

二(三苯基膦)水杨酸铜(I)乙醇溶剂配合物的晶体结构

建方方* 肖海连 孙萍萍

(青岛科技大学新材料与功能配合物实验室, 青岛 266042)

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Crystal Structure of Bis(triphenylphosphine) Copper (I) hydroxylbenzoate Ethanol Solvate: $[(PPh_3)_2Cu(O_2CPhOH)] \cdot CH_3CH_2OH$

JIAN Fang-Fang* XIAO Hai-Lian SUN Ping-Ping

(New Material & Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao 266042)

The crystal and molecular structure of $[(PPh_3)_2Cu(O_2CPhOH)] \cdot CH_3CH_2OH$ has been determined by X-ray crystallography. It crystallizes in the monoclinic system, space group $P2_1/c$, with $M_r = 771.26$ ($C_{45}H_{41}CuO_4P_2$), $a = 0.96413(19)$ nm, $b = 1.5780(3)$ nm, $c = 2.5426(5)$ nm, $\beta = 100.27(3)^\circ$, $V = 3.8065(13)$ nm³. The title compound consists of discrete copper (I) bis(triphenylphosphine) salicylate molecules and ethanol solvate. Each Cu is coordinated to two phosphorus atoms of triphenylphosphine ligands and one of carboxylate oxygens in a trigonal planar geometry. In the solid, the intramolecular hydrogen bond and extensive intermolecular interaction connecting $(PPh_3)_2Cu(O_2CPhOH)$ molecules and ethanol solvate form hydrogen bonds network which stabilize the crystal structure. CCDC: 208730.

Keywords: triphenylphosphine ligand crystal structure copper (I) complex trigonal geometry
hydrogen bond

0 Introduction

The study of copper (I) complexes is investigated in many laboratories. Among the reasons for carrying out the investigation of such species are their structural features^[1], the usefulness of copper (I) compounds in organic syntheses^[2] and the well-documented importance of copper (I) centers at the active sites of a number of protein^[3]. Concerning copper (I) carboxy-

lates a further interest exists, stemming from their use in homogeneous catalysed hydrogenation^[4]. The copper (I) bis(triphenylphosphine) cation is a soft, but flexible acceptor ion that can accommodate a range of coordinating anions to form air-stable complexes of the type $[(PPh_3)_2CuX]$. The weak adducts formed with hard carboxylate anions, $[RCO_2]^-$, are of interest as copper coordination environments ranging from four-coordinate P_2CuO_2 , with bidentate coordination of

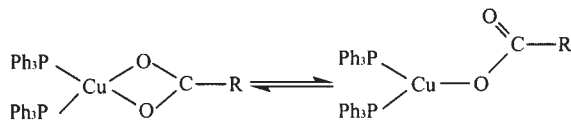
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* 通讯联系人。E-mail: ffj2001@public.qd.sd.cn

第一作者: 建方方, 男, 39岁, 教授; 研究方向: 配位化学和资源化学。

the anion, to three-coordinate P_2CuO , with unidentate coordination of the anion, are possible as below^[5]:



In the present paper, we report the crystal structure of bis(triphenylphosphine) copper (I) salicylate ethanol solvate, $[(PPh_3)_2Cu(O_2CPhOH)] \cdot CH_3CH_2OH$ to expand knowledge in this area.

1 Experimental Section

All chemicals used were of analytical reagent grade and used directly without further purification. $(o\text{-HO} \cdot C_6H_4COO)_2 \cdot Cu$ was prepared by mixing aqueous solutions of copper(II) sulfate and sodium salicylate according to the literature method^[6]. To a warm solution of triphenylphosphine (0.26g, 1mmol) in EtOH (50mL) was added with stirring $Cu(O_2CPhOH)_2$ (0.10g, 0.4mmol) and the mixture was refluxed for 20min. At this time, we should find blue solution to become to colorless solution gradually. This phenomenon suggests Cu^{2+} complex change to Cu^+ (d^{10}) complex. The resulting colorless solution was filtered and was left to stand overnight. A colorless solid was formed and collected by filtration. Single crystal suitable for X-ray analysis was obtained by recrystallizing this colorless solid from ethanol solution. Upon slow evaporation at room temperature for a few days, the colorless crystalline solid appeared and was collected by filtration. The C and H and N content were determined by elemental analysis (Found(%): C, 69.91; H, 4.83; for $C_{45}H_{41}CuO_4P_2$ Calc. (%): C, 70.08; H, 5.36).

