

Synthesis and properties of the chain-like polymeric copper(II) complexes bridged by bis(diphenylphosphino oxide)ethane

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At room temperature, the chain-like polymeric copper(II) complexes bridged by bis(diphenylphosphino oxide)ethane (dppeO₂), [Cu(dppeO₂)X₂]_n [X = Cl(1), Br(2)] have been prepared and characterized by elemental analysis, ³¹P NMR, TG-DTA and X-ray analysis for [CuBr₂(dppeO₂)]_n. The chain is composed of subunits containing tetrahedron coordinated copper(II) atoms. The four-coordinated copper(II) atom is ligated to another four-coordinated copper(II) atom through dppeO₂. The coordination sphere of copper(II) atom is completed by two monodentate bromide and two oxygen atoms from bridging dppeO₂. Crystal data are as follows: C₂₆H₂₄CuP₂Br₂O₂, 0.50 mm × 0.40 mm × 0.40 mm, monoclinic, space group: C₂/c, λ = 0.07107 nm(Mo K_α), a = 1.2286(2) nm, b = 2.0555(8) nm, c = 1.0652(2) nm, β = 97.366(9)°, V = 2.668 nm³, Z = 4, D_{calc} = 1.628 g·cm⁻³, R = 0.066; R_w = 0.091.

Keywords Crystal structure, copper(II), complex, bis(diphenylphosphino oxide)ethane

Introduction

Copper(II) displays wide diversity in its structural chemistry. Procedures to synthesize copper(II) complexes are of great interest because of the diversity of products resulting from almost the same methodology. The synthesis and stereochemistry of copper(I,II) complexes of tertiary phosphines are of current interest because of the wide variety of structural types that have been found.¹⁻⁸

Although several copper complexes can be synthesized by the reduction of the tertiary phosphine, the scope of this preparative method has not been explored. Now we have extended the reaction of copper(II) nitrate bis(diphenylphosphino)ethane. In this work, we report the preparation and crystal structure of the novel polymeric copper(II) complexes containing bridging bis(diphenylphosphino oxide)ethane.

Experimental

General considerations

Solvents were dried by standard methods and distilled under nitrogen prior to use. Reagent grade chemicals were used in all experiments without further purification. 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. TG-DTA spectra were recorded on a PE-TGS-2 instrument. ³¹P NMR spectra were taken on a Bruker AM-500 spectrometer in CDCl₃ with 85% H₃PO₄ as external reference. XPS spectra were recorded on VGESCALAB MK II instrument with Al K_α radiation. High voltage, electric current and vacuum were set at 12.5 kV, 20 mA and 6 × 10⁻⁶ Pa, respectively.

Received August 11, 1999; accepted January 5, 2000.

Project supported by the National Natural Science Foundation of China(No. 29871009), Henan Province Outstanding Youth Science Foundation and Henan Natural Science Foundation.

Preparation

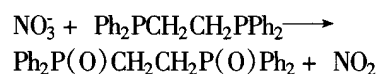
$[\text{Cu}(\text{dppe})_2](\text{NO}_3)_2$ Dppe (1.536 g, 4 mmol) and solid $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.482 g, 2 mmol) were added to hot ethanol (60 mL) to form a colorless solution. The resulting solution was subsequently allowed to evaporate slowly at room temperature to a final volume of 20–25 mL. Colorless crystals of $[\text{Cu}(\text{dppe})_2](\text{NO}_3)_2$ were obtained, separated by filtration, washed with ethanol, and dried in air. Yield: 69%. mp 189–191 °C. ν_{max} : 1482(m), 1436(s), 1405(m), 1381(s), 1041(s), 828(m) cm^{-1} . δ_{H} : 7.8–7.0(40H, 8 \times C₆H₅), 2.45–2.30(8H, 4 \times CH₂). Anal. C₅₂H₄₈P₄CuN₂O₆. Calcd.: C, 63.45; H, 4.88; P, 12.6; Cu, 6.46; N, 2.85. Found: C, 63.08; H, 4.68; P, 12.1; Cu, 6.12; N, 2.68.

