Inorganica Chimica Acta, 128 (1987) L21–L22

Preparation and Structure of Poly-bis(μ-diphenylphosphinato)copper(II)

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(Received November 5, 1986)

Poly(metalphosphinates) have been extensively investigated because of their interesting structural, magnetic and other properties [1–8]. Structural X-ray studies of several dialkylphosphinates of copper(II) showed that they are one dimensional polymers consisting of Cu atoms with flattened tetrahedral coordination geometry linked by double phosphinate bridges [3–5]. A similar polymer of lead(II) with diphenylphosphinate $Pb[O_2P(C_6H_5)_2]_2$ was characterized and the coordination geometry of the lead atom was described as a distorted trigonal bipyramid [6]. This work reports the preparation and structure of poly-bis(μ-diphenylphosphinato)-copper(II) which is the first example of a copper–phosphinate polymer with a square-planar geometry.

Experimental

$Cu(NO_3)_2 \cdot 2.5H_2O$ (0.05 g) and $(C_6H_5)_2PO_2H$ (0.12 g) were dissolved in 20 ml of methanol. The solution was stirred at 50 °C until most of the solvent was evaporated. The resulting slurry was dissolved in a minimum volume of dimethylformamide and the solution was kept in a sealed vile. Blue crystals of $Cu[O_2P(C_6H_5)_2]_2$ were obtained after two weeks.

The crystals are monoclinic, space group $C2/c$ with $a = 16.698(2)$, $b = 5.081(1)$, $c = 25.582(2)$ Å, $\beta = 96.39(2)°$, $V = 2157(1)$ Å^3 and $Z = 4$.

A total of 1850 unique data were collected in the range $4° < 2\theta < 50°$, of which 1302 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 4.87%.

Results and Discussion

The positional parameters are presented in Table I and 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 in the structure.

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

Atom	*x*	*y*	*z*
Cu	0.25000	0.25000	0.50000
P	0.25040(7)	0.7500(3)	0.57689(5)
O(1)	0.2605(2)	0.4636(7)	0.5619(1)
O(2)	0.2851(2)	0.9517(7)	0.5423(1)
C(1)	0.3010(3)	0.785(1)	0.6427(2)
C(2)	0.3555(4)	0.986(2)	0.6539(3)
C(3)	0.3976(4)	1.005(2)	0.7049(3)
C(4)	0.3825(4)	0.835(2)	0.7437(3)
C(5)	0.3263(6)	0.635(2)	0.7327(3)
C(6)	0.2850(5)	0.611(2)	0.6817(3)
C(7)	0.1452(3)	0.819(1)	0.5806(2)
C(8)	0.1202(8)	0.919(3)	0.6256(6)
C(9)	0.0358(9)	0.966(3)	0.6285(6)
C(10)	−0.0175(4)	0.929(1)	0.5872(3)
C(11)	0.0089(8)	0.836(3)	0.5389(6)
C(12)	0.0920(8)	0.777(3)	0.5374(5)
C(13)	0.1207(7)	1.061(2)	0.6000(4)
C(14)	0.0403(7)	1.115(3)	0.6050(5)
C(15)	0.0015(9)	0.682(3)	0.5703(6)
C(16)	0.0854(7)	0.621(3)	0.5675(5)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

TABLE II. Bond Distances (Å) and Angles (°) for $Cu[O_2P(C_6H_5)_2]_2$

Cu–O(1)	1.911(3)
Cu–O(2)	1.916(3)
P–O(1)	1.519(3)
P–O(2)	1.510(3)
P–C(1)	1.807(5)
P–C(7)	1.803(5)
O(1)–Cu–O(2)′	90.7(1)
O(1)–Cu–O(2)″	89.3(1)
Cu–O(1)–P	138.7(2)
Cu–O(2)′–P′	139.0(2)
O(1)–P–O(2)	116.2(2)

