CORP KING OF PRUSSIA PA RESEARCH AND DEVELO--ETC F/G 7/2
THE SYNTHESIS AND CHARACTERIZATION OF THE POLY(METAL PHOSPHINAT--ETC(U)
JUN 77 B P BLOCK, H D GILLMAN, P NANNELLI   N00014-69-C-0122

UNCLASSIFIED   NL

1 OF 1
AD
A041511

END
DATE
FILMED
8-77

12

OFFICE OF NAVAL RESEARCH

(15) Contract N00014-69-C-0122

Task No. NR 356-408

(9) FINAL REPORT.

15 October 1968 - 31 March 1977

(6) THE SYNTHESIS AND CHARACTERIZATION OF THE POLY(METAL PHOSPHINATES).

by

(10) B. P./Block, H. D./Gillman, and P./Nannelli

Pennwalt Corporation
Central Research and Development Department
King of Prussia, Pennsylvania

(11) June 1977

(12) 30p.

Reproduction in whole or in part is permitted for any purpose of the United States Government

Approved for Public Release; Distribution Unlimited

404 871

JB

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
THE SYNTHESIS AND CHARACTERIZATION
OF THE POLY(METAL PHOSPHINATES)

5. TYPE OF REPORT & PERIOD COVERED
Final Report
10/15/68 - 3/31/77

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
B. P. Block, H. D. Gillman, and
P. Nannelli

8. CONTRACT OR GRANT NUMBER(s)
N00014-69-C-0122

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Pennwalt Corporation
900 First Avenue
King of Prussia, Pa. 19406

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 356-408

11. CONTROLLING OFFICE NAME AND ADDRESS
Department of the Navy
Office of Naval Research
Arlington, Virginia 22217

12. REPORT DATE
June 1977

13. NUMBER OF PAGES
26

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)
Office of Naval Research
Chemistry Branch
Arlington, Virginia 22217

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Available to the public from NTIS. No limitations on distribution.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES
None

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Inorganic polymers
Coordination polymers
Poly(metal phosphinates)
Chromium compounds
Zinc compounds
Phosphorus compounds
Transition metal compounds
High temperature coatings
Grease thickeners
Metal-loaded laminates

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A general investigation of the synthesis and characterization of poly(metal phosphinates), which covered a wide range of materials including numerous metal centers and bridging phosphinate groups, resulted in a much more comprehensive understanding of them, permitting their development for a variety of applications. Technical reports, publications, issued and allowed patents, and oral presentations are tabulated. Daughter contracts stemming from this fundamental program are also cited.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Table of Contents

Abstract

A general investigation of the synthesis and characterization of poly(metal phosphinates), which covered a wide range of materials including numerous metal centers and bridging phosphinate groups, resulted in a much more comprehensive understanding of them, permitting their development for a variety of applications. Technical reports, publications, issued and allowed patents, and oral presentations are tabulated. Daughter contracts stemming from this fundamental program are also cited.

The Synthesis and Characterization of the Poly(Metal Phosphinates)

A. General Comments

The purpose of the present investigation was to continue the investigation of the poly(metal phosphinates), a unique family of inorganic polymers first recognized during our work on ONR Contract Nonr 2687(00), the forerunner of ONR Contract N00014-69-C-0122. It has two broad goals, (1) the development of a more complete understanding of the chemistry and physical properties of the poly(metal phosphinates) and (2) the synthesis and characterization of new poly(metal phosphinates) designed for a variety of applications.

The structures and properties of the new metal phosphinates differ to a greater or lesser extent depending on the central metal, the side groups of the phosphinate, and other ligands that may be present. In addition to further studies with chromium(III), zinc(II), cobalt(II), copper(II), titanium(IV), zirconium(IV), and iron(II) and (III), work was undertaken with manganese(II), nickel(II), molybdenum(II), ruthenium(II), rhodium(II), hafnium(IV), tantalum(V), tungsten(II) and (VI), lead(II), europium(II), thorium(IV), and uranium(VI). A variety of phosphinate groups was also studied, primarily as the zinc derivatives.

In a number of cases the phosphinate group does not function merely as a symmetrical bridge via O,O' bonding, and in particular there is evidence for bridges involving unsymmetrical bonding in some poly(metal phosphinates). Structural rearrangements have been observed for some poly(metal phosphinates) upon dissolution and/or upon melting. Molecular weights of soluble poly(metal phosphinates) vary over a wide range, corresponding to degrees of polymerization from two to several thousand. In some cases the molecular weights are quite sensitive to the type and purity of the solvent, indicating that dissociation can occur in solution.

The magnetic properties of selected poly(metal phosphinates) were investigated in a joint effort with physicists at the University of Pennsylvania. The phosphinate groups were found to provide a path for antiferromagnetic supercharge J/k~0-5K. An interesting result of this investigation is the observation that disorder in the polymer plays an important role in determining the magnetic properties, limiting the range of spin correlation.

New poly(metal phosphinates) have been supplied for investigation in application work sponsored by other agencies. A number of very promising high temperature coatings based on zinc and zirconium phosphinates have been developed for the Air Force. These coatings have properties superior to those of current standards. Evaluation of some phosphinates as plasma sprayed coatings is currently underway for the Naval Air Development Center.

Recently it has been shown with Air Force support that some zirconium phosphinates are excellent thickeners for a number of high temperature fluids and convert them to promising greases. Both pyrolyzed and unpyrolyzed metal-loaded laminates with good properties have been prepared with ONR and Air Force support.

The remainder of this report consists of compilations of technical reports with summaries, publications, patents, oral presentations, and daughter Pennwalt contracts based at least in part on work performed on this contract or contract Nonr 2687(00). It is anticipated that work on applications for poly(metal phosphinates) will continue at Pennwalt.

