

β -二酮双核铜(I)配合物的合成与结构

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室温下, 通过双二苯基膦甲烷还原[Cu(tfac)₂]直接合成了双核铜(I)配合物[Cu(dppm)(tfac)]₂(**1**), dppm = 双二苯基膦甲烷, tfac = 2-噁吩甲酰三氟丙酮, 研究了配合物的物理化学和光谱性质, 并经 X-射线单晶结构分析确定了配合物(**1**)的分子结构, 晶体属单斜晶系, 空间群 $P2_1/n$, $a = 1.3028(5)$, $b = 1.3744(4)$, $c = 2.0278(5)$ nm, $\beta = 94.48(2)^\circ$, $D_c = 1.351 \text{ g} \cdot \text{cm}^{-3}$, $Z = 2$, $V = 3.6199 \text{ nm}^3$, $R = 0.04978$, 中心铜离子分别由来自两个不同 dppm 的 P 原子和 tfac 的两个氧原子形成四面体配位结构。

关键词: 铜 配合物 还原 晶体结构

分类号: O611.622

Synthesis and Structure of Binuclear Copper (I) Complex with β -Diketone

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At room temperature, the binuclear copper (I) complex [Cu(dppm)(tfac)]₂(**1**) [dppm = bis (diphenylphosphine) methane, tfac = 2-thenoyltrifluoroacetone] was prepared by reduction reaction between dppm and Cu(tfac)₂. The structure of the complex was characterized by IR, ³¹P NMR, XPS spectra and X-ray diffraction analysis. Crystal(**1**) belongs to monoclinic, space group $P2_1/n$, $a = 1.3028(5)$, $b = 1.3744(4)$, $c = 2.0278(5)$ nm, $\beta = 94.48(2)^\circ$, $D_c = 1.351 \text{ g} \cdot \text{cm}^{-3}$, $Z = 2$, $V = 3.6199 \text{ nm}^3$, $R = 0.04978$. Each copper (II) ion is coordinated by the phosphorus of dppm and two oxygen atoms of tfac to form tetrahedron coordination structure.

Keywords: copper complex reduction crystal structure

0 Introduction

Copper(I) complex displays wide diversity in its structural chemistry, the copper coordination

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number ranging from two to six. Procedures to synthesize copper (I) complexes are of great interest because of the diversity of products resulting from almost the same methodology. Binuclear copper(I) complexes containing diphosphine ligands have been the focus of investigation in the last few years. It has been pointed out and confirmed that the four-electron-donor diphosphine ligand(dppm) is very efficient bridging bidentate ligand^[1]. Many examples of complexes containing this kind diphosphine ligands are known with a variety of metals, oxidation state and stereochemistries^[2-4]. In general, the complexes consist of bridging diphosphine compound dppm to give a M_2P_4 core structure with the two metal atoms held in close distance (regardless of whether a metal-metal bond is present or not). This feature is presumably one of the chief reasons for the unusual bonding, reactivity, and catalytic properties of $M_2(\text{diphosphine})_2$ compounds. These compounds require additional ligands, since each metal ion in M_2P_2 framework is coordinatively unsaturated. In the present paper we describe an easy way to synthesize copper (I) β -diketone(tfac) complex using the diphosphine ligand(dppm). Structural results allowed us to interpret some properties of the title complex, such as molecular weight and conductivity measurement.

1 Experimental

1.1 Physical measurements

The compound(dppm) were synthesized according to literature^[3]. All other chemicals were reagent grade obtained from commercial sources and used without further purification. All solvents were dried by standard methods. Elemental analysis was performed on an ERBA-1106 instrument (Italy). Cu and P contents were determined using a JA96-970 spectrometer. IR spectra were recorded on a Nicolet 170SX IR spectrophotometer. Room temperature ³¹P-NMR spectra were taken on a DPX-400 NMR spectrometer, and measured in $CDCl_3$ with 85% H_3PO_4 as external reference. Molecular weight determinations were made on $CHCl_3$ solutions at 25° using CORONA-117 analyser (American instrument). Conductivity measurement was carried out in thermostatical acetone solution at 25° and a Shanghai DDS-11A conductometer and DJS-1 type platinum black electrode was used. Melting point was determined and emission spectrum was recorded on a Luminescence Spectrophotometer(Aminco Bowman Series 2). XPS spectra were recorded on VG ESCALAB MK II instrument with $AlK\alpha$ radiation. High voltage, electric current and vacuum were set at 12.5kV, 20mA and 6×10^{-6} Pa, respectively.

