

Inorganic Coordination Polymers. XXII. * Manganese(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Bis[Bis(N-phenylaminomethyl)phosphinates]. Effects of Coordinating Side Groups

H. D. GILLMAN and J. L. EICHELBERGER

Pennwalt Corporation Technological Center, King of Prussia, Pennsylvania 19406 (U.S.A.)

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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.

Introduction

Investigations at our laboratories have been partly directed at preparing inorganic coordination polymers suitable for high temperature applications. In this regard we have studied a variety of metal(II) bis(phosphinates) and have found that a number of structures occur for these materials, including octahedrally coordinated metal atoms linked by unsymmetrical phosphinate bridges [2, 3]. We wished, as part of this general investigation, to determine what effects coordinating substituents on the phosphorus would have on the structures and properties of these polymers. With this system it may be possible to prepare linear polymeric metal(II) bis(phosphinates) with octahedral metal centers. Such a linear polymer would likely be soluble, whereas the previously studied octahedral metal(II) bis(phosphinates) were not [2]. It was also of interest to evaluate the effect of chelating side groups on the thermal stability of these polymers.

Experimental Section

The bis(N-phenylaminomethyl)phosphinic acid was prepared as described by Il'na and Shermgorn, m.p. 180-1 °C (lit. 180-1 °C) [4]. All other materials were reagent grade and were used without further purification.



All of the metal(II)bis[bis(N-phenylaminomethyl)phosphinates] were synthesized by the same general procedure. The phosphinic acid was first neutralized in an aqueous solution by treatment with 0.5 mol of K_2CO_3 per mol of acid. An excess of K_2CO_3 was avoided, so that metal(II) hydroxy phosphinates would not be formed in the next step. This solution was then treated with an aqueous solution of the appropriate metal(II) sulfate or chloride (0.5 mol of metal(II) salt per mol of potassium phosphinate). In most cases a precipitate of metal(II) phosphinate formed immediately, whereupon it was filtered, washed with water, and dried in a vacuum desiccator. For $Ni\{OP[CH_2NH(C_6H_5)]_2O\}_2$ it was necessary to heat the solution to 90 °C for 2 hr and then cool before precipitation occurred. The nickel phosphi-

TABLE I. Summary of Analytical Data for $M\{OP[CH_2NH(C_6H_5)]_2O\}_2^a$.

| M | C | H | P | N | M | M.P. |
|----|----------------|--------------|--------------|--------------|--------------|----------|
| Zn | 54.4 (54.6) | 5.25 5.24 | 9.9 10.1 | 9.04 9.10 | 10.5 10.6 | 185-191d |
| Cu | 54.5 (54.8) | 5.28 5.25 | 10.0 10.1 | 9.06 9.12 | 10.1 10.4 | 205d |
| Ni | 55.2 (55.2) | 5.43 5.29 | 10.1 10.2 | 9.21 9.20 | 9.24 9.64 | d |
| Co | 55.2 (55.2) | 5.28 5.29 | 10.0 10.2 | 8.87 9.19 | 10.5 9.67 | d |
| Mn | 55.7 (55.5) | 5.39 5.33 | 10.2 10.2 | 8.98 9.25 | 10.9 9.1 | 255d |

*For part XXI see ref. 1.

^aCalculated values in parentheses. ^dDecomposes.

TABLE II. N-H, PO₂, and M-N Stretching Frequencies of M{OP[CH₂NH(C₆H₅)₂O]₂} and [(C₆H₅)NHCH₂]₂P(O)OH.

| M | N-H Str. Freq., cm ⁻¹ | PO ₂ Str. Freq., cm ^{-1a} | M-N Str. Freq., cm ⁻¹ |
|--|----------------------------------|---|----------------------------------|
| [(C ₆ H ₅)NHCH ₂] ₂ P(O)OH | 3350 | 1148 1035 (1182, 1000) | |
| Zn | 3375 3360 | 1132 1052 (1142, 1038) | - |
| Cu | 3380 3310 | 1132 1030 (1195, 1010) | 540 475 |
| Ni | 3360 3175 | 1132 1038 (1195, 995, 980) | 500 |
| Co | 3375 3220 | 1132 1038 (1190, 962) | 500 478 |
| Mn | 3375 3220 | 1132 1030 (1185, 923) | 492 470 |

^aThe bands which appear in brackets are very weak and may be either overtones, combination bands, or PO₂ stretching frequencies caused by phosphinate structures not predominant in the bulk polymer.

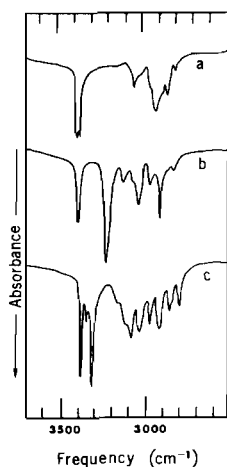


Figure 1. Infrared spectra in hexachlorobutadiene mull of: a, Zn{OP[CH₂NH(C₆H₅)₂O]₂}; b, Co{OP[CH₂NH(C₆H₅)₂O]₂} and c, Cu{OP[CH₂NH(C₆H₅)₂O]₂}.

nate was worked up in the same manner as the other metal(II) phosphinates. The analytical data for these phosphinates appear in Table I.