B. Summary of Technical Reports Issued

Technical Report No. 1. "Inorganic Coordination Polymers. XI. A new Family of Chromium(III) Bis(phosphinate) Polymers, $[Cr(OH)(OPRR'O)_2]_x$." P. Nannelli, H. D. Gillman, and B. P. Block. May, 1971. AD-724 768. Manuscript for Publication No. 6.

Heating hydroxyaquochromium(III) bis(phosphinates) at temperatures up to 200°C under vacuum yields the corresponding anhydrous polymers $[Cr(OH)(OPRR'O)_2]_x$. The infrared and visible spectra and solution properties lead to the following conclusions. When R and R' are phenyl groups, the hydroxyl groups appear to bridge between adjacent chromium atoms in the chain together with the phosphinate ligands to yield a linear, triple-bridged polymer. When at least one substituent on the phosphorus is an alkyl group, some of the hydroxyl groups crosslink between chains to yield less soluble polymers. Comparison of the properties of these new polymers with the parent polymers suggests that the latter should be formulated $[Cr(H_2O)_n(OH)(OPRR'O)_2]_x \cdot pH_2O$ and that they contain more than one kind of monomer unit. The parent polymers can be readily prepared by a new method that involves reaction of a soluble chromium(III) salt with alkali metal phosphinates or of chromium(III) hydroxide with phosphinic acids in a water-tetrahydrofuran mixture.

Technical Report No. 2. "Inorganic Coordination Polymers. XII. Chromium(III) Tris(phosphinates)." P. Nannelli, B. P. Block, J. P. King, A. J. Saraceno, O. S. Sprout, Jr., N. D. Peschko, and G. H. Dahl. June, 1971. AD-763 691. Manuscript for Publication No. 9.

Cohesive films of a series of chromium(III) tris(phosphinates) $[Cr(OPRR'O)(OPR''R'''O)(OPR^*R^{**}O)]_y$ in which the side groups on the phosphorus are alkyl, phenyl, and/or hydrogen groups have been prepared by reaction casting or by hot pressing. The preparative reaction appears to involve conversion of an aquahydroxo or hydroxo chromium(III) bis(phosphinate) to an intermediate hydroxo bis(phosphinate) containing coordinated phosphinic acid followed by an intrachain reaction leading to the tris(phosphinate). Tensile strengths of the chromium(III) tris(phosphinates) range from 100 to 5600 psi, elongations from less than 1 to 100%. Thermogravimetric data indicate that major decomposition occurs at temperatures from 200 to 435°C in air and from 410 to 510°C in nitrogen. Infrared spectra and physical properties are interpreted to support a structure for the chromium(III) tris(phosphinates) that is based on linear, triple-bridged chains. The presence of octyl or other long alkyl side groups on the phosphorus improves the physical properties, presumably by internal plasticization, but leads to decreased thermal stability.

Technical Report No. 3. "Inorganic Coordination Polymers. XIII. Chromium(III) Halo bis(phosphinates)." H. D. Gillman, J. P. King, and B. P. Block. June, 1971. AD-763 692. Manuscript for Publication No. 10.

μ-Halo-bis(μ-phosphinato)-chromium(III) polymers, $[CrX(OPRR'O)_2]_n$ (with $R=R'=C_6H_5$, $R=R'=C_8H_{17}$, and $R=CH_3$ and $R'=C_6H_5$; X=Cl, Br, and I), have been investigated. The chloro polymers were prepared by the reaction of anhydrous chromium(III) chloride with the appropriate phosphinic acid. The bromo and iodo polymers were prepared by oxidizing chromium(II) phosphinates with bromine and iodine, respectively. The chloro and bromo diphenylphosphinato polymers are soluble in common organic solvents and have molecular weights corresponding to degrees of polymerization of 10-12. They are hydrolytically unstable, forming first an aquated halo species and eventually the corresponding aqua hydroxo polymer $\{Cr(H_2O)_p(OH)[OP-$

$(C_6H_5)_2O]_2\}_n \cdot qH_2O$. They are quite stable thermally and exhibit initial weight loss at 360° and 310°, respectively, by thermogravimetric analysis. The iodo polymer, on the other hand, starts evolving iodine below 100°. The solubility and visible and infrared spectra of these polymers indicate a linear structure similar to that previously suggested for μ-hydroxo-bis(μ-phosphinato)-chromium(III) polymers. In this structure all three anions function as bridging groups.

Technical Report No. 4. "Phosphinylmethyl Derivatives." J. P. King, I. C. Popoff, and B. P. Block. June, 1971. AD-763 693.

Diphenylphosphinylmethanol, methylphenylphosphinylmethanol, and dimethylphosphinylmethanol have been prepared by fusion reactions of sodium acetate and the corresponding P,P-disubstituted chloromethylphosphine oxide at elevated temperatures followed by acid hydrolysis. The intermediate phosphinylmethyl acetates have been isolated and characterized. Both infrared and hydrogen nmr results show that there is extensive intramolecular hydrogen bonding in these phosphinylmethanols.

Technical Report No. 5. "Various Phosphonitrilates of Chromium(III)." J. P. King and B. P. Block. June, 1971. AD-763 694.

A series of chelates of chromium(III)--$Cr(OPPh_2NPPh_2O)_3$, $Cr(OPPh_2NPPh_2O)_2(AcCHAc)$, and $Cr(OPPh_2NPPh_2O)(AcCHAc)_2$--has been synthesized and characterized by elemental analyses, melting points, infrared spectra, and molecular weights. TGA data show that the chromium(III) tris(phosphonitrilate) is stable to 410° in air.