1.2 Synthesis

Dppm(2mmol, 0.768g) was added to a green solution of $[Cu(\text{tfac})_2]$ (1mmol, 0.505g) in acetone. At room temperature, the mixture was stirred for 48h giving a yellow precipitate. The product was collected by filtration and washed with acetone. Yellow crystals were obtained by re-crystallization of the product from $CHCl_3$ and THF. The crystals are stable in air. Yield: 66%. Anal. calcd. for $C_{66}H_{52}P_4S_2O_4F_6Cu_2$: C, 59.24; H, 3.92; P, 9.3; Cu, 9.5%, Found: C, 59.48; H, 4.01; P, 9.4; Cu, 9.3%. ³¹P NMR: -13.5 ppm. $\nu_{(C=O)} = 1610\text{cm}^{-1}$, $\nu_{(C=C)} = 1550\text{cm}^{-1}$.

1.3 Crystallographic Data Collection and Structure Determination

A yellow single crystal of the title compound with dimensions of $0.10 \times 0.10 \times 0.15\text{mm}^3$ was

selected and mounted on the tip of a glass fiber with epoxy resin for X-ray diffraction studies. The determination of the unit cell and the data collection were performed with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Nonius CAD4 diffractometer. A total of 7743 independent reflections were collected in the range of $1^\circ < \theta < 25^\circ$ by ω - 2θ scan technique at room temperature, of which 2605 reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in the succeeding structural solution and refinements. No significant change was detected in the intensities of the three standard reflections. Lorentz, polarization and absorption corrections (empirical method, ψ -scan) were applied to the intensity data. Positional and thermal parameters were refined by the full-matrix least-squares method. The structure was solved by direct methods and Fourier syntheses. Computations were performed using the SDP program on a PDP11/44 computer. All hydrogen atoms were located in calculation positions and isotropically refined. Atomic parameters and equivalent isotropic thermal parameters of non-H atoms for the title complex are given in Table 1. Table 2 gives selected bond lengths and angles, respectively.

Crystal data: $C_{66}H_{52}P_4S_2O_4F_6Cu_2$, monoclinic, space group $P2_1/n$, $a = 1.3028(5)$, $b = 1.3744(4)$, $c = 2.0278(5)$ nm, $\beta = 94.48(2)^\circ$, $D_c = 1.351 \text{ g} \cdot \text{cm}^{-3}$, $V = 3.6199 \text{ nm}^3$, $Z = 2$, $\mu(\text{Mo } K\alpha) = 7.87 \text{ cm}^{-1}$, $\rho_{\text{max}}/\rho_{\text{min}} = 473/148 \text{ e} \cdot \text{nm}^{-3}$, $F(000) = 1512$, $R = 0.04978$, $R_w = 0.05531$.