The selected crystal of $[(PPh_3)_2Cu(O_2CPhOH)] \cdot CH_3CH_2OH$ with approximate dimensions of 0.42mm \times 0.26mm \times 0.14mm was mounted on a glass fiber. The data were collected on a SMART CCD diffractometer with graphite monochromated $MoK\alpha$ ($\lambda = 0.071073\text{nm}$) radiation at the temperature of 293(2) K, using an ω -2 θ scan mode ($1.53^\circ < \theta < 29.50^\circ$). Intensities were corrected for Lorentz and polarization

effects and empirical absorption, and the data reduction using SADABS^[7] program.

The structure was solved by direct methods using SHELXS-97^[8]. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. All hydrogen atoms were placed in calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in structure-factor calculations. The total reflections were 27062 and the final cycle of full-matrix least-squares refinement was based on 9624 observed reflections ($R_{\text{int}} = 0.1127$) and 500 variable parameters and converged with unweighted and weighted agreement factors. The final least-square cycle gave $R_1 = 0.0564$, $wR_2 = 0.1221$ for 5490 observed reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0547P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$, the maximum shift (Δ/σ)_{max} = 0.000 and $S = 0.890$. The maximum and minimum peaks on the final difference Fourier map corresponded to $695e \cdot \text{nm}^{-3}$ and $-1077e \cdot \text{nm}^{-3}$, respectively. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray Crystallography^[9].

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2 Results and Discussion

Fig. 1 shows a perspective view of the title compound with atomic numbering scheme, and Fig. 2 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths and bond angles are presented in Table 1.

The title compound consists of discrete copper (I) bis(triphenylphosphine) hydroxylbenzoate molecules and ethanol solvate. The molecular structure shows that the copper atom is bonded to the phosphine ligands and to one oxygen atom of the carboxylate group, giving rise to a nearly trigonal planar coordination. In fact, the O(1) atom is 0.1021nm out of the plane through P(1)-P(2)-Cu(1). The hydroxylbenzoate anion behaves as

Table 1 Selected Bond Lengths(nm) and Bond Angles(°)

Cu(1)-O(1)	0.2045(2)	Cu(1)-P(2)	0.2212(1)	Cu(1)-P(1)	0.2254(1)
O(2)-C(43)	0.1275(4)	P(1)-C(7)	0.1820(3)	P(2)-C(19)	0.1827(3)
P(1)-C(1)	0.1825(3)	P(2)-C(25)	0.1827(3)	P(1)-C(13)	0.1834(3)
P(2)-C(31)	0.1830(3)	C(43)-C(37)	0.1481(4)	O(3)-C(38)	0.1347(4)
O(1)-C(43)	0.1253(4)	C(64A)-C(61A)	0.161(2)	C(64B)-(61B)	0.122(2)
C(64A)-O(5A)	0.148(2)				
O(1)-Cu(1)-P(2)	118.24(7)	O(1)-Cu(1)-P(1)	106.08(7)	P(2)-Cu(1)-P(1)	135.42(4)
C(7)-P(1)-Cu(1)	112.50(1)	C(1)-P(1)-Cu(1)	114.60(1)	C(13)-P(1)-Cu(1)	114.36(1)
C(19)-P(2)-Cu(1)	115.06(1)	C(31)-P(2)-Cu(1)	113.39(1)	C(25)-P(2)-Cu(1)	116.22(1)
C(43)-O(1)-Cu(1)	102.6(2)				