Technical Report No. 6. "Four- and Six-Coordinate Cobalt(II) Dioctylphosphinate." H. D. Gillman. June, 1972. AD-744 960. Manuscript for Publication No. 7.

A new form of cobalt(II) dioctylphosphinate (form II) was prepared by the reaction of cobalt(II) chloride with dioctylphosphinic acid in absolute ethanol. Visible and near infrared spectra indicate that form II contains octahedrally coordinated cobalt(II), whereas the previously reported form (form I) contains tetrahedrally coordinated cobalt(II). Form II is irreversibly converted to form I by heating above 68° or by dissolving it in nonpolar solvents. Infrared spectra, X-ray powder patterns, and DSC thermograms for both forms are presented and compared. This appears to be the first example of a poly(metal phosphinate) that exists both in four- and six-coordinate forms.

Technical Report No. 7. "Polymeric Chromium(III) Bis(phosphinates)." H. D. Gillman, P. Nannelli, and B. P. Block. June, 1972. AD-744 961. Manuscript for Publication No. 21.

General procedures avoiding the use of chromium(II) intermediates are presented for the synthesis of two types of chromium(III) bis(phosphinate) polymers, $[Cr(H_2O)(OH)(OPRR'O)_2]_x$ and $[Cr(OH)(OPRR'O)_2]_x$.

Technical Report No. 8. "Observations on Some Poly(metal phosphinates)." B. P. Block, H. D. Gillman, P. Nannelli, and P. T. Grzymala. June, 1972. AD-744 962. Manuscript of a paper presented at the 164th American Chemical Society meeting, New York, N. Y., August, 1972.

Dioctylphosphinates of the bivalent first-transition-series elements from chromium through zinc have been prepared and characterized. The variety of forms found is discussed. Cobalt(II), iron(II), and manganese(II) yield a form based on octahedral centers that requires multiple sharing of some individual phosphinate oxygens. Chromium(II) and nickel(II) may give similar derivatives. Uranyl phosphinates can be divided into two groups based on solubility. The viscosity and molecular weight data obtained for some of the soluble species indicate that they are polymeric although their solution behavior is not ideal. Infrared and Raman spectra suggest that the uranyl oxygen atoms are not shared in the soluble species and consequently that the bridging is via phosphinate groups. It has proved possible to prepare flexible, strong, crystalline films of the chromium tris-(phosphinate) $Cr[OP(CH_3)(C_6H_5)O]_2[OP(C_8H_{17})_2O]$ reproducibly. Brittle, amorphous films result, however, under certain conditions. The differences in the films are accounted for on the basis of the plasticizing action of octyl groups spaced in regular fashion along the backbone of the polymer in the flexible form.

Technical Report No. 9. "Inorganic Coordination Polymers. XIV. Chromium(III) Phosphinate Perfluorocarboxylate Polymers." H. D. Gillman and P. Nannelli. September, 1973. AD-766 837. Manuscript for Publication No. 11.

A series of polymers, $\{Cr(OH)(OPRR'O)[OOC(CF_2)_{\underline{n}}CF(CF_3)_2]\}$ has been prepared and studied. The polymers with $R=R'=C_6H_5$ are soluble in CCl_2FCClF_2, whereas those with $R=CH_3$ and $R'=C_6H_5$ and with $R=R'=C_8H_{17}$ are insoluble in all solvents. Attempts to prepare similar materials without hydroxyl groups gave the polymers $\{Cr(OH)_{\underline{r}}(OPRR'O)_{\underline{p}}[OOC(CF_2)_{\underline{n}}CF(CF_3)_2]_{\underline{q}}\}_{\underline{x}}$ with $0 < r < 1$. The latter polymers are much more tractable than the former; however, they are also less thermally stable. The perfluorocarboxylate groups in these materials can either be chelating or bridging depending on the other ligands present.

Technical Report No. 10. "Inorganic Coordination Polymers. XV. Dioctylphosphinates of Chromium(II), Manganese(II), Iron(II), Nickel(II), and Copper(II)." H. D. Gillman. November, 1973. AD-770 156. Manuscript for Publication No. 12.

The dioctylphosphinates $Cr[OP(C_8H_{17})_2O]_2$, $Mn[OP(C_8H_{17})_2O]_2$, $Fe[OP(C_8H_{17})_2O]_2$, $Ni[OP(C_8H_{17})_2O]_2$, and $Cu[OP(C_8H_{17})_2O]_2$ 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.

Technical Report No. 11. "Inorganic Coordination Polymers. XVI. Zinc(II) Phosphinate Polymers Containing Polyphenylene and Poly(Phenylene Oxide) Side Groups." P. Nannelli, H. D. Gillman, H. G. Monsimer, and S. B. Advani. April, 1974. AD-780 465. Manuscript for Publication No. 13.

The synthesis and characterization of a series of new phosphinic acids and the zinc polymers prepared from them are reported. These compositions are characterized by the presence of short polyphenylene and poly(phenylene oxide) chains as side groups. Some of the zinc derivatives were found to be tractable polymers with good thermal stability.

Technical Report No. 12. "Inorganic Coordination Polymers. XVII. The Preparation and Properties of Tantalum(V) Diphenylphosphinates." H. D. Gillman. August, 1974. AD-783 946. Manuscript for Publication No. 17.

Tantalum diphenylphosphinate alkoxides and oxides were prepared with one, two, and three diphenylphosphinate groups per tantalum. They were found to be low molecular weight polymers in solution. The infrared spectra of the tantalum diphenylphosphinate oxides indicate that the phosphinate groups have predominately one mode of coordination (probably symmetrical bridging) in $Ta[OP(C_6H_5)_2O]$-$O_2 \cdot H_2O$, whereas in $Ta[OP(C_6H_5)_2O]_2O_{3/2} \cdot xH_2O$ and $Ta[OP(C_6H_5)_2O]_3$-$O \cdot xH_2O$ they have a variety of coordination modes. The thermal stabilities of tantalum diphenylphosphinate dioxide and tantalum bis(diphenylphosphinate) sesquioxide were considerably greater than tantalum tris(diphenylphosphinate) oxide.

