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A New Class of Metalphosphinates Containing Bridging Formamide Ligands

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Abstract

Methylphenylphosphinic acid reacts with Mn^{2+}, Co^{2+} and Cu^{2+} in formamide forming polymeric compounds of the formula $ML_2Fa \cdot Fa$ ($L = O_2P(CH_3)(C_6H_5)$; Fa = formamide; M = Mn, **1**; M = Co, **2**; M = Cu, **3**).

The structures consist of one dimensional polymeric chains in which two phosphinate groups form double bridges and a formamide oxygen atom forms a μ-O bridge between metal atoms. The intrachain metal distances in **1**, **2** and **3** are 4.020(1), 3.947(1) and 4.056(1) Å respectively. Compounds **1** and **2** are isomorphous and crystallize in the monoclinic system, space group $C2/m$. In **1**, $a = 22.446(3)$, $b = 8.041(1)$, $c = 11.612(2)$ Å, $\beta = 92.20(4)°$, $V = 2094(1)$ Å^3 and $Z = 4$. In **2**, $a = 22.352(3)$, $b = 7.894(1)$, $c = 11.638(2)$ Å, $\beta = 92.74(3)°$, $V = 2051(1)$ Å^3 and $Z = 4$. Compound **3** is triclinic, space group $P\bar{1}$ with $a = 11.550(2)$, $b = 11.569(1)$, $c = 8.113(1)$ Å, $\alpha = 107.98(5)$, $\beta = 90.86(4)$, $\gamma = 91.32(4)°$, $V = 1031(1)$ Å^3 and $Z = 2$.

Introduction

One dimensional polymers of metalphosphinates consist of metal ions linked by OPO bridges. Several coordination modes and polymer configurations of metalphosphinates have been reported in the last two decades. One example is $Zn[O_2P(C_4H_9)(C_6H_5)]_2$ in which two metal atoms are doubly bridged by three phosphinates and each pair is connected to its neighbour via an OPO bridge of another phosphinate group [1]. In $Pb[O_2P(C_6H_5)_2]_2$ the structure consists of polymeric chains of lead atoms linked by double-phosphinate bridges. The geometry around the metal atom is described as a distorted trigonal bipyramid with a lone pair of electrons occupying an equatorial site. The Pb...Pb separation is 5.55 Å [2]. In $Mn[O_2P(CH_3)_2]_2(H_2O)_2$ the chains are formed by manganese atoms doubly bridged by phosphinate groups [3]. Four oxygen atoms from four different phosphinates form a square planar array around the metal atoms and two coordinated water ligands complete the octahedral geometry around the manganese atoms in the polymer. The intrachain M...M distance is 4.865 Å.

In copper(II) phosphinates $Cu[O_2PR_2]_2$, the geometry around the metal atom depends upon the nature of the R groups. With dialkylphosphinates the copper atoms have a flattened tetrahedral geometry [4] whereas with diphenylphosphinate a square-pyramidal coordination is obtained [5]. The Cu...Cu separations in these polymers are within the range of 4.94–5.1 Å.

Recently, we reported the preparation of $\{Mn[O_2P(C_6H_5)_2]_2(DMF)\} \cdot DMF$ in which pentacoordinated manganese atoms are doubly bridged by $O_2P(C_6H_5)_2$ groups and coordinated to a DMF molecule, completing a slightly distorted trigonal bipyramidal geometry [6]. The Mn...Mn separation in this polymer is 4.58 Å, shorter by 0.28 Å from that found in $Mn[O_2P(CH_3)_2]_2(H_2O)_2$.

We report here the structure of a new kind of poly(metalphosphinates) in which the metal atoms are linked by two bridges of methylphenylphosphinate groups and an additional single μ-O(formamide) bridge. The intrachain distance between the metal atoms in these polymers, about 4 Å, is significantly shorter than in any of the other types of polymers reported so far.

We have prepared three compounds having the general formula $\{M[O_2P(CH_3)(C_6H_5)]_2(OCHNH_2)\} \cdot OCHNH_2$ (M = Mn, Co, Cu) and we report here the results of their X-ray structural analysis.

Experimental

Preparation of $MnL_2(Fa) \cdot Fa$ (1) ($L = O_2P(CH_3)(C_6H_5)$; Fa = formamide, $OCHNH_2$)

$Mn(ClO_4)_2$ (0.127 g) and $(C_6H_5)(CH_3)PO_2H$ (0.156 g) were dissolved in 25 ml of formamide. The solution was placed in an open beaker for evaporation in a hood. Colorless crystals of **1** were deposited after several weeks.