2 Results and discussion

2.1 Preparation of the complex

Table 1 Atomic Coordinates and Isotropic Thermal Parameters

atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} / (10^{-2}nm^2)	atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} / (10^{-2}nm^2)
Cu(1)	0.29243(9)	0.19307(8)	0.16599(5)	4.42(2)	S(1)	0.3952(4)	0.2181(4)	-0.0628(2)	13.8(2)
P(1)	0.1676(2)	0.3051(2)	0.1516(1)	4.04(5)	P(2)	0.4358(2)	0.2432(2)	0.2248(1)	4.20(5)
F(1)	0.3155(5)	-0.1804(4)	0.0994(3)	9.2(2)	F(2)	0.3474(5)	-0.1347(4)	0.1999(3)	8.8(2)
F(3)	0.1920(5)	-0.1400(4)	0.1574(4)	9.3(2)	O(1)	0.2707(5)	0.0469(4)	0.1665(3)	4.8(1)
O(2)	0.3282(5)	0.1780(5)	0.0655(3)	6.1(2)	C(1)	0.0902(7)	0.3424(6)	0.2188(4)	4.4(2)
C(2)	0.2950(7)	-0.0103(6)	0.1230(4)	4.8(2)	C(3)	0.3255(7)	0.0081(7)	0.0616(5)	5.7(2)
C(4)	0.3387(7)	0.1001(7)	0.0351(4)	5.2(2)	C(5)	0.2861(8)	-0.1175(7)	0.1447(5)	6.8(3)
C(11)	0.2300(7)	0.4186(6)	0.1294(4)	4.6(2)	C(12)	0.2172(8)	0.5071(7)	0.1584(5)	5.7(2)
C(13)	0.276(1)	0.5872(7)	0.1405(6)	7.8(3)	C(14)	0.342(1)	0.5796(9)	0.0941(7)	10.0(4)
C(15)	0.354(1)	0.4938(9)	0.0645(7)	11.4(4)	C(16)	0.2993(9)	0.4121(8)	0.0820(6)	9.0(3)
C(21)	0.0701(7)	0.2897(7)	0.0839(4)	5.3(2)	C(22)	0.0564(9)	0.1987(9)	0.0564(5)	7.5(3)
C(23)	-0.024(1)	0.184(1)	0.059(6)	10.3(4)	C(24)	-0.084(1)	0.262(1)	-0.0153(6)	11.0(4)
C(25)	-0.0683(9)	0.350(1)	0.0101(5)	9.1(4)	C(26)	0.0065(8)	0.3648(9)	0.0592(5)	7.2(3)
C(31)	0.5099(6)	0.1553(6)	0.2753(4)	4.5(2)	C(32)	0.6108(8)	0.1731(8)	0.2998(6)	8.6(3)
C(33)	0.6647(9)	0.105(1)	0.3370(8)	11.7(5)	C(34)	0.6192(8)	0.0158(9)	0.3498(7)	9.3(4)
C(35)	0.5221(8)	-0.0024(7)	0.3266(6)	6.6(3)	C(36)	0.4672(7)	0.0669(7)	0.2890(5)	5.0(2)
C(41)	0.5302(7)	0.2960(7)	0.1743(4)	5.3(2)	C(42)	0.5599(8)	0.2643(9)	0.1225(5)	7.6(3)
C(43)	0.6331(9)	0.283(1)	0.0825(6)	9.8(4)	C(44)	0.679(1)	0.368(1)	0.0954(7)	12.9(4)
C(45)	0.650(1)	0.414(1)	0.1466(8)	20.4(5)	C(46)	0.575(1)	0.382(1)	0.1840(7)	16.0(4)
C(51)	0.3710(7)	0.1062(8)	-0.0327(5)	5.9(3)	C(52)	0.3872(7)	0.0305(8)	-0.0796(4)	5.6(2)
C(53)	0.412(1)	0.072(1)	-0.1331(7)	13.5(5)	C(54)	0.422(1)	0.163(1)	-0.1367(5)	12.3(5)

$$B_{\text{eq}}: (4/3) \cdot [a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + abc \cos \gamma B(1,2) + acc \cos \beta B(1,3) + bcc \cos \alpha B(2,3)]$$

Table 2 Selected Bond Lengths(nm) and Angles(°)

bond distances					
Cu(1)-P(1)	0.2242(3)	Cu(1)-P(2)	0.2245(3)	Cu(1)-O(1)	0.2029(5)
Cu(1)-O(2)	0.2136(6)	O(1)-C(02)	0.1239(10)	O(2)-C(04)	0.1248(12)
P(1)-C(01)	0.1831(9)	P(1)-C(11)	0.1832(9)	P(1)-C(21)	0.1808(9)
angle					
P(1)-Cu(1)-P(2)	115.1(1)	P(1)-Cu(1)-O(1)	125.5(2)		
P(1)-Cu(1)-O(2)	98.8(2)	P(2)-Cu(1)-O(1)	114.3(2)		
P(2)-Cu(1)-O(2)	107.6(2)	O(1)-Cu(1)-O(2)	87.01(2)		
Cu(1)-P(1)-C(01)	122.1(3)	Cu(1)-P(1)-C(11)	106.6(3)		
Cu(1)-P(1)-C(21)	118.6(3)	Cu(1)-P(2)-C(31)	118.7(3)		
Cu(1)-P(2)-C(41)	113.3(3)	Cu(1)-O(1)-C(02)	125.5(6)		
Cu(1)-O(2)-C(04)	126.5(6)	O(1)-C(02)-C(03)	129.9(8)		

