Crystal Structure of Poly-bis(μ-phenylmethylphosphinato)copper(II)(dimethylformamide)

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Structural studies of several poly(copperphosphinates) showed the existence of two different types of geometries about the metal atoms in the polymeric chains. The structure of dialkylphosphinates of Cu(II) consists of copper atoms with flattened tetrahedral coordination geometry linked by double phosphinate bridges [1]. Recently we reported the preparation and structure of poly-bis(μ-diphenylphosphinato)copper(II) in which the metal atom is four-coordinated with a square planar geometry [2].

In all these polymers, only phosphinato oxygen atoms were coordinated to the metal atoms. In principle, other monodentate ligands can be incorporated to the metal center within the polymeric framework. This may alter the coordination geometry, the magnetic and the spectroscopic properties of the material. One such example is the compound $Mn(H_2O)_2[O_2P(CH_3)_2]_2$ in which two water ligands complete the octahedral coordination sphere of the manganese atom [3].

We report here the preparation and structure of poly-bis(μ-phenylmethylphosphinato)copper(II)-(DMF) which is an example of a metal phosphinate with a square-pyramidal geometry.

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Experimental

$Cu(NO_3)\cdot 2.5H_2O$ (0.116 g) and $(C_6H_5)(CH_3)PO_2H$ (0.156 g) were dissolved in 40 ml of DMF and the solution was placed in an open beaker in the hood. After several days large blue prisms of $Cu[O_2P(C_6H_5)(CH_3)]_2(DMF)$ were deposited. The crystals are triclinic, space group $P\bar{1}$ with $a = 10.104(1)$, $b = 11.110(2)$, $c = 9.998(1)$ Å, $\alpha = 112.47(3)$, $\beta = 102.01(3)$, $\gamma = 90.97(2)°$, $V = 1009(1)$ Å^3 and $Z = 2$.

A total of 2622 unique data were collected in the range $4° < 2\theta < 45°$, of which 1693 were found to have $I > 3\sigma(I)$ and used in the refinement. The structure was refined by least-squares methods to a conventional R factor of 7.77%.

Results and Discussion

The positional parameters are presented in Table I. Table II gives some important bond distances and angles. Figure 1 shows a stereoview of a section of the polymeric chain and Fig. 2 shows the numbering scheme. The structure consists of infinite chains of centrosymmetric eight membered rings formed by two metal atoms bridged by two phosphinato groups. Each copper atom is bonded to five oxygen atoms, four of which belong to four different $O_2P\phi Me$ groups, forming a roughly square planar array. The deviation of the copper atom from the plane defined by these four oxygen atoms is 0.16 Å. One molecule of dimethylformamide is coordinated to the metal atom with a Cu–O distance of 2.316(8) Å completing a square pyramidal coordination geometry. The two crystallographically independent Cu...Cu intrachain distances of 5.199(5) and 5.181(4) Å are similar to that found in square planar $Cu[O_2P(C_6H_5)_2]_2$

TABLE I. Positional Parameters for $Cu[O_2P(C_6H_5)(CH_3)]_2(DMF)$

Atom	x	y	z	Atom	x	y	z
Cu	−0.0566(2)	−0.0468(2)	0.2187(2)	C(6)	−0.465(2)	0.325(2)	0.525(2)
P(1)	−0.1517(4)	0.0946(4)	0.5249(4)	C(7)	−0.383(2)	0.221(2)	0.484(2)
P(2)	−0.0254(4)	0.1741(3)	0.0879(4)	C(8)	0.149(2)	0.201(1)	0.189(2)
O(1)	−0.135(1)	0.0762(9)	0.371(1)	C(9)	−0.093(1)	0.328(1)	0.176(2)
O(2)	−0.0239(9)	0.1287(9)	0.645(1)	C(10)	−0.096(2)	0.426(1)	0.122(2)
O(3)	−0.1012(9)	0.0677(8)	0.108(1)	C(11)	−0.146(2)	0.544(2)	0.193(2)
O(4)	−0.0347(9)	0.1570(8)	0.072(1)	C(12)	−0.192(2)	0.562(2)	0.317(2)
O(5)	−0.2592(9)	−0.183(1)	0.111(1)	C(13)	−0.193(2)	0.468(2)	0.372(2)
C(1)	−0.245(2)	−0.050(2)	0.514(2)	C(14)	−0.144(2)	0.348(2)	0.297(2)
C(2)	−0.261(1)	0.224(1)	0.576(2)	N	−0.484(2)	−0.180(1)	0.080(2)
C(3)	−0.219(2)	0.329(2)	0.705(2)	C(15)	−0.358(2)	−0.127(2)	0.118(2)
C(4)	−0.299(2)	0.437(2)	0.749(2)	C(16)	−0.509(3)	−0.329(3)	0.020(3)
C(5)	−0.424(2)	0.424(2)	0.653(2)	C(17)	−0.604(3)	−0.105(3)	0.096(3)