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TABLE I. Crystallographic Data

Compound	1	2	3
Formula	$C_{16}H_{22}MnN_2O_6P_2$	$C_{16}H_{22}CoN_2O_6P_2$	$C_{16}H_{22}CuN_2O_6P_2$
Formula weight	455.24	459.24	463.85
Space group	$C2/m$	$C2/m$	$P\bar{1}$
a (Å)	22.446(3)	22.352(3)	11.550(2)
b (Å)	8.041(1)	7.894(1)	11.569(1)
c (Å)	11.612(2)	11.638(2)	8.113(1)
α (°)			107.98(5)
β (°)	92.20(4)	92.74(3)	90.86(4)
γ (°)			91.32(4)
V (Å^3)	2094(1)	2051(1)	1031(1)
Z	4	4	2
μ (cm^{-1})	7.52	9.58	11.80
Range of 2θ (°)	4–45	4–45	4–45
No. unique data	1564	1536	2703
Data with $F_o^2 > 3\sigma(F_o^2)$	1061	1082	1833
R	0.077	0.072	0.081
R_w	0.080	0.080	0.093

Preparation of CoL$_2$(Fa)·Fa (2) and CuL$_2$(Fa)·Fa (3)

These two compounds were prepared as **1** using 0.183 g of $Co(ClO_4)_2\cdot 6H_2O$ and 0.116 g of $Cu(NO_3)_2\cdot 2.5H_2O$ respectively. Pale pink crystals of **2** and very pale blue crystals of **3** were obtained after several weeks.

X-ray Crystallography

Data were collected at 20 ± 2 °C on a Philips PW 1100 four-circle diffractometer. Mo Kα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 20 reflections in the range of $12° < \theta < 16°$. Data were measured by using ω–2θ motion. Crystallographic data and other pertinent information are given in Table I. For each crystal Lorentz and polarization corrections were applied. The heavy atom positions in all structures were obtained by using the results of SHELX 86 direct method analysis. Compounds **1** and **2** are isomorphous, their structures were refined* in space group $C2/m$ to convergence by using anisotropic thermal parameters for all non-hydrogen atoms of the polymeric chain and isotropic ones for the formamide molecules of crystallization atoms. Both the coordinated and the uncoordinated formamide molecules are subjected to a two fold disorder. In the coordinated one, O(3) and C(11) reside on a crystallographic mirror plane and in the uncoordinated one C(12) and N(2) reside on this plane. Therefore, N(1) and O(4) which occupy general positions were refined using occupancy factors of 0.5 for each. Structure **3** was refined in space group $P1$ using anisotropic thermal parameters for all copper, phosphorous, and oxygen atoms in the first coordination sphere and isotropic ones for the rest of the non-hydrogen atoms. The discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table I.

Results

MnL$_2$(Fa)·Fa (1)

The atomic positional parameters are listed in Table II. Table III presents important bond lengths and angles. Figure 1 shows the structure and the numbering scheme. Figure 2 shows a stereoview of the chain in **1**, **2** and **3**.

The structure consists of polymeric chains, propagating along the crystallographic b axis, in which two phosphinate groups form double bridges and the formamide oxygen forms a μ-O bridge between manganese atoms (Fig. 1). Each metal atom

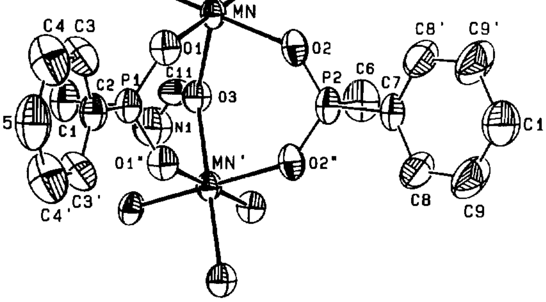

Fig. 1. A section of the polymeric chain of $Mn[O_2P(C_6H_5)(CH_3)]_2(OCHNH_2)$. Only one orientation of N(1) is shown.

