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JAN 77 J L EICHELBERGER, H J GILLMAN N00014-69-C-0122  
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TECHNICAL REPORT NO. 19

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.

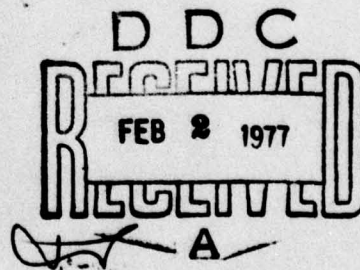
by

J. L. Eichelberger and H. D. Gillman

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The metal(II) bis[bis(N-phenylaminomethyl)phosphinates] $M[OP(CH_2NHC_6H_5)_2-O]_2$ (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		

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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.

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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.<sup>2,3</sup> 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.<sup>2</sup> 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 Shermergorn, m. p. 180-1° (lit. 180-1°).<sup>4</sup> All other materials were reagent grade and were used without further purification.

$M\{OP[CH_2NH(C_6H_5)]_2O\}_2$ . 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 mole of  $K_2CO_3$  per mole 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 mole of metal(II) salt per mole 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  $\text{Ni}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$  it was necessary to heat the solution to  $90^\circ$  for 2 hr and then cool before precipitation occurred. The nickel phosphinate 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.

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

---

a. Calculated values in parentheses.

d. Decomposes.

## Results

All of the metal(II) bis[bis(N-phenylaminomethyl)-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.

$M\{OP[CH_2NH(C_6H_5)]_2O\}_2$ ; M=Mn, Co, and Ni. The infrared spectrum of  $[(C_6H_5)NHCH_2]_2P(O)OH$  contains only one absorption band ( $3350\text{ cm}^{-1}$ ) due to N-H stretching vibrations, and the position of this band is consistent with N-H stretching of non-protonated N-H groups.<sup>5</sup> Similarly, the spectra of the cobalt(II), nickel(II), and manganese(II) derivatives of this acid all contain an absorption band at  $3360\text{--}3375\text{ cm}^{-1}$  assigned to uncoordinated N-H groups. Their spectra also contain an additional sharp band at  $3175\text{--}3220\text{ cm}^{-1}$  that we assign to coordinated N-H groups.

In the  $PO_2$  stretching region all these new phosphinates contain two strong bands at  $1132$  and  $1030\text{--}1052\text{ cm}^{-1}$ , although they also contain additional weaker bands in this region. The strong absorption bands are due to the  $PO_2$  symmetric and antisymmetric vibrations,<sup>6</sup> and they should be sensitive to

Table II

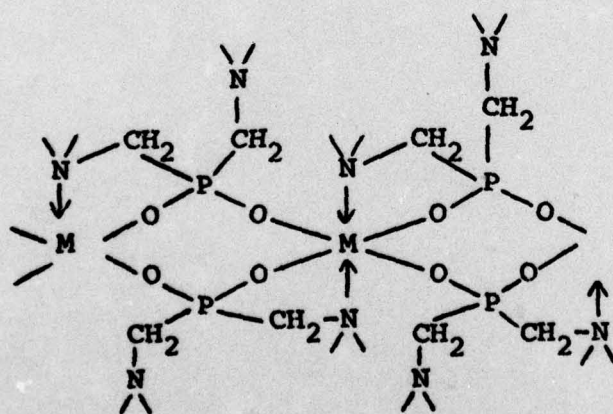
N-H, PO<sub>2</sub>, and M-N Stretching Frequencies of M(OP[CH<sub>2</sub>NH(C<sub>6</sub>H<sub>5</sub>)]<sub>2</sub>O)<sub>2</sub> and [(C<sub>6</sub>H<sub>5</sub>)NHCH<sub>2</sub>]<sub>2</sub>P(O)OH

M	N-H Str. Freq., cm <sup>-1</sup>		PO <sub>2</sub> Str. Freq., cm <sup>-1</sup> <sup>a</sup>		M-N Str. Freq., cm <sup>-1</sup>	
[(C <sub>6</sub> H <sub>5</sub> )NHCH <sub>2</sub> ] <sub>2</sub> 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

a. The bands which appear in brackets are very weak and may be either overtones, combination bands, or PO<sub>2</sub> stretching frequencies caused by phosphinate structures not predominant in the bulk polymer.

the way in which the phosphinate group coordinates<sup>2</sup>. The positions of these absorption bands are similar to those found in other chromium,<sup>7</sup> cobalt,<sup>8</sup> and zinc<sup>9</sup> phosphinate polymers, all of which have been assigned structures with symmetrical 0,0' 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  $\text{Ni}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$  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 0,0' phosphinate groups the most likely structures involve phosphinate bridges<sup>10</sup> as depicted in I and II.