Elemental analyses were performed 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. Reflectance spectra were obtained in the visible region with a Perkin Elmer 450 spectrophotometer. Thermogravimetric analyses were recorded on a DuPont 950 thermogravimetric analyzer. The DSC curves were obtained with a DuPont DSC cell module and a DuPont 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. An AEI model MS30 single beam mass spectrometer was used in the thermal decomposition studies.

Results

All of the metal(II) bis[bis(N-phenylamino-methyl)phosphinates] in this study are crystalline solids and are insoluble in all noncoordinating solvents tested. We assume that the phosphinates in this study are polymers because of this insolubility as well as the fact that all of the soluble metal phosphinates previously studied were found to be polymeric. Their X-ray powder patterns indicate that the cobalt and manganese derivatives are isomorphous with one another, the nickel derivative appears similar to these two, and the copper and zinc compounds each have unique structures. The infrared spectra (Fig. 1 and Table II) in the N-H stretching region of these compounds clearly reflect the similarities and differences as observed in their X-ray patterns.

M{OP[CH₂NH(C₆H₅)₂O]₂}; *M* = Mn, Co, and Ni

The infrared spectrum of [(C₆H₅)NHCH₂]₂P(O)OH contains only one absorption band (3350 cm⁻¹) due to N-H stretching vibrations, and the position of this band is consistent with N-H stretching of non-protonated N-H groups [5]. Similarly, the spectra of the cobalt(II), nickel(II), and manganese(II) derivatives of this acid all contain an absorption band at 3360–3375 cm⁻¹ assigned to uncoordinated N-H groups. Their spectra also contain an additional sharp band at 3175–3220 cm⁻¹ that we assign to coordinated N-H groups.

In the PO₂ stretching region all these new phosphinates contain two strong bands at 1132 and 1030–1052 cm⁻¹, although they also contain additional weaker bands in this region. The strong absorption bands are due to the PO₂ symmetric and anti-symmetric vibrations [6], and they should be sensitive to the way in which the phosphinate group coordinates [2]. The positions of these absorption bands are similar to those found in other chromium [7], cobalt [8], and zinc [9] phosphinate polymers,

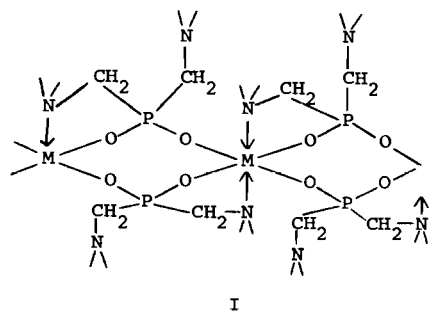
TABLE III. Spectral and Magnetic Properties of $M\{OP[CH_2NH(C_6H_5)]_2O\}_2$ ^a.

| M | Color | Electronic Spectra ^b ν, cm^{-1} | μ_{eff} B.M. |
|----|--------|--|----------------------------|
| Cu | Yellow | 13,800 25,000 (vbr) | 1.8 |
| Ni | Green | 14,300 22,000(vw) 24,200 27,500 (vw) | 3.0 |
| Co | Violet | 15,000 (sh) 18,400 20,300 (sh) 21,300 (sh) 25,000 (sh) | c |
| Mn | White | White | 5.5 |

^aKey: sh, shoulder; vw, very weak; vbr, very broad. ^bDiffuse reflectance in the 13,400–28,500 cm^{-1} range. ^cNot measured.

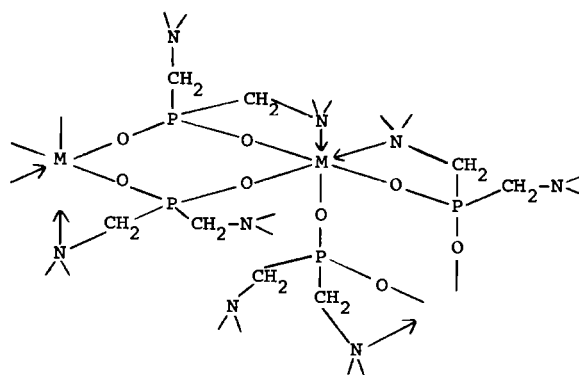
all of which have been assigned structures with symmetrical O, O' phosphinate groups.

The visible spectra and colors of the manganese, cobalt, and nickel derivatives are characteristic of octahedral metal centers, and the magnetic moment of $Ni\{OP[CH_2NH(C_6H_5)]_2O\}_2$ agrees with this structural assignment (Table III). It is reasonable to assume that both oxygen atoms and one amine group per phosphinate ligand is coordinating in order to satisfy a coordination number of six for each metal center. This assumption is consistent with the IR spectra, which shows that both coordinated and uncoordinated N–H groups are present. For symmetrical O, O' phosphinate groups the most likely structures involve phosphinate bridges [10] as depicted in I and II.