$[\text{Cu}(\text{dppeO}_2)\text{Br}_2]_n$ CuBr₂ (0.448 g, 2 mmol) was added in a solution of $[\text{Cu}(\text{dppe})_2](\text{NO}_3)_2$ (0.984 g, 1 mmol) of 30 mL CHCl₃. The addition of CuBr₂ caused the colorless solution immediately turn to grey and then dark yellow with evolution of brown fumes (nitrogen dioxide). The mixture was stirred at room temperature for 48 h. At last red powder was precipitated and filtered out, washed with CHCl₃ then dried *in vacuo* at room temperature. Yield: 78%. ν_{max} : 1483(m), 1437(s), 1405(m), 1148(s), 1122(s), 1093(m), 743(s), 728(s), 692(s) cm^{-1} .⁹ Anal. C₂₆H₂₄CuP₂Br₂O₂. Calcd.: C, 47.74; H, 3.67; P, 9.49; Cu, 9.72. Found: C, 47.51; H, 3.38; P, 9.16; Cu, 9.39.

$[\text{Cu}(\text{dppeO}_2)\text{Cl}_2]_n$ can be prepared using a similar procedure with CuCl₂ as metal center. Yield: 72%. ν_{max} : 1485(m), 1438(s), 1409(m), 1162(s), 1123(s), 1097(s), 743(s), 729(s), 693s cm^{-1} .⁹ Anal. C₂₆H₂₄CuP₂Cl₂O₂. Calcd.: C, 55.27; H, 4.25; P, 10.98; Cu, 11.25. Found: C, 55.01; H, 4.38; P, 10.5; Cu, 10.9.

At room temperature, the title complexes are crystalline, and fairly stable in air in the solid state, and soluble in such polar organic solvents as DMF, DMSO, MeOH and EtOH, sparingly soluble in benzene, THF and hexane.

Noticeably, the title polymers $[\text{Cu}(\text{dppeO}_2)\text{X}_2]_n$ [X = Cl(1), Br(2)] can only be obtained in chlorated alkyl hydrocarbon. Bis(diphenylphosphino) ethane, which is used as an auxiliary ligand in the system, simultaneously undergoes oxidation to form bis(diphenylphosphino oxide)ethane.



This is confirmed by the IR spectra. The title complexes show several strong bands in the infrared between 1093–1162 cm^{-1} due to P=O stretching, such as 1097, 1123, 1162 (1) and 1093, 1122, 1148 cm^{-1} (2), which shift slightly compared with free dppeO₂, pointing out to the fact that the coordination of dppeO₂ occurs through oxygen in the prepared complexes. In the 1500–700 cm^{-1} range, the characteristic absorption bands of nitrate anion of $[\text{Cu}(\text{dppe})_2](\text{NO}_3)_2$ disappear in the title compounds, showing that nitrate has been substituted.

Raney Ni catalyst

Tetrahydrophthalic anhydride (THPA): Merck chemicals, Ni-Al alloy: Shanghai Chemical Industry Company. Keeping the temperature at 90–95 °C, 40 g of Ni-Al alloy were added in 600 mL of 10% NaOH water solution during 30 min. The mixture was stirred for 1 h, and Raney Ni was washed with water and ethanol for three times, respectively. Raney Ni was stored in ethanol. Improved Raney Ni catalyst was prepared by the following method: 5g of Raney Ni were put in 50 mL of ethanol solution containing 0.35 g of $[\text{Cu}(\text{dppeO}_2)\text{Cl}_2]_n$, stirred slowly for 45 min.

Catalytic reactions took place in a 500 mL stainless steel pressure container. Catalyst, THPA (100 g) and solvent were added. Nitrogen gas passed through the container five times, then hydrogen gas twice. When hydrogen pressure reached assigned value, the reaction happened.

Crystallography

Single crystals were obtained by recrystallization of the product $[\text{CuBr}_2(\text{dppeO}_2)]_n$ from CHCl₃ and MeOH at room temperature for 5–7 days in yield of 75%. The deep red prismatic crystal having approximate dimensions of 0.50 mm \times 0.40 mm \times 0.40 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromatized Mo K_α radiation. Data were collected at a temperature of 289 \pm 1 K to a maximum 2θ value of