According to color change correlative with the procedure for preparing the complex(1), copper(II) 2-thenoyltrifluoroacetone(tfac) has reacted with the phosphine ligand(dppm) and to form the copper(I) complex. Therefore, direct reduction of copper(II) ion is characteristic of the present synthetic method. Molecular weight was measured in CHCl_3 solution. The complex was soluble enough for measurements. Results are quite reproducible and seem to be scarcely influenced by concentration in the accessible range. The molecular weight determination (Found: 1339, calcd.: 1337) strongly suggests that the title complex is binuclear. The copper(I) complex $[\text{Cu}(\text{dppm})(\text{tfac})]_2$ can be obtained with high yield. The elemental analysis of the complex(1) agreed well with its formula. Conductance data ($3.6\text{S} \cdot \text{cm}^{-2} \cdot \text{mol}^{-1}$) show that the complex(1) belongs to non-electrolyte. At room temperature, the title complex is crystalline, diamagnetic compound and is fairly stable in air, and soluble in CH_2Cl_2 , DMF and CHCl_3 , sparingly soluble in benzene, THF and hexane.

2.2 Spectral properties

The characteristic band of free tfac ($\nu_{\text{C}=\text{O}}$: 1650cm^{-1}) shifts to lower frequency in the copper(I) complex $[\text{Cu}(\text{dppm})(\text{tfac})]_2$. β -Diketone(tfac) in the complex is in the enol form and is bonded to the metal as chelate mode. The C=O and C=C stretching vibration of the enol ring in the title complex were assigned at 1610 and 1550cm^{-1} , respectively. The vibrational absorption peak shape and intensity change obviously in the range $1000 \sim 1400\text{cm}^{-1}$ ^[5]. The P-Ph absorption, at about 1100cm^{-1} , shows an increase in frequency and intensity, which is characteristic of P-metal coordination.

In ^{31}P NMR spectra of the complex(1), the corresponding phosphorus resonance (-13.5ppm) shifted to higher field compared to that of free ligand (dppm: -23ppm). ^{31}P NMR spectra at room temperature appear only a single resonance showing that all phosphorus atoms in each molecule are chemically equivalent^[3].

XPS of the complex(1) gave information concerning copper-ligand binding. The C_{1s} , O_{1s} , S_{2p} , P_{2p} and Cu_{2p} binding energy of the complex(1) are at $288.62(3)$, $536.23(3)$, $168.21(3)$, $133.56(3)$ and $936.13(3)$ eV, respectively. The binding energy P_{2p} of phosphine ligand in (1) is larger than the relative value (P_{2p} : 132.5eV) of free ligand(dppm). This is attributed to electronic density re-

duction of P atom because of the formation of $P \rightarrow Cu$ bond in the complex(1).

2.3 Luminescence property

Excitation of solid sample of the title complex at $\lambda = 355\text{nm}$ at room temperature produces long-lived luminescence at $\lambda = 525\text{nm}$. There is extensive literature on the emission of copper(I) complexes^[6-8]. In the tri-nuclear copper(I) complex $[Cu_3(dpmp)_2(MeCN)_2Cl_2]^+$, where dpmp is bis(diphenylphosphinomethyl) methyl, an emission at 560 nm was assigned as a metal-centered $3d^9 4s^1 \rightarrow 3d^{10}$ transition^[6]. In the binuclear copper(I) complex $[(PPh_3)_2Cu_2Cl_2(py)]$ a similar type of assignment has been made^[7]. Based on a literature assignment of analogous compounds and our experimental observation, the low-energy and long lifetime emission(525 ~ 540nm) is most likely associated with the metal-centered excited state $3d^9 4s^1$ of Cu(I). Copper(I) centre, a d^{10} system is very electron rich in nature and can be stabilised by ligands having π -acid character, viz. PPh_3 , bpy, phen and tfac etc.