I

None of these materials are soluble, so it is very likely that they are not linear. Crosslinking can occur either through phosphinate or amine linkages.



II

$Cu\{OP[CH_2NH(C_6H_5)]_2O\}_2$

The infrared spectra of the copper derivative contains an absorption band at 3380 cm^{-1} , assigned to uncoordinated N–H groups and one at 3310 cm^{-1} assigned to coordinated N–H groups. The higher frequency of N–H stretching vibrations for the coordinated N–H groups of the copper derivative as compared to that of the nickel, cobalt, and manganese compounds is probably associated with structural differences. Copper complexes have a propensity to form tetragonal complexes, so that structure I with the amine–copper bonds elongated is reasonable. This elongation is probably responsible for the relatively high M–N and coordinated N–H stretching frequencies of the copper complex. The magnetic moment of the copper derivative indicates that at room temperature little if any spin coupling occurs.

$Zn\{OP[CH_2NH(C_6H_5)]_2O\}_2$

For this zinc complex no absorption bands due to coordinated N–H vibrations are observed. Similarly the spectrum of the zinc derivative contains no absorption bands in the M–N stretching region, whereas the spectra of the manganese, cobalt, nickel, and copper derivatives all do. Thus the structure of the zinc polymer is probably similar to that of other insoluble zinc phosphinates that probably contain tetrahedral zinc atoms bridged in a three-dimensional lattice by the phosphinate groups [3].

Thermal Properties

The thermal stabilities of these materials (Table IV and Fig. 2) differ markedly from one another. Except for $Cu\{OP[CH_2NH(C_6H_5)]_2O\}_2$ the order of stability corresponds to that expected on the basis of the ligand field stabilization energy of the various metallic ions. The thermal decomposition temperatures of $Zn\{OP[CH_2NH(C_6H_5)]_2O\}_2$ and $Mn\{OP[CH_2NH(C_6H_5)]_2O\}_2$ are similar, and neither material is thermodynamically stabilized by the ligand field. This indicates that these polymers are not thermally

TABLE IV. Thermal Properties of $M\{OP[CH_2NH(C_6H_5)]_2O\}_2$ ^a.

| M | Temp. for Indicated Wt. Loss, °C | | DSC Transitions, °C | |
|----|----------------------------------|-----|---------------------|---------------|
| | Initial | 10% | | |
| Zn | 250 | 305 | 160 >250 | en ex (br) |
| Cu | 180 | 240 | 185 | ex |
| Ni | 340 | 360 | 270 | ex (br) |
| Co | 300 | 310 | 310 325 | en ex |
| Mn | 250 | 320 | 260 | en |

^aIn all cases a nitrogen atmosphere and a heating rate of 5 °C/min were used. Key: en, endotherm; ex, exotherm; br, broad.

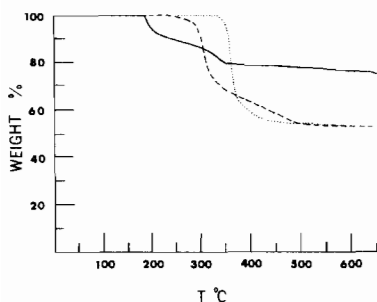


Figure 2. Thermogravimetric analysis in N_2 of: (...) $Ni\{OP[CH_2NH(C_6H_5)]_2O\}_2$, (----) $Zn\{OP[CH_2NH(C_6H_5)]_2O\}_2$, and (—) $Cu\{OP[CH_2NH(C_6H_5)]_2O\}_2$.

stabilized by chelation of the side groups because the zinc derivative does not contain chelate rings and the manganese derivative does.

The observed DSC transitions for these materials are also given in Table IV. All of the observed transitions are probably due to decompositions except for the endotherm at 160 °C of $Zn\{OP[CH_2NH(C_6H_5)]_2O\}_2$ which is due to melting.

The copper, zinc, and nickel derivatives were thermally decomposed in a mass spectrometer in order to determine the reason for the lower decomposition temperature and higher percent residue of the copper

compound. The volatile decomposition products were determined from their characteristic mass spectra. Each of these three compounds predominately liberated aniline and moderate amounts of N-methylaniline and N-methylethaniline. Traces of higher molecular weight species such as N-ethylaniline and N,N'-diphenylethylenediamine were also detected. The only apparent difference among the decomposition products of the three derivatives was that a slightly greater relative quantity of methylaniline and N-methylethaniline was obtained from the copper compound than from the others. Thus all three phosphinates appear to decompose via similar paths, and the lower decomposition temperature for the copper derivative is a consequence of other reasons such as the stability of the decomposition products or intermediates in the decomposition.

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