Technical Report No. 13. "The Effects of Structural Disorder on One-Dimensional Antiferromagnetic Chains: Poly-Chromium-Phosphinates." J. C. Scott, A. F. Garito, A. J. Heeger, P. Nannelli, and H. D. Gillman. December, 1974. AD/A-002 449. Manuscript for Publication No. 16.

The magnetic properties of several poly(metal phosphinates) have been measured. In particular ESR spectra and the temperature dependence of the static susceptibility of three poly(chromium phosphinates) imply that these polymers comprise a class of one-dimensional antiferromagnetic chains with $J/k \sim 4K$ and with a varying degree of crystallinity. Structural disorder is found to limit the range of spin correlations and, in the extreme case, prohibits extended short-range order. The data are analyzed in terms of a model of chains of constant exchange but finite length. Comparison is made with an alternative model of infinite chains with Heisenberg exchange J varying randomly about a mean. The width of the distribution of J provides a direct measure of the disorder in each system.

Technical Report No. 14. "Inorganic Coordination Polymers. XVIII. Observations on Brittle and Flexible Films of $\{Cr[OP(CH_3)(C_6H_5)O]_2[OP(C_8H_{17})_2O]\}$." P. Nannelli, H. D. Gillman, and B. P. Block. May, 1975. AD-A010 554. Manuscript for Publication No. 19.

Films of $\{Cr[OP(CH_3)(C_6H_5)O]_2[OP(C_8H_{17})_2O]\}_x$ formed during the reaction of $\{Cr(OH)[OP(CH_3)(C_6H_5)O]_2\}_x$ with dioctylphosphinic acid, are either brittle or flexible depending on the details of the preparation of the chromium(III) bis(phosphinate) precursor. Both kinds of film appear to contain mainly triple-bridged chains. Differing degrees of randomness in distribution of the two kinds of phosphinate bridges and, hence, of the internally plasticizing octyl groups along the chain acount for the observed differences in flexibility, X-ray diffraction patterns, and birefringence. The observed intrinsic viscosities of 9-18 dl/g probably indicate that these tris(phosphinates) form microgels rather than true solutions. The thermal degradation of these films proceeds by the oxidation and cleavage of the organic side groups. Addition of antioxidants to the flexible films significantly increases the longevity of their flexibility at 200°C.

Technical Report No. 15. "The Specific Heat of Disordered Antiferromagnetic Chains: Poly(Metal Phosphinates)." T. S. Wei, J. C. Scott, A. F. Garito, A. J. Heeger, P. Nannelli, and H. D. Gillman. December, 1975. AD-A020 183. Manuscript for Publication No. 18.

The specific heat of some poly(chromium phosphinates) and of their non-magnetic analogues, poly(zinc phosphinates), have been measured in the temperature range $1.6 \leqslant T \leqslant 10K$. The vibrational contribution to the specific heat is consistent with the polymeric nature of the materials, changing from T^3 to $T^{5/2}$ dependence as the temperature increases. The magnetic specific heat can then be extracted and is found to be in qualitative agreement with a model that includes disorder in the spin chains. We believe that this is the first measurement of the specific heat of a disordered one-dimensional magnetic system.

Technical Report No. 16. "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)." J. L. Eichelberger and H. D. Gillman. December, 1975. AD-A020 184. Manuscript for Publication No. 22.

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 that 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.

Technical Report No. 17. "Inorganic Coordination Polymers. XX. Zinc(II) Phosphinate Polymers and Copolymers Containing Phenyl Sulfone Side Groups." P. Nannelli, H. D. Gillman, H. G. Monsimer, and S. B. Advani. December, 1975. AD-A020 185. Manuscript for Publication No. 23.

The synthesis and characterization of a series of new phosphinic acids and the zinc polymers and copolymers prepared from them are reported. These compositions are characterized by the presence of phenyl sulfone side groups.

The zinc derivatives were found to be among the most thermally stable tractable poly(metal phosphinates) yet studied.

Technical Report No. 18. "Synthesis, Properties, and Structural Characterization of Lead(II) Bis(diphenylphosphinate), $Pb[OP(C_6H_5)_2O]_2$." P. Colamarino, P. L. Orioli, W. D. Benzinger, and H. D. Gillman. December, 1975. AD-A020 186. Manuscript for Publication No. 20.

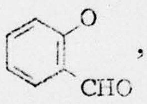
Pure polymeric $Pb[OP(C_6H_5)_2O]_2$ has been prepared, and its structure has been determined by three-dimensional single-crystal X-ray techniques. The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a = 12.167\ (5)$, $b = 10.937\ (4)$, $c = 8.695\ (6)$ Å; $\alpha = 96.40\ (3)$, $\beta = 105.96\ (4)$, $\gamma = 91.05\ (5)°$; $V = 1104$ Å^3; $d_{calcd} = 1.93\ g\ cm^{-3}$. Least-squares refinement of 3737 independent reflections gave a final R factor of 3.5%. The structure consists of polymeric chains of lead atoms linked by double-phosphinate bridges. The coordination around each lead atom can be described as a distorted trigonal bipyramid with a lone pair of electrons occupying an equatorial site. Mean equatorial and axial Pb-O distances are 2.233 (6) and 2.435 (6) Å, respectively. The corresponding O-Pb-O angles are 88.2 (2) and 167.6 (2)°. This polymer was found to dissociate in solution, and its infrared spectrum suggests that changes in the mode of coordination of the phosphinate groups take place upon dissolution. Other forms including crystalline and amorphous modifications were found in the solid state.