The crystal structure of $Cu[O_2P(C_6H_5)_2]_2$ is similar to those of $Cu[O_2PR_2]_2$ ($R = C_2H_5$, n-C_4H_9, n-C_6H_{13}) [3–5] and of $Pb[O_2P(C_6H_5)_2]_2$ [6]. It consists of infinite chains of centrosymmetric eight membered rings formed by two copper atoms bridged by two phosphinato groups. The copper atom resides on a crystallographic center of symmetry having a nearly square planar coordination geometry. The two crystallographically independent Cu–O distances 1.911(3) and 1.916(3) Å and the two O–Cu–O angles, 90.7(1)° and 89.3(1)°, deviate slightly from a perfect D_{4n} symmetry (the CuO_4 unit is planar by definition). One of the phenyl rings is subjected

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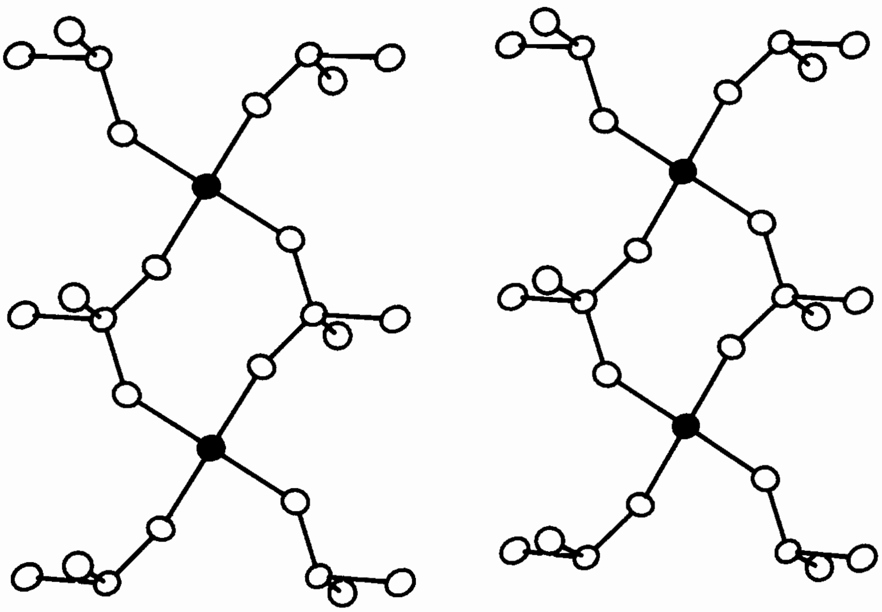

Fig. 1. Stereoview of a section of poly-bis-(μ-diphenylphosphinato)copper(II). Only α carbon atoms of the phenyl groups are depicted.

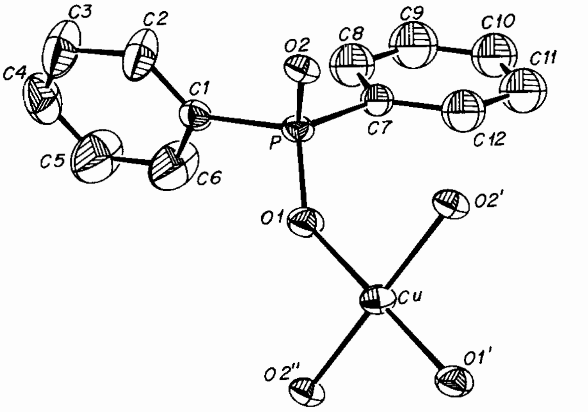

Fig. 2. The structure of $Cu[O_2P(C_6H_5)_2]_2$. Only one position of the disordered phenyl ring C(7)–C(12) is shown.

to a two-fold disorder around the C(7)–C(10) axis. The atoms C(8), C(9) and C(11) through C(16) were refined with a half occupancy factor. The dihedral angle between the planes of the disordered rings is 51.5°. The Cu•••Cu separation of 5.081(1) Å is slightly longer than those found for the other copper phosphinates (~4.94 Å) [3–5].

It is not very clear why substitution of the linear alkyl groups with phenyl rings causes a transition in the coordination sphere of the copper(II) atom. This transition from flattened tetrahedra to a square-planar geometry may cause a considerable change in the spectroscopic and magnetic properties of the system and we intend to explore these changes.

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