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*All crystallographic computing was done on a CYBER 855 Computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE II. Positional Parameters for **1**[a]

Atom	x	y	z	Atom	x	y	z
Mn	0.250	0.250	0.000	C(6)	0.4062(8)	0.000	0.073(1)
P(1)	0.1402(2)	0.000	0.0745(3)	C(7)	0.3666(5)	0.000	0.308(1)
P(2)	0.3406(2)	0.000	0.1580(3)	C(8)	0.3751(5)	−0.151(2)	0.3669(9)
O(1)	0.1752(3)	0.1593(9)	0.0913(5)	C(9)	0.3930(6)	−0.151(2)	0.484(1)
O(2)	0.3069(3)	0.1606(9)	0.1371(5)	C(10)	0.4031(8)	0.000	0.539(1)
O(3)	0.2578(4)	0.000	−0.0952(7)	C(11)	0.2585(8)	0.000	−0.202(1)
C(1)	0.1004(7)	0.000	−0.065(1)	N(1)	0.248(1)	−0.117(3)	−0.276(2)
C(2)	0.0812(6)	0.000	0.177(1)	O(4)	0.784(1)	0.130(3)	0.644(2)
C(3)	0.0597(5)	0.153(2)	0.2153(9)	C(12)	0.784(1)	0.000	0.598(2)
C(4)	0.0128(5)	0.151(2)	0.294(1)	N(2)	0.7705(8)	0.000	0.489(2)
C(5)	−0.0089(7)	0.000	0.333(1)				

[a] e.s.d.s in the least significant digits are given in parentheses.

TABLE III. Important Bond Lengths (Å) and Angles (°) for **1**

Mn–O(1)	2.148(6)
Mn–O(2)	2.127(6)
Mn–O(3)	2.304(4)
P(1)–O(1)	1.511(7)
P(2)–O(2)	1.511(7)
O(1)–Mn–O(2)	88.5(2)
O(1)–Mn–O(2)′	91.5(2)
O(1)–Mn–O(3)	90.9(3)
O(1)–Mn–O(3)′	89.1(3)
O(2)–Mn–O(3)	90.5(3)
O(2)–Mn–O(3)′	89.5(3)
Mn–O(3)–Mn′	121.5(4)
Mn–O(1)–P(1)	129.6(4)
Mn–O(2)–P(2)	133.7(4)

resides on a crystallographic center of symmetry. The $M_2O[O_2P(CH_3)(C_6H_5)]_2$ unit is bisected by a crystallographic mirror plane passing through O(3), P(1), P(2), the methyl carbon atoms C(2) and C(6) and the phenyl carbon atoms C(1), C(5), C(7) and C(10). The geometry about the metal atom is octahedral with four oxygen atoms of four different phosphinate groups and two of the two coordinated formamide ligands.

The intrachain metal–metal distance is half of the *b* axis which is 4.020(1) Å in **1**.

$CoL_2(Fa)\cdot Fa$ (2)

The atomic positional parameters are listed in Table IV. Table V shows the important bond lengths and angles in **2**. The labeling scheme used for **2** is identical with that of **1**.

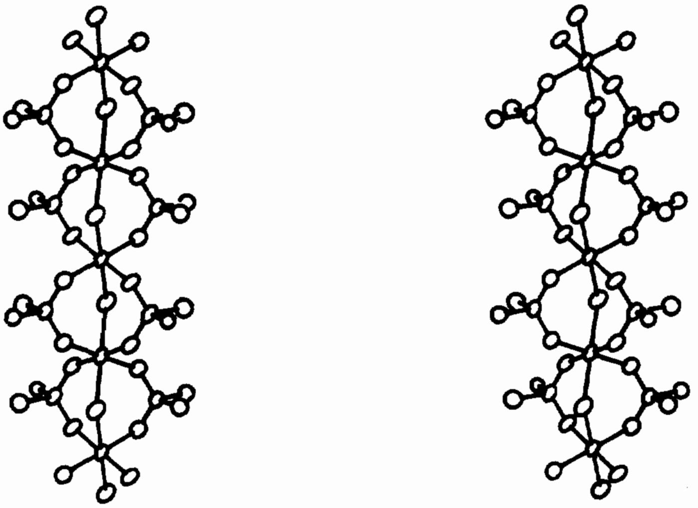

Fig. 2. A stereoview of the chain in $\{M[O_2P(C_6H_5)(CH_3)]_2(OCHNH_2)\}$. The phenyl carbon atoms and the carbon and nitrogen atoms of the formamide ligand were omitted for clarity.