Technical Report No. 19. "Inorganic Coordination Polymers. XXI. Manganese(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Bis[Bis(N-Phenylaminomethyl)phosphinates]. Effects of Coordinating Side Groups." J. L. Eichelberger and H. D. Gillman. January, 1977. AD-A035 099. Manuscript for Publication No. 24.

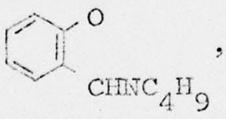
The metal(II) bis[bis(N-phenylaminomethyl)phosphinates] $M[OP(CH_2NHC_6H_5)_2O]_2$ (with M = Mn, Co, Ni, Cu, and Zn) have been investigated. The manganese, cobalt, and nickel derivatives all have similar structures with octahedrally coordinated metal centers, the copper derivative is probably tetragonally distorted octahedral, and the zinc derivative is tetrahedral. All of these compounds contain some coordinating amine groups except the zinc complex in which no amine groups coordinate. Most likely, all of these compounds contain symmetrically bridging O,O' phosphinate groups. The thermal stabilities of these complexes are markedly different from one another and appear to be dependent on the ligand field stabilization energies but not on the chelation of the amine groups.

<u>Technical Report No. 20</u>. "Inorganic Coordination Polymers. XXII. Chromium(III) Bis(phosphinate) Polymers Containing Some Organic Anions." H. D. Gillman and P. Nannelli. January, 1977. AD-A035 100. Manuscript for Publication No. 25.

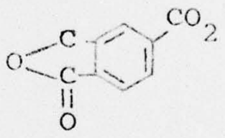
The preparation and characterization of a variety of chromium(III) bis(phosphinate) polymers $\{Cr(L)[OPRR'O]_2\}_x$ [with $R=R'=C_6H_5$ and $R=CH_3$, $R'=C_6H_5$; $L=OCH_3$, $(OCH_2CH_2O)_{0.5}$, $OCH_2CH_2NH_2$,



,

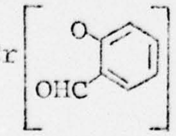


, and



] is reported. These alkoxides, aryloxides, and carboxylate derivatives were prepared by the reaction of μ-chloro-bis(μ-phosphinato)-chromium(III) with the appropriate alcohol or carboxylic acid in the presence of excess triethylamine in THF. The imines were prepared by treating

Cr



$[OPRR'O]_2$ with the appropriate amine in benzene.

These materials are generally soluble in organic solvents in which their molecular weights range from 1,600 to 10.600. In both the solid state and in solution these polymers are hydrolytically stable. Their properties suggest octahedral chromium(III) centers bridged by double phosphinate bridges as well as bridging (L) groups.

Technical Report No. 21. "^{31}P NMR Studies of the Linear Chain Magnets: Poly(Metal Phosphinates)." L. S. Smith, P. R. Newman, A. J. Heeger, A. F. Garito, H. D. Gillman, and P. Nannelli. June, 1977. AD- . Manuscript for Publication No. 26.

The paramagnetic shift and linewidth of the ^{31}P NMR have been measured for three magnetic polymers $Co[OP(C_4H_9)_2O]_2$, $Cr[OP(CH_3)(C_6H_5)O]_2OH$, and $Cr[OP(CH_3)(C_6H_5)O]_2[OP(C_8H_{17})_2O]$ for $77K \leq T \leq 300K$. Analysis of the paramagnetic shift as a function of the static magnetic susceptibility yields a value for the hyperfine coupling constant $A \approx 4 \times 10^{-4}$ cm^{-1}. Previously measured and calculated hyperfine constants for an electron in the 3s and 3p orbitals are used to show the paramagnetic shift is due mainly to transferred magnetic spin density ($\approx$0.1%) in the phosphorus 3s orbital. The linewidths of these materials are approximately 10 Oe at room temperature and broaden slightly with decreasing temperature. The temperature dependences of the linewidths are used to deduce an upper limit ($\lesssim$ 1 %) for the amount of transferred spin density in the phosphorus 3p orbital.

Technical Report No. 22. "Crystal Structure and Magnetic Studies of Bis(μ-Dibutylphosphinato)Copper(II)." R. Cini, P. Colamarino, P. L. Orioli, L. S. Smith, P. R. Newman, H. D. Gillman, and P. Nannelli. June, 1977. AD- .

The structure of $Cu[OP(C_4H_9)_2O]_2$ in the solid state has been determined by three-dimensional single-crystal x-ray techniques. The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions: $\underline{a} = 12.245(6)$, $\underline{b} = 9.863(5)$, $\underline{c} = 9.819(5)$ Å; $\underline{\alpha} = 101.18(4)$, $\underline{\beta} = 105.78(5)$, $\underline{\gamma} = 93.77(4)$ °; $V = 1110.7$ $Å^3$, $d_c = d_m = 1.25$ g cm^{-3}. The structure was solved by the heavy-atom technique, and least squares refinement gave an R factor of 0.061. The structure consists of polymeric chains of copper atoms linked by double phosphinate bridges. The coordination around each copper atom can be described as a very flattened tetrahedron. The g tensors for oriented single crystals were determined by ESR and range from 2.07 to 2.41, with the larger value in a direction nearly normal to a mean plane formed by the copper atoms and the ligands. The spin orbit coupling constant suggests considerable mixing of metal and ligand orbitals in this polymer.

C. List of Publications

1. "The Poly(Metal Phosphinates)", B. P. Block in "Coordination Chemistry", S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, pp. 241-7.