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

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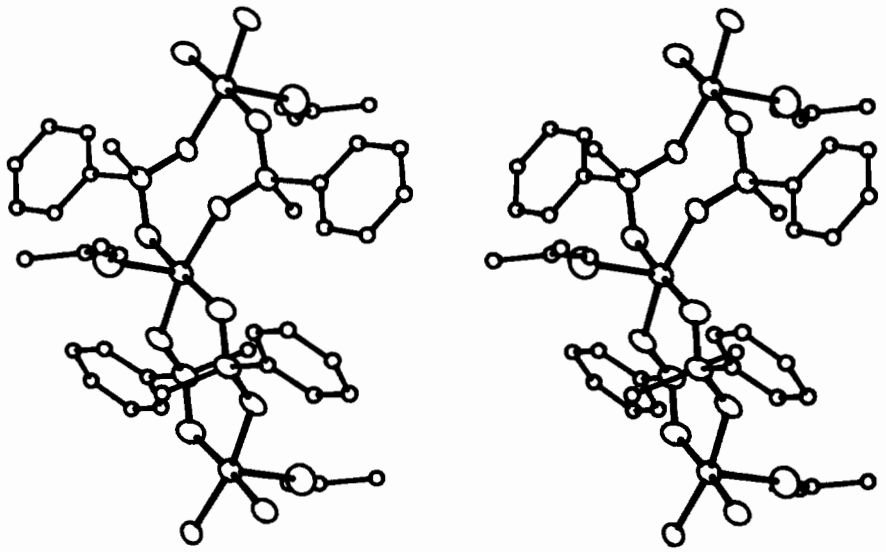

Fig. 1. Stereoview of a section of $Cu[O_2P(C_6H_5)(CH_3)]_2(DMF)$.

TABLE II. Important Bond Lengths (Å) and Angles (°) for $Cu(O_2POMe)_2(DMF)$

Cu–O(1)	1.944(9)
Cu–O(2)′	1.97(1)
Cu–O(3)	1.98(1)
Cu–O(4)′	1.931(9)
Cu–O(5)	2.316(8)
O(1)–Cu–O(2)′	90.8(4)
O(1)–Cu–O(3)	86.5(4)
O(1)–Cu–O(4)′	175.0(5)
O(1)–Cu–O(5)	91.8(5)
O(2)′–Cu–O(3)	166.5(5)
O(2)′–Cu–O(4)′	89.9(4)
O(2)′–Cu–O(5)	97.6(4)
O(3)–Cu–O(4)′	91.7(4)
O(3)–Cu–O(5)	95.7(4)
O(4)′–Cu–O(5)	93.1(5)

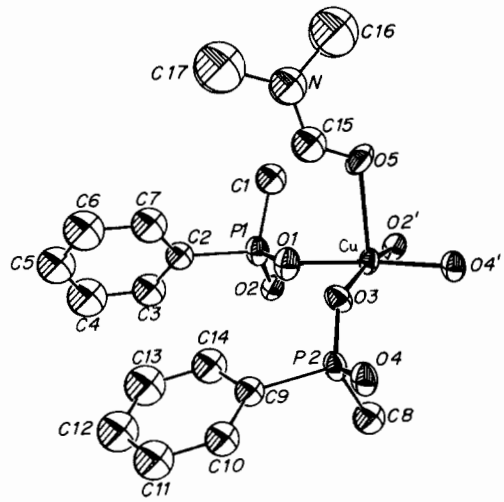

Fig. 2. View of $Cu[O_2P(C_6H_5)(CH_3)]_2(DMF)$ showing the numbering scheme and the coordination about the copper atom.

(5.0181 Å) [2] and slightly longer than those found for other copper phosphinates (4.9 Å) [1].

It should be noted that a DMF molecule is not incorporated to the copper atom when the methyl group of the phosphinate is substituted by a phenyl group. In $Cu[O_2P\phi Me]_2$, the two phenyl groups constitute a steric barrier and the copper atoms remain four-coordinated. If formamide (Fa) is used instead of DMF a new polymer, $Cu[O_2P\phi Me]_2(Fa)$, with μ-O (Fa) bridges having a totally different conformation is obtained [4]. This and other results will be included in subsequent publications.

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