55°. A total of 2405 reflections were collected. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1899 observed reflections [$I > 3\sigma(I)$] and 151 variable parameters. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.¹⁰ Crystal data are as follows: $C_{26}H_{24}CuP_2Br_2O_2$, monoclinic, space group: C_2/c , $\lambda = 0.071070$ nm, $a = 1.2286(2)$ nm, $b = 2.0555(8)$ nm, $c = 1.0652(2)$ nm, $\beta = 97.366(9)^\circ$, $V = 2.668$ nm³, $Z = 4$, $D_{\text{calc}} = 1.628$ g·cm⁻³, $\mu = 39.6$ cm⁻¹, $F(000) = 1300$, $\Delta/\sigma = 0.00$, $\rho_{\text{max/min}} = 1850/-1430$ e/nm³, Goodness of fit indicator: 1.16, $R = 0.066$; $R_w = 0.091$, $R = \sum \|F_o| - |F_c|\| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$.

Atomic coordinates, the selected bond lengths and bond angles are given in Tables 1 and 2, respectively. An ORTEP drawing is given in Fig. 1 and a view of the

skeleton of the polymeric chain in Fig. 2.

Table 1 Atomic coordinates and equivalent isotropic displacement parameters (nm² × 10⁻²)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Br(1)	-0.49525(7)	-0.12279(4)	0.91814(7)	4.09(2)
Cu(1)	-0.5000	-0.19613(5)	0.7500	2.58(2)
P(1)	-0.6203(1)	-0.30635(8)	0.9199(2)	2.42(3)
O(1)	-0.5937(4)	-0.2620(2)	0.8164(4)	3.3(1)
C(1)	-0.4144(6)	-0.2935(4)	1.0517(8)	3.9(2)
C(2)	-0.3182(6)	-0.3169(5)	1.1237(9)	4.4(2)
C(3)	-0.3100(7)	-0.3802(5)	1.1620(8)	4.7(2)
C(4)	-0.3944(7)	-0.4238(5)	1.1273(10)	4.9(2)
C(5)	-0.4901(6)	-0.4023(4)	1.0524(9)	4.1(2)
C(6)	-0.4992(5)	-0.3383(4)	1.0151(6)	2.9(1)
C(7)	-0.7716(6)	-0.4092(4)	0.9183(7)	3.6(2)
C(8)	-0.8372(6)	-0.4575(4)	0.8585(9)	4.8(2)
C(9)	-0.8352(6)	-0.4702(4)	0.7335(8)	4.6(2)
C(10)	-0.7678(8)	-0.4347(5)	0.6660(7)	5.0(2)
C(11)	-0.7003(7)	-0.3873(4)	0.7237(8)	4.2(2)
C(12)	-0.7027(5)	-0.3730(3)	0.8516(6)	2.8(1)
C(13)	-0.6958(5)	-0.2652(3)	1.0317(6)	3.0(1)

Table 2 Selected bond lengths (0.1 nm) and bond angles (°)

Br(1)—Cu(1)	2.336(1)	Cu(1)—O(1)	1.967(4)
P(1)—O(1)	1.498(5)	P(1)—C(6)	1.813(7)
P(1)—C(12)	1.801(7)	P(1)—C(13)	1.811(7)
Br(1)—Cu(1)—Br(1*)	99.62(6)	Br(1)—Cu(1)—O(1)	97.3(1)
Br(1)—Cu(1)—O(1*)	139.6(1)	O(1)—Cu(1)—O(1*)	93.0(3)
Cu(1)—O(1)—P(1)	151.2(3)	O(1)—P(1)—C(6)	113.0(3)
O(1)—P(1)—C(12)	109.3(3)	O(1)—P(1)—C(13)	112.2(3)
C(12)—P(1)—C(13)	108.2(3)	P(1)—C(6)—C(1)	116.2(6)

* Symmetry operators: (1) x, y, z ; (2) $-x, y, 1/2 - z$; (3) $-x, -y, -z$; (4) $x, -y, 1/2 + z$; (5) $1/2 + x, 1/2 + y, z$; (6) $1/2 - x, 1/2 + y, 1/2 - z$; (7) $1/2 - x, 1/2 - y, -z$; (8) $1/2 + x, 1/2 - y, 1/2 + z$.

Results and discussion

XPS spectra

The XPS spectra of the complex **2** give information concerning copper-ligand binding. The binding energy of C1s, O1s, Br3d, P2p and Cu2p in the complex **2** are 291.00, 538.05, 75.10, 138.80 and 939.25 eV, respectively. The P2p binding energy (138.80 eV) of dppe in the complex **2** is larger than the relative value of

free dppe (P2p: 132.4 eV), and that of the precursor complex $[Cu(dppe)_2](NO_3)_2$ (P2p: 133.5 eV, Cu2p: 935.8 eV). This is attributed to electronic density reduction of P atom caused by the formation of O = P bond in the complex **2**.