2. "The Reaction of Molybdenum(II) Cluster Alkoxides with Phenol", P. Nannelli and B. P. Block, *Inorg. Chem.*, 8 (8), 1767-71 (1969).

3. "Problems in the Nomenclature of Inorganic Polymers", B. P. Block, P. M. Thomas, and K. M. Donovan, *J. Chem. Doc.*, 9 (4), 242-4 (1969).

4. "Polymeric Metal Phosphinates", B. P. Block, *Inorg. Macromol. Rev.*, 1 (2), 115-25 (1970).

5. "Molybdenum(II) Halides", P. Nannelli and B. P. Block, *Inorg. Syn.*, 12, 170-8 (1970).

6. "Inorganic Coordination Polymers. XI. A New Family of Chromium(III) Bis(phosphinate) Polymers, $[Cr(OH)(OPRR'O)_2]_x$", P. Nannelli, H. D. Gillman, and B. P. Block, *J. Polym. Sci., Part A-1*, 9 (10), 3027-38 (1971).

7. "A Novel Form of Cobalt(II) Dioctylphosphinate", H. D. Gillman, *Inorg. Chem.*, 11 (12), 3124-6 (1972).

8. "Disodium Hexaalkoxy-octa-μ_3-chloro-hexamolybdate", P. Nannelli and B. P. Block, *Inorg. Syn.*, 13, 99-103 (1972).

9. "Inorganic Coordination Polymers. XII. Chromium(III) Tris(phosphinates)", P. Nannelli, B. P. Block, J. P. King, A. J. Saraceno, O. S. Sprout, Jr., N. D. Peschko, and G. H. Dahl, *J. Polym. Sci.*, *Polym. Chem.*, 11 (10), 2691-2701 (1973).

10. "Inorganic Coordination Polymers. XIII. The Preparation and Characterization of Some μ-Halo-bis(μ-phosphinato)-chromium(III) Polymers", H. D. Gillman, P. Nannelli, and B. P. Block, *J. Inorg. Nucl. Chem.*, 35 (12), 4053-9 (1973).

11. "Inorganic Coordination Polymers. XIV. Chromium(III) Phosphinate Perfluorocarboxylate Polymers", P. Nannelli and H. D. Gillman, *J. Polym. Sci., Polym. Chem.*, **12** (1), 221-9 (1974).

12. "Inorganic Coordination Polymers. XV. Dioctylphosphinates of Chromium(II), Manganese(II), Iron(II), Nickel(II), and Copper(II)", H. D. Gillman, *Inorg. Chem.*, **13** (8), 1921-4 (1974).

13. "Inorganic Coordination Polymers. XVI. Zinc(II) Phosphinate Polymers Containing Polyphenylene and Poly-(phenylene oxide) Side Groups", P. Nannelli, H. D. Gillman, H. G. Monsimer, and S. B. Advani, *J. Polym. Sci., Polym. Chem.*, **12** (11), 2525-34 (1974).

14. "Friction and Shear Strength of a Chromium Tris(phosphinate) Polymer Under High Pressure", L. C. Towle and P. Nannelli, *ASLE Trans.*, **17**, 224-8 (1974).

15. "Clusters Metallici", P. Nannelli, in "Enciclopedia della Chimica", Florence, Italy, 1974, Vol. 3, pp. 559-63.

16. "Magnetic Properties of Poly(metal phosphinates): The Effects of Structural Disorder on One-dimensional Antiferromagnetic Chains", J. C. Scott, A. F. Garito, A. J. Heeger, P. Nannelli, and H. D. Gillman, *Phys. Rev. B*, **12** (11), 356-61 (1975).

17. "Inorganic Coordination Polymers. XVII. The Preparation and Properties of Tantalum(V) Diphenylphosphinates", H. D. Gillman, *J. Inorg. Nucl. Chem.*, **37** (9), 1909-12 (1975).

18. "The Specific Heat of Disordered Antiferromagnetic Chains: Poly(metal phosphinates)", T. S. Wei, J. S. Scott, A. F. Garito, A. J. Heeger, H. D. Gillman, and P. Nannelli, *Phys. Rev. B*, **12** (11), 5297-301 (1975).

19. "Inorganic Coordination Polymers. XVIII. Observations on Brittle and Flexible Films of $\{Cr[OP(CH_3)(C_6H_5)O]_2-[OP(C_8H_{17})_2O]\}_x$", P. Nannelli, H. D. Gillman, and B. P. Block, *J. Polym. Sci., Polym. Chem.*, **13** (12), 2849-56 (1975).

20. "Synthesis, Properties, and Structural Characterization of Lead(II) Bis(diphenylphosphinate), $Pb[OP(C_6H_5)_2O]_2$", P. Colamarino, P. L. Orioli, W. D. Benzinger, and H. D. Gillman, *Inorg. Chem.*, **15** (4), 800-04 (1976).

21. "Polymeric Chromium(III) Bis(phosphinates)", H. D. Gillman, P. Nannelli, and B. P. Block, *Inorg. Syn.*, **16**, 89-92 (1976).

22. "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)", H. D. Gillman and J. L. Eichelberger, *Inorg. Chem.*, **15** (4), 840-3 (1976).

23. "Inorganic Coordination Polymers. XX. Zinc(II), Phosphinate Polymers and Copolymers Containing Phenyl Sulfone Side Groups", P. Nannelli, H. D. Gillman, H. G. Monsimer, and S. B. Advani, *Makromol. Chem.*, **177** (9), 2607-16 (1976).

24. "Inorganic Coordination Polymers. XXI. Manganese(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Bis[Bis(N-Phenyl-aminomethyl) Phosphinates]. Effects of Coordinating Side Groups". H. D. Gillman and J. L. Eichelberger, *Inorg. Chim. Acta*, in press.