I.

Table III

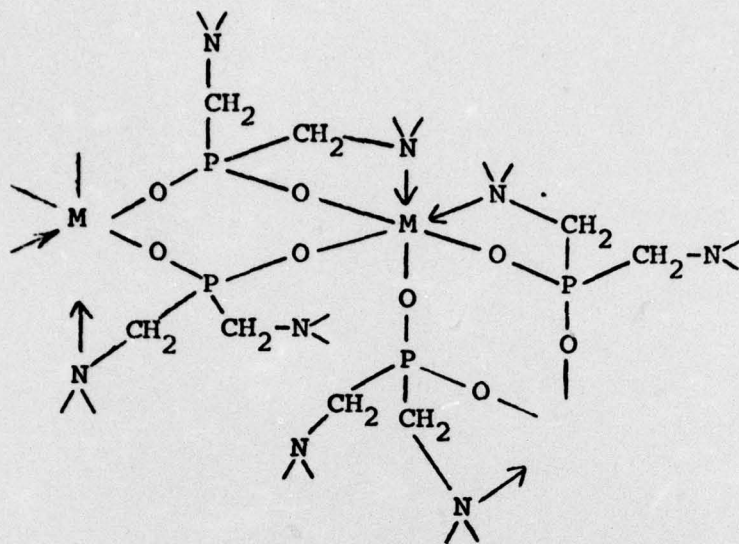
Spectral and Magnetic Properties of  $M\{OP[CH_2NH(C_6H_5)]_2O\}_2^a$ 

M	Color	Electronic Spectra <sup>b</sup> $\gamma, \text{cm}^{-1}$	$\mu_{\text{eff}}$ 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		5.5

a. Key: sh, shoulder; vw, very weak; vbr, very broad.

b. Diffuse reflectance in the 13,400-28,500  $\text{cm}^{-1}$  range.

c. Not measured.



II.

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.

$\text{Cu}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$ . The infrared spectra of the copper derivative contains an absorption band at  $3380\text{ cm}^{-1}$ , assigned to uncoordinated N-H groups and one at  $3310\text{ cm}^{-1}$  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.

$\text{Zn}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$ . 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.<sup>3</sup>

Thermal Properties. The thermal stabilities of these materials (Table IV and Fig. 2) differ markedly from one another. Except for  $\text{Cu}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$  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  $\text{Zn}\{\text{OP}(\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$  and  $\text{Mn}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}$  are similar, and neither material is thermodynamically stabilized by the ligand field. This indicates that these polymers are not thermally 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

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 en >250 ex (br)
Cu	180	240	185 ex
Ni	340	360	270 ex (br)
Co	300	310	310 en 325 ex
Mn	250	320	260 en

a. In all cases a nitrogen atmosphere and a heating rate of 5°/min were used.

Key: en, endotherm; ex, exotherm; br, broad.

due to decompositions except for the endotherm at 160° 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-methylenedianiline. 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-methylenedianiline 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.

#### Acknowledgment

The authors wish to thank Dr. Campbell Scott of the University of Pennsylvania for making the magnetic measurements on the Faraday balance. We acknowledge Dr. B. P. Block for originating the study of poly(metal phosphinates) with chelating side groups at our laboratories. This work was supported in part by the Office of Naval Research and the Advanced Research Projects Agency.