TABLE IV. Positional Parameters for 2[a]

Atom	x	y	z	Atom	x	y	z
Co	0.250	0.250	0.000	C(6)	0.4042(7)	0.000	0.066(1)
P(1)	0.1427(2)	0.000	0.0699(3)	C(7)	0.3658(6)	0.000	0.301(1)
P(2)	0.3392(2)	0.000	0.1521(3)	C(8)	0.3757(5)	−0.154(1)	0.360(1)
O(1)	0.1780(3)	0.1644(8)	0.883(5)	C(9)	0.3946(6)	−0.153(2)	0.476(1)
O(2)	0.3045(3)	0.1645(8)	0.1326(5)	C(10)	0.4040(9)	0.000	0.533(1)
O(3)	0.2574(4)	0.000	−0.0888(7)	C(11)	0.2590(8)	0.000	−0.193(1)
C(1)	0.1041(9)	0.000	−0.071(2)	N(1)	0.261(1)	−0.100(3)	−0.268(2)
C(2)	0.0848(7)	0.000	0.170(1)	O(4)	0.783(1)	0.105(4)	0.646(2)
C(3)	0.0616(5)	0.154(1)	0.211(1)	C(12)	0.784(2)	0.000	0.587(4)
C(4)	0.0155(5)	0.154(2)	0.290(1)	N(2)	0.772(1)	0.000	0.480(2)
C(5)	−0.0072(8)	0.000	0.329(1)				

[a] e.s.d.s in the least significant digits are given in parentheses.

The intrachain cobalt–cobalt separation in 2 is 3.947(1) Å.

CuL₂(Fa)·Fa (3)

The atomic positional parameters are listed in Table VI. Table VII shows the important bond lengths and angles. Figure 3 shows a section of the polymeric chain in 3 and the labeling scheme. There are two independent copper atoms residing on two crystallographic centers of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$ and the intrachain copper–copper separation is 4.056(1) Å. Structure 3 differs from 1 and 2 by the absence of the crystallographic mirror plane that bisects the phosphinate groups and the bridging and uncoordinated formamide molecules. Otherwise, the polymeric chains in **1**, **2** and **3** are basically identical.

Discussion

The series of compounds, described here, represent a new class of polymeric metalphosphinates. The introduction of μ-O bridges into the chains causes a substantial decrease in the metal–metal separation from about 5 Å in polymers such as $M(O_2PR_2)_2$ [2–5] to about 4 Å. The overall geometry of each pair of metal atoms (Fig. 1) is reminiscent of the structure of $\{Fe_2O[O_2P(OC_6H_5)_2][HB(Pz)_3]_2\}$ [HB-(Pz)$_3$ = hydrotris(1-pyrazolyl)-borate] and other related compounds in which the OPO bridges are replaced by acetato bridges [7]. The main difference is the much weaker interactions of the metal atoms in the polymers with the bridging oxygen atom. The M–O(Fa) bond distances in 1, 2 and 3 are 2.304(4), 2.237(4) and 2.38(1) Å respectively whereas in the $Fe_2O(O_2PR_2)_2$ system this distance is about 1.8 Å and the Fe–Fe separation is 3.337 Å [7a].

Replacement of the formamide ligand with dimethylformamide causes a dramatic structural change in the polymeric chain. In the case of $Cu(O_2P\phi Me)_2$, the substitution transforms the coordination geometry of the metal atom from octahedral in 3 to square pyramidal in $\{Cu[O_2P(CH_3)(C_6H_5)]_2(DMF)\}$ [8]. This transformation is accompanied by an in-

TABLE V. Important Bond Lengths (Å) and Angles (°) for 2

Co–O(1)	2.064(6)
Co–O(2)	2.035(6)
Co–O(3)	2.237(4)
P(1)–O(1)	1.528(6)
P(2)–O(2)	1.524(6)
O(1)–Co–O(2)	88.1(2)
O(1)–Co–O(2)′	91.9(2)
O(1)–Co–O(3)	91.0(3)
O(1)–Co–O(3)′	89.0(3)
O(2)–Co–O(3)	90.2(3)
O(2)–Co–O(3)′	89.8(3)
Co–O(3)–Co′	116.2(4)
Co–O(1)–P(1)	128.2(4)
Co–O(2)–P(2)	132.7(4)

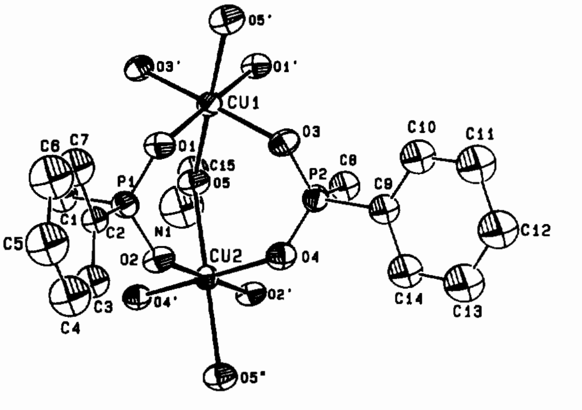

Fig. 3. A section of the polymeric chain and the labeling scheme in $\{Cu[O_2P(C_6H_5)(CH_3)]_2(OCHNH_2)\}$.