25. "Inorganic Coordination Polymers. XXII. Chromium(III) Bis(phosphinate) Polymers Containing Some Organic Anions", H. D. Gillman and P. Nannelli, *Inorg. Chim. Acta*, in press.

26. "^{31}P NMR Studies of the Linear Chain Magnets: Poly-Metal Phosphinates)", L. S. Smith, P. R. Newman, A. J. Heeger, A. F. Garito, H. D. Gillman, and P. Nannelli, *J. Chem. Phys.*. in press.

D. List of Patents Issued and Allowed

	U. S. Pat. No.	Date	Inventors	Title
1.	3,426,050[a]	2/4/69	G. H. Dahl	Tetra(phenylphosphinates) of Titanium and Zirconium
2.	3,432,532[a]	3/11/69	J. P. King	Halo-chromium salts of acids of Phosphorus and their Esters
3.	3,440,186[a]	4/22/69	S. H. Rose	Inorganic Polymers
4.	3,444,103[a]	5/13/69	K. D. Maguire	Preparation of Inorganic Polymers
5.	3,449,367[a]	6/10/69	J. P. King and B. P. Block	Chromium Phosphinate Complexes
6.	3,457,195[a]	7/22/69	B. P. Block and G. H. Dahl	Process for Titanyl Phosphinate Polymers
7.	3,483,142	12/9/69	A. J. Saraceno	Process for Making Inorganic Polymers
8.	3,483,143	12/9/69	J. P. King, A. J. Saraceno, and B. P. Block	Inorganic Polymers
9.	3,487,095	12/30/69	P. L. Nannelli and B. P. Block	Octa-μ_3-Halo and Alkoxy Hexamolybdenum(II) Alkoxides
10.	3,517,060[a]	6/23/70	B. P. Block and G. H. Dahl	Carborane Compounds
11.	3,522,178[b]	7/28/70	N. D. Peschko, B. P. Block, G. H. Dahl, and L. R. Ocone	Grease Compositions
12.	3,624,244	11/30/71	P. L. Nannelli and H. D. Gillman	Method of Preparing Inorganic Polymers

	U. S. Pat. No.	Date	Inventors	Title
13.	3,621,129	12/28/71	P. L. Nannelli and H. D. Gillman	Method of Preparing Inorganic Polymers
14.	3,663,274[b]	5/16/72	B. P. Block, O. S. Sprout, Jr., and G. H. Dahl	Method of Minimizing Accumulation of Electrostatic Charge in Polyethylene
15.	3,663,460	5/16/72	B. P. Block, P. L. Nannelli, H. D. Gillman, and P. M. Thomas	Chromium(III) and Iron(III) Hydroxy Bis(phosphinate) and Bis(arsinate) Polymers
16.	3,966,486[b]	6/29/76	J. P. King, J. Simkin, and P. F. Radice	High-temperature Pigmented Coatings Based on Zirconium Phosphinate Polymer Binders Crosslinked with Phosphinic Acids
17.	4,001,034[b]	1/4/77	J. Simkin	High-temperature Coatings Based on Poly(Zinc Phosphinates)
18.	4,026,830	5/31/77	H. D. Gillman	Tantalum Phosphinates

---

[a] Listed as allowed in Final Report for Nonr 2687(00)

[b] Based on work on a daughter contract

[c] Application number of allowed but unissued patent

[d] Date of application

E. List of Oral Presentations

American Chemical Society National and Regional Meetings

2nd Central Regional Meeting, 1970

Inorganic Paper 77. B. P. Block, Coordination Polymers. (Invited)

6th Middle Atlantic Regional Meeting, 1971

Polymer Paper 27. H. D. Gillman, P. Nannelli, and B. P. Block, A New Family of Chromium(III) Bis(phosphinate) Polymers.

164th National Meeting, New York, 1972

Polymer Paper 33. B. P. Block, H. D. Gillman, P. Nannelli, and P. T. Grzymala, Observations on Some Poly(Metal Phosphinates). *Polym. Preprints*, **13**(2), 784 (1972). (Invited)

8th Middle Atlantic Regional Meeting, 1973

Inorganic Paper E35. B. P. Block, P. Nannelli, O. S. Sprout, Jr., N. D. Peschko, G. H. Dahl, J. P. King, and A. J. Saraceno, A Survey of Some Chromium(III) Tris(Phosphinates).

Inorganic Paper E36. H. D. Gillman and B. P. Block, μ-Halo-Bis(μ-phosphinato)-chromium(III) Polymers.

172nd National Meeting, San Francisco, 1976

Inorganic Paper 26. B. P. Block, The Poly(Metal Phosphinates). (Invited)

10th Middle Atlantic Regional Meeting, 1976

Inorganic Paper 46. P. Nannelli, J. P. King, P. F. Radice, and J. Simkin, Poly(metal phosphinate) Coatings. (Invited)

Informal Presentation. H. D. Gillman, P. Nannelli, K. F. Watterson, and B. P. Block, Poly(Metal Phosphinates) with Fluorinated Side Groups.

Other

International Symposium on Inorganic Polymers, London, England, April 9-11, 1969.

B. P. Block, Polymeric Metal Phosphinates. (Invited)

John C. Bailar, Jr. Symposium on Coordination Chemistry, Urbana, Illinois, June 22-25, 1969.

B. P. Block, The Poly(Metal Phosphinates). (Invited)

Gordon Conference on Inorganic Chemistry, New Hampton, N. H., August 3-7, 1970.

B. P. Block, Recent Developments in Poly(Metal Phosphinates). (Invited)

American Chemical Society, Western New York Section Meeting, March 19, 1970.

B. P. Block, Present Status of Coordination Polymers.

Seminar, U. S. Dept. of Agriculture, Beltsville, Maryland, June 9, 1971.