2.4 Crystal structure

The molecular structure of $[Cu(dpmp)(tfac)]_2$ is depicted in Fig. 1. The title complex consists of a central symmetry dimeric molecular unit with the two copper atoms bridged by a pair of dpmp ligands. In addition, each copper atom is bound by tfac in a chelating fashion. Two copper atoms are bridged by two dpmp ligands to form an eight-membered $Cu_2P_4C_2$ ring. The slightly distorted coordination tetrahedron of copper is formed by two phosphorus atoms from dpmp ligand and two oxygen atoms from tfac. It has been observed that Cu-P bond lengths in the complexes are affected by the number of phosphorus atoms bonded to the same copper atom. The Cu-P distances in (1) of

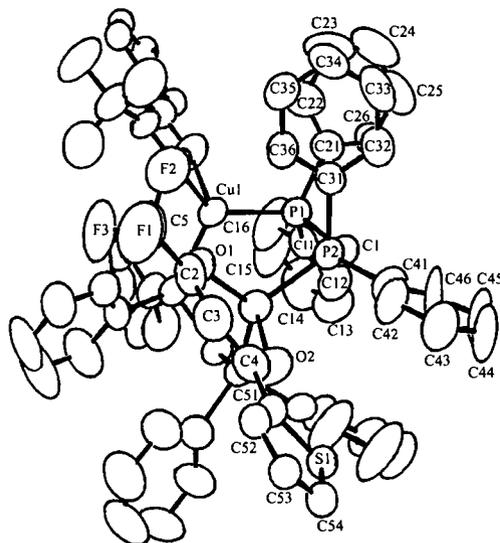


Fig. 1 Structure of the complex $[Cu(dpmp)(tfac)]_2$

0. 2242(3) and 0. 2245(3) nm are in good agreement with the 0. 2240(6) and 0. 2249(6) nm found in $[Cu(S_2CC_6H_4Me-o)(dpmp)]_2$ ^[9]. The Cu-Cu separation of 0. 3646(10) nm is significantly longer than the range of copper-copper bond lengths [0. 2494(5) to 0. 2674(5) nm] found in $H_6Cu_6(PPh_3)_6 \cdot DMF$ ^[10], indicating that the copper atoms in the title compound are not involved in metal-metal bonding interactions. The magnitude of C-O and C-C bond lengths in tfac are in the region expected for a localized symmetrical bonding of the β -diketone ligand(tfac). The bond lengths of C(5) -C(2), C(2) -C(3), C(3) -C(4) and C(4) -C(51) are 1. 545(13), 1. 361(13), 1. 390(14) and 1. 471(12) Å respectively. The bond lengths of C(2) -C(3) and C(3) -C(4) are shorter than of C(5) -C(2) and C(4) -C(51), because C(2), C(3) and C(4) form a conjugated system. The bond C(4) -C(51) linking to thiophene ring is fall in the limits of single and double

bond lengths. It certifies that there is conjugated system formed between chelating ring and thiophene ring.

The observed Cu-O distances of 0.2029(5) nm and 0.2136(6) nm are comparable to the Cu-O distances [0.1954(11) nm] found in the complex $[\text{Cu}(2, 2'\text{-bipy})(\text{tfac})]^{[11]}$. Only a few structural studies about binuclear phosphine species of other transition metals have been frequent, in general, also reveal the linear P-M-P fragments and planar M_2P_4 structure^[12, 13]. For d^{10} complexes, however, the P-M-P units are distinctly nonlinear^[14, 15]. X-ray structural characterization of the title complex clearly reveals that the P-M-P angles are not restricted by steric crowding of dppm phenyl rings. The P-Cu-P angles in (1), in particular, are of much less linearity [115.1(1)°] than the corresponding P-M-P values [131.8(2)°] found in $[\text{Cu}(\text{dppm})(\text{NO}_3)]_2^{[13]}$, but close to the corresponding P(1)-Cu-P(2) angle of 119.9(1)° found in the related binuclear (dppm)₂ complex $[\text{Cu}(\text{dppm})(\text{MeCN})_2]_2(\text{ClO}_4)_2^{[16]}$. Two bis(diphenylphosphine)methane in (1) are respectively located on the opposite sides to minimise repulsion between the ligands. The complex (1) contains folded Cu_2P_4 core structures, and the $\text{Cu}_2(\text{dppm})_2$ framework in the complex is quite flexible. The nonlinearity of Cu_2P_4 core and coordinative features of the dimer should particularly facilitate the combination of larger substrate species than presently possible with known square-planar $\text{M}_2(\text{dppm})_2$ complexes^[17]. In addition, the property of the complex $[\text{Cu}(\text{dppm})(\text{tfac})]_2$ suggests yet another pattern for the binding of small ligands by M_2P_2 complexes^[18-20].