TABLE VI. Positional Parameters for 3[a]

Atom	x	y	z	Atom	x	y	z
Cu(1)	0.500	0.500	0.000	C(6)	0.040(2)	0.192(2)	−0.046(2)
Cu(2)	0.500	0.500	0.500	C(7)	0.158(1)	0.233(1)	−0.023(2)
P(1)	0.3574(3)	0.3271(3)	0.1714(4)	C(8)	0.579(1)	0.790(1)	0.380(2)
P(2)	0.4400(3)	0.7124(3)	0.3426(4)	C(9)	0.334(1)	0.831(1)	0.393(2)
O(1)	0.3718(7)	0.3955(8)	0.041(1)	C(10)	0.299(1)	0.884(1)	0.267(2)
O(2)	0.3738(7)	0.3960(8)	0.360(1)	C(11)	0.216(1)	0.974(1)	0.305(2)
O(3)	0.4200(7)	0.6444(8)	0.154(1)	C(12)	0.169(1)	1.008(1)	0.472(2)
O(4)	0.4223(7)	0.6446(8)	0.471(1)	C(13)	0.202(1)	0.959(2)	0.600(2)
O(5)	0.6051(7)	0.4754(9)	0.240(1)	C(14)	0.287(1)	0.868(1)	0.561(2)
C(1)	0.450(1)	0.195(1)	0.117(2)	C(15)	0.712(1)	0.479(1)	0.237(2)
C(2)	0.208(1)	0.269(1)	0.144(2)	N(1)	0.779(2)	0.457(2)	0.356(3)
C(3)	0.145(1)	0.266(1)	0.285(2)	O(6)	0.850(2)	0.425(2)	0.807(3)
C(4)	0.028(1)	0.227(2)	0.263(2)	C(16)	0.926(6)	0.422(6)	0.718(8)
C(5)	−0.022(2)	0.188(2)	0.098(2)	N(2)	1.017(2)	0.419(2)	0.718(3)

[a] e.s.d.s in the least significant digits are given in parentheses.

crease in the Cu...Cu distance of about 1.2 Å.

Substitution of the phosphinate group from $O_2P\phi Me$ to $O_2P\phi H$ causes a structural transformation in compounds such as $\{Mn[O_2P(C_6H_5)H]_2(Fa)_2\}$ or its cobalt analogue [9]. In these compounds the formamide ligands do not bridge the metal atoms and serve as terminal ligands.

These results indicate that conformations of polymers of metalphosphinates can be determined by several factors such as the size and the nature of the R groups in the O_2PR_2 ligands and of the monodentate ligand. The variety in coordination geometries, intrachain M–M distances and types of metal atoms, participating in the construction of polymetalphosphinates, may produce some interesting magnetic and spectroscopic properties that we are currently investigating.

TABLE VII. Important Bond Lengths (A) and Angles (°) for 3

Cu(1)–O(1)	1.987(9)
Cu(1)–O(3)	2.005(8)
Cu(1)–O(5)	2.38(1)
Cu(2)–O(2)	1.972(7)
Cu(2)–O(4)	1.989(9)
Cu(2)–O(5)	2.390(9)
P(1)–O(1)	1.51(1)
P(1)–O(2)	1.499(8)
P(2)–O(3)	1.502(8)
P(2)–O(4)	1.50(1)
O(1)–Cu(1)–O(3)	88.2(4)
O(1)–Cu(1)–O(3)′	91.8(4)
O(1)–Cu(1)–O(5)	89.8(3)
O(1)′–Cu(1)–O(5)	90.2(3)
O(3)–Cu(1)–O(5)	91.3(4)
O(3)′–Cu(1)–O(5)	88.7(4)
O(2)–Cu(2)–O(4)	89.0(4)
O(2)–Cu(2)–O(4)′	91.0(4)
O(2)–Cu(2)–O(5)	89.0(3)
O(2)′–Cu(2)–O(5)	91.0(3)
O(4)–Cu(2)–O(5)	91.0(3)
O(4)′–Cu(2)–O(5)	89.0(3)
Cu(1)–O(5)–Cu(2)	116.7(3)
Cu(1)–O(1)–P(1)	132.3(5)
Cu(2)–O(2)–P(1)	134.1(5)
Cu(1)–O(3)–P(2)	130.2(5)
Cu(2)–O(4)–P(2)	131.0(6)

Supplementary Material

Tables of structure factors, thermal parameters, non-essential bond distances and angles for **1**–**3** (34 pages) are available from the authors.

Acknowledgement

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