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Fig. 1. Infrared spectra in Hexachlorobutadiene mull of:  
a,  $\text{Zn}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$ ; b,  $\text{Co}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$ ;  
and c,  $\text{Cu}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$

Fig. 2. Thermogravimetric analysis in  $\text{N}_2$  of:  
(...)  $\text{Ni}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$ , (---)  $\text{Zn}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$ ,  
and (—)  $\text{Cu}\{\text{OP}[\text{CH}_2\text{NH}(\text{C}_6\text{H}_5)]_2\text{O}\}_2$

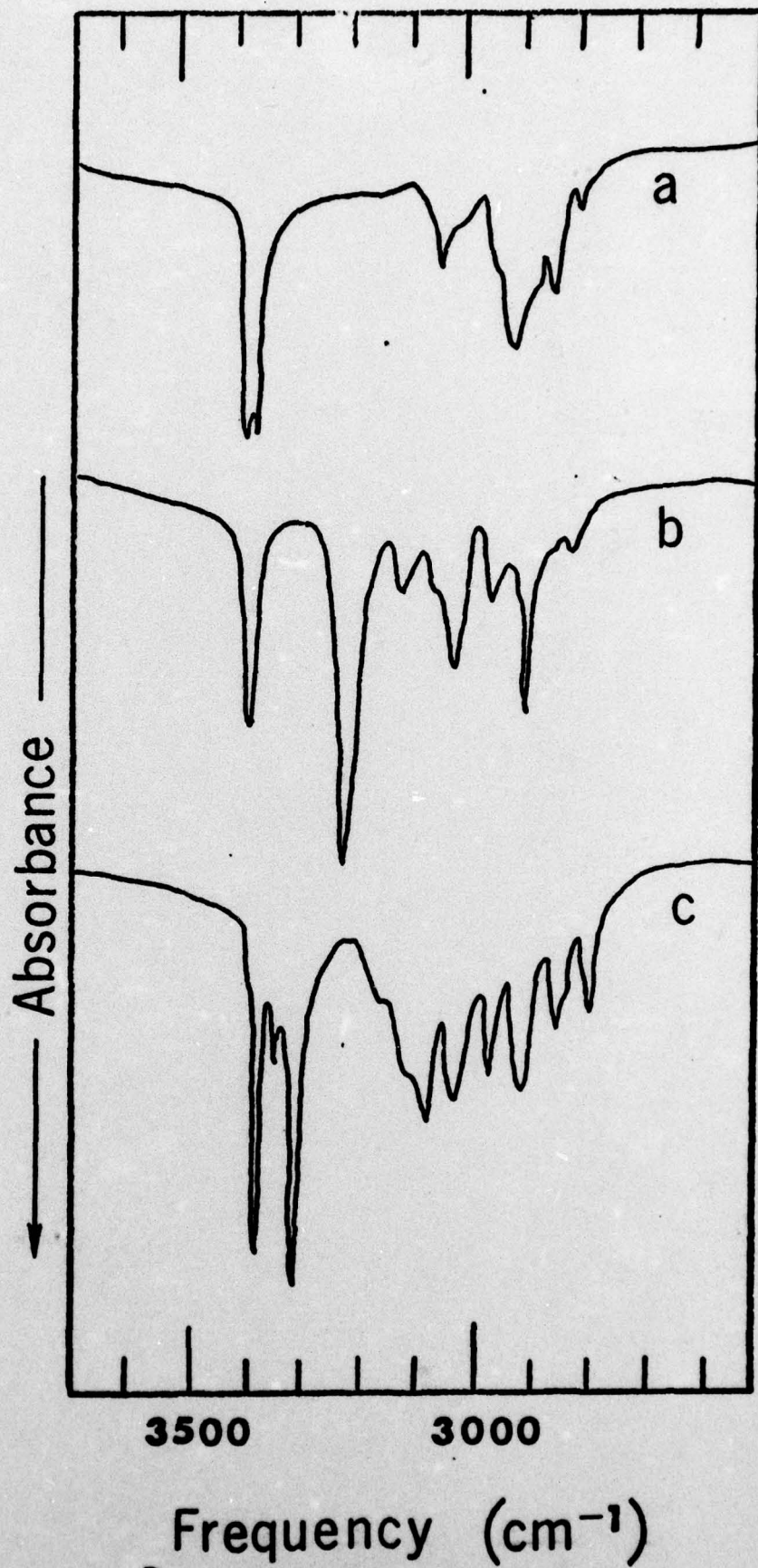


Figure 1

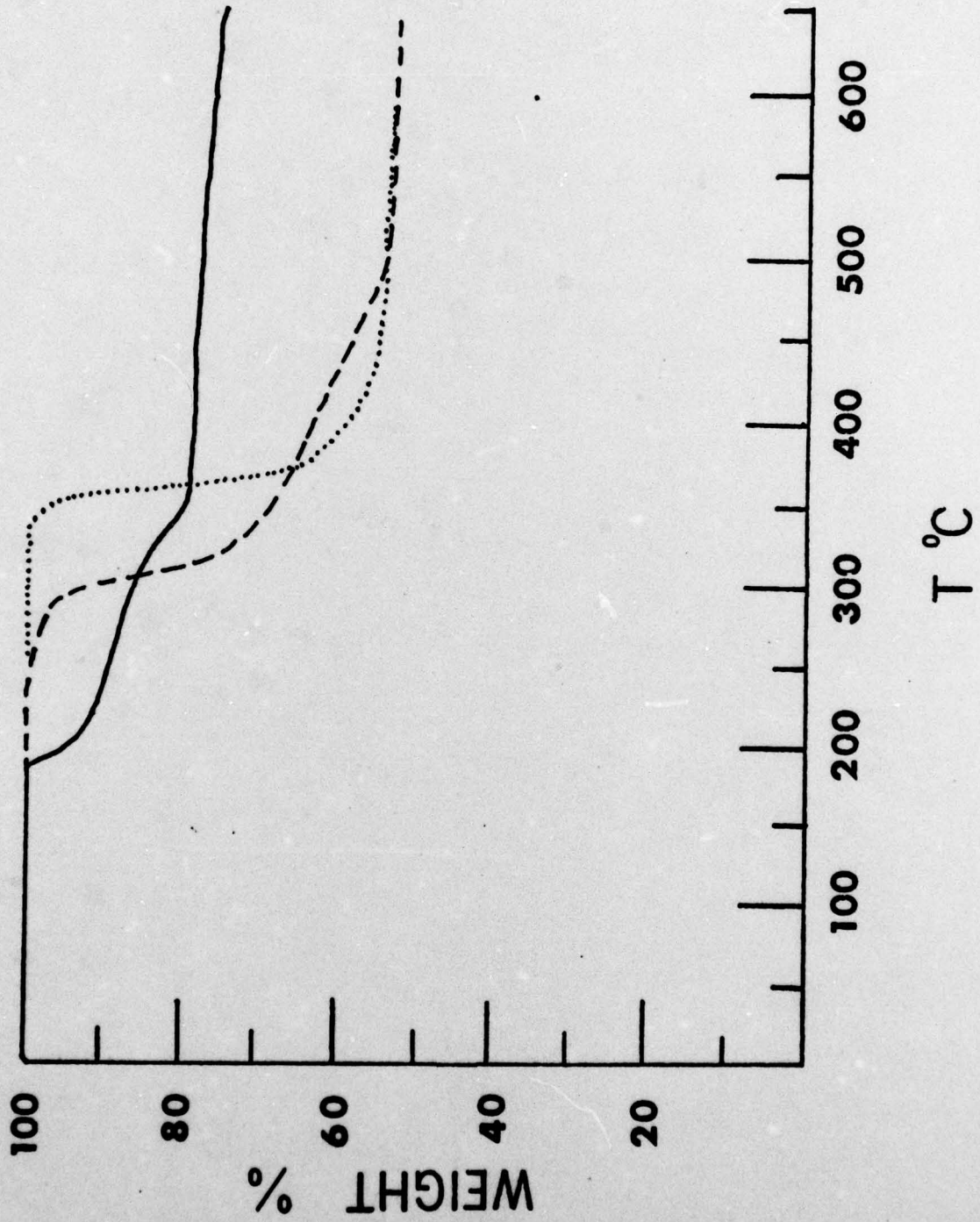


Figure 2

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