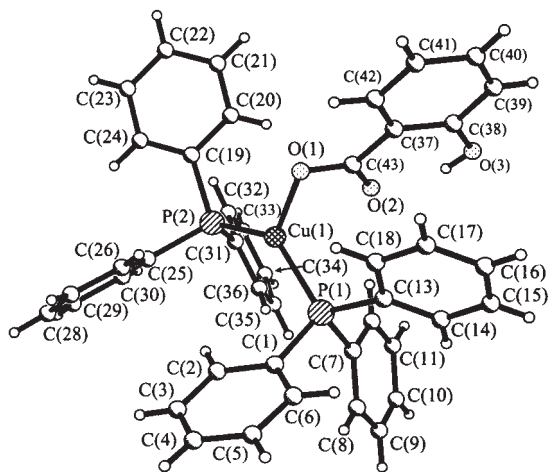
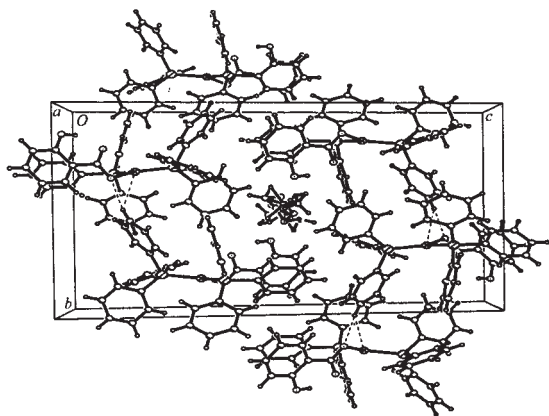


Fig. 1 Molecular structure along with the labeling atoms

Fig. 2 A view of the crystal packing down the *a* axis for $[(\text{PPh}_3)_2\text{Cu}(\text{O}_2\text{CPhOH})] \cdot \text{CH}_3\text{CH}_2\text{OH}$

a monodentate carboxylate ligand making the shortest interaction with the copper atom $[\text{Cu}(1)-\text{O}(1) = 0.2044(4) \text{ nm}]^{[10]}$. The $\text{Cu}(1)-\text{O}(2)$ distance at $0.25665(2) \text{ nm}$ indicates a very weak interaction, which is less than the sum of the van der Waals radii,

$0.29 \text{ nm}^{[11]}$. The $\text{Cu}(1)-\text{P}(1)$ and $\text{Cu}(1)-\text{P}(2)$ bond distances are $0.2254(1) \text{ nm}$ and $0.2212(2) \text{ nm}$, respectively. The corresponding $\text{P}(1)-\text{Cu}(1)-\text{P}(2)$ bond angle is $135.42(4)^\circ$. This obtuse angle is typical for triphenylphosphine copper (I) complexes and reflects the steric requirements of the triphenylphosphine ligand^[12]. Distorted tetrahedral Cu (I) triphenylphosphine complexes have P-Cu-P bond angles ranging from 120° to 133° ^[13, 14]. It has been reported that the P-Cu-P bond angle decreases as the nonplanarity and size of the anion increases; therefore, the largest bond angles would be anticipated for small planar chelating anions^[14]. In this paper, the salicylate is best considered monodentate, since the $\text{Cu}(1)-\text{O}(2)$ distance is $0.25665(2) \text{ nm}$, which is considering that there are weak covalence interaction between them. It might be expected that increasing the basicity of the carboxylate would strengthen the interaction between O(2) and the Cu(1) center; therefore, carboxylates of higher basicity would be predicted to have tetrahedral structures and carboxylates of lower basicity would favor three-coordinate trigonal planar complexes^[15, 16]. The O(5), C(61) and C(64) atoms of ethanol solvate molecules are disordered and result in higher thermal parameter of these three atoms. The occupied ratios are 0.3 for O(5A), 0.4 for C(61A) and 0.4 for C(64A), respectively.

In the structure, there is one intramolecular hydrogen bond between hydroxyl oxygen O(3) and carbonyl oxygen O(2) having a contact distance of $0.25469(1) \text{ nm}$. Also, there are the potentially weak (C-H...Y hydrogen bonds, Y = O, N and Cl) inter-

molecular interactions^[17,18]. The crystal packing are stabilized by these extensive hydrogen bondings. The O(1) with C(34) atoms in alkyl form potentially weak C-H...O intermolecular interactions, the donor and acceptor distances are C(34)...O(1) 0.32928(2) nm [symmetry code: $2-x, -1/2+y, 1/2-z$]. This extensive hydrogen bond connected $(\text{PPh}_3)_2\text{Cu}(\text{O}_2\text{CPhOH})$ molecule and ethanol solvate form hydrogen bonds network which stabilize the crystal structure.

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