B. P. Block, Coordination Polymers

Seminar, University of Florida, Oct. 27, 1972.

B. P. Block, Recent Developments in Poly(Metal Phosphinates).

ASLE/ASME Lubrication Conference, Atlanta, Georgia, Oct. 16-18, 1973.

L. C. Towle and P. Nannelli, Friction and Shear Strength of a Chromium Tris(Phosphinate) Polymer Under High Pressure.

Seminar, Drexel University, Philadelphia, Pa., Jan. 8, 1974.

B. P. Block, Poly(Chromium Phosphinates).

21st Annual Conference on Magnetism and Magnetic Materials, Philadelphia, Pa., Dec. 9-12, 1975.

Paper 6C-2. J. C. Scott, T. S. Wei, A. F. Garito, A. J. Heeger, H. D. Gillman, and P. Nannelli, Poly(Metal Phosphinates): Antiferromagnetism in Disordered Linear Polymers. (Invited)

General Meeting of the American Physical Society, Atlanta, Georgia, March 29-April 1, 1976.

L. S. Smith, P. R. Newman, A. F. Garito, A. J. Heeger, P. Nannelli, and H. D. Gillman, ^{31}P NMR Investigation in Poly(Metal Phosphinates).

F. Daughter Pennwalt Contracts

Period	Contract No.	Sponsor	Title	Date of Final Report
4/22/65-4/21/69	DA-31-124-ARO-D-362	ARO-D	New Materials from High-Temperature High-Pressure Processes	May, 1969
8/15/68-7/15/69	N00156-68-C-0602	NADA	Solid Lubricant Materials - Phase II	August, 1969
8/25/68-3/24/69	NAS 9-8356	NASA	Development of Nonflammable, Antistatic, Heat-Sealable Films	May, 1969
4/1/69-8/22/69	F33615-69-C-1619	AFML	Protective Materials	January, 1970
4/1/69-2/28/71	N00014-69-C-0305	ONR	Development of High Energy Resistant Materials	May, 1971
6/5/69-5/4/71	F29601-69-C-0112	AFWL	Characterization of Composites Containing Metallic Resins	September, 1971
8/13/69-11/12/71	N00156-70-C-1132	NADA	Solid Lubricant Materials - Phase III	November, 1971
12/1/69-11/30/70	N00019-70-C-0255	NASC	Basic Solid Lubricant Studies	May, 1971
2/22/71-2/21/72	N00019-71-C-0322	NASC	Basic Solid Lubricant Studies - Phase II	May, 1972
6/2/71-6/1/72	F29601-71-C-0095	AFWL	Characterization of Advanced Resins for Reentry Vehicle Systems	August, 1972

Period	Contract No.	Sponsor	Title	Date of Final Report
7/1/71-1/31/73	N00014-72-C-0174	ONR	Resins for Advanced Reentry Systems Applications	March, 1973
5/1/72-5/15/74	F33615-72-C-1662	AFML	High Temperature Polymeric Coating Materials	August, 1974
11/30/72-3/15/74	N60921-73-C-0140	NOL	Metal Carbide Loaded Carbon Systems Derived from Poly-(metal phosphinates)	May, 1974
3/1/75-	F33615-75-C-5187	AFML	Development of High Temperature Thickeners for High Performance Greases	
9/22/76-	N62269-76-C-0507	NADC	Poly(metal phosphinates) in Plasma Spray Applications	

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. T. C. Williams Union Carbide Corp. Chemicals & Plastics Tarrytown Technical Center Tarrytown, New York 10591	1
Dr. K. A. Reynard Horizons Inc. 23800 Mercantile Road Cleveland, Ohio 44122	1
Dr. A. G. MacDiarmid University of Pennsylvania Department of Chemistry Philadelphia, Pennsylvania 19174	1
Dr. E. Hedaya Union Carbide Corp. Corporate Research Laboratory Tarrytown Technical Center Tarrytown, New York 10591	1
Dr. A. Rheingold SUNY Plattsburg Department of Chemistry Plattsburg, New York 12901	1
Dr. C. Pittman University of Alabama Department of Chemistry University, Alabama 35486	1
Dr. H. Allcock Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. M. Kenney Case-Western University Department of Chemistry Cleveland, Ohio 44106	1
Dr. R. Lenz Department of Chemistry University of Massachusetts Amherst, Massachusetts 01002	1

	No. Copies
Dr. M. Good Department of Chemistry University of New Orleans Lakefront New Orleans, Louisiana 70122	1
Douglas Aircraft Co. 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library CI 290/36-84 AUTO-Sutton	1
NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serafini, MS 49-1	1
Dr. J. Griffith Naval Research Laboratory Chemistry Section, Code 6120 Washington, D. C. 20375	1
Dr. G. Goodman Globe-Union Inc. 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. E. Fischer, Code 2853 Naval Ship Research and Development Center Annapolis Division Annapolis, Maryland 21402	1
Dr. Martin H. Kaufman, Head Materials Research Branch (Code 4542) Naval Weapons Center China Lake, California 93555	1
Professor Lydia M. Frenzel University of New Orleans Department of Chemistry New Orleans, Louisiana 70122	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP	6
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1
Director, Naval Research Laboratory Washington, D. C. 20390 Attn: Library, Code 2029 (ONRL)	6
Technical Info. Div.	1
Code 6100, 6170	1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D. C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D. C. 20360 Attn: Code 310C (H. Rosenwasser)	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U. S. Army Research Office P. O. Box 12211 Research Triangle Park, N. C. 27709 Attn: CRD-AA-IP	1
Commander Naval Undersea Research & Development Center San Diego, California 92132 Attn: Technical Library, Code 133	1
Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D. C. 20380	1