References

- [1] Puddephatt R. J. *Chem. Soc. Rev.*, **1983**, **12**, 99.
- [2] Yang Rui-Na, Sun Yu-An, Hu Xiao-Yuan, Jin Dou-Man *Chin. J. Chem.*, **1999**, **17**, 284.
- [3] Yang Rui-Na, Lin Kun-Hua, Jin Dou-Man *Trans. Met. Chem.*, **1997**, **22**, 254.
- [4] Shin H. K., Hampden-Smith M. J., Kodas T. T. *Polyhedron*, **1991**, **10**, 645.
- [5] Jin Dou-Man, Zhu Wen-Xiang *Research Methods of Coordination Chemistry*, Beijing: Science Publishing House, **1996**, p85.
- [6] Li D., Yip H. K., Che C. M., Zhou Z. Y., Mak T. C. W., Liu S. T. *J. Chem. Soc., Dalton Trans.*, **1992**, 2445.
- [7] Henry M., Wotton J. L., Khan S. I., Zink J. I. *Inorg. Chem.*, **1997**, **36**, 796.
- [8] Yam V. W., Lee W., Lai T. F. *J. Chem. Soc., Chem. Commun.*, **1993**, 1571.
- [9] Manotti Lanfredi A. M., Ugozzoli F. *Inorg. Chim. Acta*, **1985**, **99**, 111.
- [10] Churchill M. R., Bezman S., Osborn J. A. *Inorg. Chem.*, **1972**, **11**, 1818.
- [11] Wang Dong-Mei, Xue Bao-Yu, Yang Rui-Na, Jin Dou-Man *Chin. J. Struct. Chem.*, **1997**, **16**, 287.
- [12] Commons C. J., Hoskins B. F. *Aust. J. Chem.*, **1975**, **28**, 1663.
- [13] Abbott E. H., Bose K. S., Cotton F. A. *Inorg. Chem.*, **1978**, **17**, 3240.
- [14] Yang Rui-Na, Hu Xiao-Yuan, Jin Dou-Man *Trans. Met. Chem.*, **2000**, **25**, 174.
- [15] Yang Rui-Na, Hou Yi-Min, Hu Xiao-Yuan, Jin Dou-Man *Inorg. Chim. Acta*, **2000**, **304**, 1.
- [16] Josefina Diez M. Pilar, Jose Gimeno *J. Chem. Soc., Dalton Trans.*, **1987**, 1275.
- [17] JIN Dou-Man (金斗满), YANG Rui-Na (杨瑞娜), WANG Dong-Mei (王冬梅), HU Xiao-Yuan (胡晓院) *Wuji Huaxue Xuebao (Chin. J. Inorg. Chem.)*, **2000**, **16**(2), 335.
- [18] YANG Rui-Na (杨瑞娜), SUN Yu-An (孙雨安), HU Xiao-Yuan (胡晓院), JIN Dou-Man (金斗满) *Huaxue Xuebao (Acta Chimica Sinica)*, **2000**, **58**, 727.
- [19] Yang Rui-Na, Sun Yu-An, Hu Xiao-Yuan, Jin Dou-Man *Chin. J. Chem.*, **2000**, **18**, 346.
- [20] YANG Rui-Na (杨瑞娜), HU Xiao-Yuan (胡晓院), DUAN Zheng (段征), JIN Dou-Man (金斗满) *Wuji Huaxue Xuebao (Chin. J. Inorg. Chem.)*, **1999**, **15**(6), 697.