Thermal analysis

The results of the thermogravimetric analysis of the complexes, compared with those of free dppeO₂ (decom-

position temperature: 135—280°C), indicate that the thermal stability of dppeO_2 increases upon complexation. The TG-DTA thermogram of the complex **1** corresponds to a pronounced weight loss of 27% due to the decomposition of the ligand dppeO_2 (weight loss calcd.: 24%)

giving CuCl_2 as the residue in the 200—489°C range. The TG-DTA pattern of the complex **2** is similar to the complex **1**. The complex **2** showed weight loss of 36% (calcd.: 34%, CuBr_2 as the residue) in the 200—439°C range.

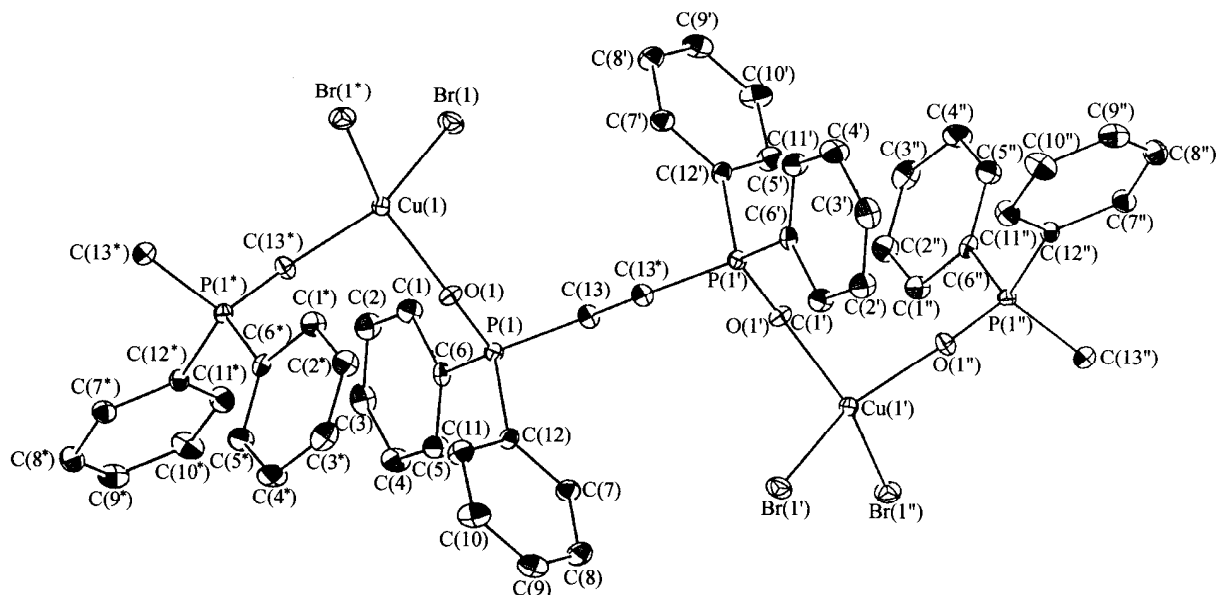


Fig. 1 ORTEP drawing of the coordination environments about the copper(II) atoms in the polymeric chain $[\text{CuBr}_2(\text{dppeO}_2)]_n$.

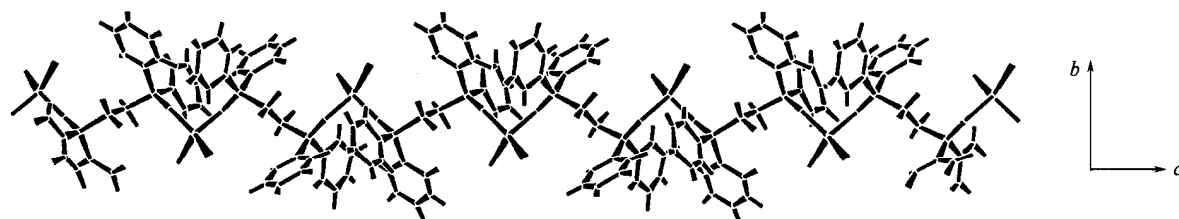


Fig. 2 Perspective view showing the skeleton of the polymeric chain in $[\text{CuBr}_2(\text{dppeO}_2)]_n$.

UV-visible spectra and ^{31}P NMR

In the ^{31}P NMR spectra of the title complexes, the peaks were at 38.2 (**1**) and 38.6 (**2**) respectively, showing that all the phosphorus atoms in each molecule are chemical equivalent. These values are similar to those of dppeO_2 . Thus the existence of dppeO_2 in the title complexes was further confirmed. The chemical shift of free ligand dppe (^{31}P) was at -12.6 .

The UV-visible spectra of complex **2** in ethanol solution was measured at room temperature. The electronic spectra of the complex **2** are noticeably different from those of the free ligand dppe (240 nm, 271 nm). Complex **2** shows a transition near $\lambda_{\text{max}} = 221, 207$ nm which

can be assigned to the high-energy transitions resulting from intraligand $\pi-\pi^*$ orbital transition.¹¹

X-Ray crystal structure

The crystal structure of the title complex comprises a packing of one-dimensional chain-like polymeric $[\text{Cu}(\text{dppeO}_2)\text{Br}_2]_n$. The chain is composed of the subunits containing two $[\text{Cu}(\text{dppeO}_2)\text{Br}_2]$ fragments related by an inversion center and extends along axis c direction. The copper atom is four-coordinated, with oxygen atoms from two different bridging dppeO_2 molecules occupying two of the coordination sites, the bromide occupying the third and the fourth, resulting in a tetrahedral coordina-

tion geometry with the most distorted bond angle to be 139.6° for Br(1)-Cu(1)-O(1*). In fact, the reported angle of Br-Cu-O (139.6°) is due to a steric effect of the phosphine-oxide groups. Although the compressed tetrahedral geometry, caused by the John-Teller effect, is well-known in tetrahedral copper(II) complexes,¹²⁻¹⁴ the bridging dppeO₂ in polymeric chain compounds is rarely reported.¹⁴ The resulting structure is an infinite polymer with the dppeO₂ molecules linking CuBr₂ units. Two Cu—O distances [0.1967(4) nm] are comparable to those in other copper(II) complexes containing Cu—O bond.^{15,16}

Application of the complex 1

Although olefin hydrogenation may happen in chemical thermodynamics, the hydrogenation of olefin can not occur without catalyst. Because hydrogen molecule is extremely stable, H—H bond is not easily broken as a result of polarization. Many transition metal elements (Ni, Pd, Pt, Co, Fe, Rh, Ru, Cu *et al.*) have catalytic activity to olefin hydrogenation reaction. The activation of hydrogen molecule has two routes including hydrogen molecule as electron acceptor or electron supplier. In general, Raney Ni is used as the catalyst of olefin hydrogenation reaction.¹⁷

Hexahydrophthalic anhydride (HHPA) is absolutely necessary for top grade quality coatings.¹⁸ The coatings tend to low pollution, low energy consumption, high solid content and high durability along with increasing environmental protection consciousness of people. The coatings made from HHPA just accord with these demands.¹⁹

It is well known that the auxiliary substances such as MnCl₂, Cu(NO₃)₂, CuCl₂ and PtCl₂ have marked promotion effect on Raney Ni hydrogenation reaction.¹⁷ The complex 1 is a chain polymer containing CuCl₂, and is better-distributed than CuCl₂. We observed the effect of the complex 1 on the Raney Ni catalyzed hydrogenation of THPA.

Our experiment results showed that the improved Raney Ni catalyst has high activity to the preparation of HHPA from THPA hydrogenation reaction. The good catalytic reaction results (the yield of HHPA: 93%, the selectivity: 100%) have been obtained under suitable reaction conditions (40% DMF solution, 95—98°C,

7% improved Raney Ni catalyst, H₂ pressure: 3.5 MPa, reaction time: 2.5 h). The byproduct was not detected in the reaction system. These results showed that this catalytic system with high catalytic efficiency has fine selectivity to the end product (HHPA) in the observed reaction condition range, and also the reaction materials were easily available. The research results offered a practical technology route for the preparation of HHPA.

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