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Synthesis and Structural Characterization of two Novel Copper(I) Complexes with Oxygen Donor

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Abstract. Two novel copper(I) complexes with Cu-O bonds, $[Cu_2L_2(PPh_3)_2](BF_4)_2$ (**1**) and $[Cu(L)(dppeo)](BF_4)$ (**2**) (**L** = 6-(4-diethylmethylphosphonatephenyl)-2,2′-bipyridine, dppeo = bis(diphenylphosphino)ethane monoxide), have been prepared and their structures characterized. In the binuclear complex **1**, the ligand **L** serves as tridentate donor with the N, N′ and O as coordination atoms, and the two Cu^I atoms are bridged through both P = O donor atoms in different ligand **L** with a triphenylphosphine molecule as auxiliary ligand. While in mononuclear complex **2**, both ligands L and dppeo behave as bidentate with N^N from L and P^O from dppeo chelating to Cu^I atom.

Keywords: Copper; Oxygen donor; Crystal structure

Introduction

Copper(I) complexes have received much attention for their being less expensive and environmentally friendly, various coordination structure, rich photochemical and photophysical properties [1−4]. Since the metal atom is generally considered a borderline soft acid, the chemistry of copper(I) is dominated by soft ligands (such as tertiary phosphine donor ligands and sulfur donor ligands) and chelating ligands (polypyridine ligands such as 2,2′-bipyridine, 1,10-phenanthroline and their substituted derivatives) [5, 6]. Copper(I) complexes with oxygen donor ligands, on the contrary, are really rare [7−9], since the oxygen site is hard donor which often prefers to complex with hard metals such as early and high valent transition metals. *Samuelson* and *Pilloni* have reported that bis(phosphine) monoxides (BPMO) such as bis(diphenylphosphino)ethane monoxide (dppeo) and diphenyl phosphino ferrocene oxide (odppf) can serve as P^O bidentate chelating ligands to copper(I) atoms [8, 9]. We envision that P=O group substituted polypyridine ligands may use as polydentate donor to construct novel copper(I) complexes with Cu-O bond. Recently, we have synthesized the new ligand, 6-(4-diethylmethylphosphonatephenyl)-2,2′-bipyridine (**L**), and found it can be used as tridentate or bidentate ligand according to the properties of the metal atom and auxiliary ligand. Here we report two novel copper(I) complexes with Cu-O bond, $[Cu_2L_2(PPh_3)_2](BF_4)_2$ (**1**) and $[Cu(L)(dppeo)](BF_4)$ (**2**), and their structural characterization.

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Experimental Section

General procedures

All reactions were performed under a dinitrogen atmosphere. Solvents were distilled using standard techniques and saturated with dinitrogen before use. $[Cu(CH_3CN)_4](BF_4)$, 4-bromophenyl-2,2′-bipyridine (**3**) and dppeo were prepared by literature methods [10−12].

Synthesis of ligand **L** *(see scheme 1)*

6-(4-bromophenyl)-2,2′-bipyridine. A solution of **3** (1.0 g, 4.1 mmol), N-bromosuccinimide (0.72 g, 4.1 mmol) and small amount of benzoyl peroxide in dry CCl_4 (30 mL) was heated to reflux for 3 h. The resulting solution was cooled to room temperature, then filtered to remove succinimide, and with small amount of warm CCl_4 washed twice the solid. On removal of the solvent, a slight yellow solid was obtained which was used in the next reaction without further purification. Yield: 0.96 g, 72 %; m.p. 128∼130 °C.

^{1}H NMR (300 Hz, $CDCl_3$): 4.58 (s, 2H), 7.55 (d, J = 8 Hz, 2H), 7.66 (m, 1H), 7.88 (d, J = 8 Hz, 1H), 8.01 (m, 1H), 8.14 (d, J =8 Hz, 1H), 8.21 (m,2H), 8.63 (d, J = 8 Hz, 1H), 8.78 (d, J = 8 Hz, 1H), 8.95 (d, J = 5 Hz, 1H).

6-(4-diethylmethylphosphonatephenyl)-2,2′-bipyridine (L). A solution of **4** (1.0 g, 3.08 mmol) in triethylphosphite (5 mL) was refluxed for 3 h. The excess phosphite was removed by distillation

Table 1 crystal data and structure refinement

Complexes	**1**·CH_2Cl_2	**2**·0.5CH_2Cl_2
Formula	$C_{40}H_{40}BCl_2CuF_4N_2O_3P_2$	$C_{47.5}H_{48}BClCuF_4N_2O_4P_3$
Fw	879.93	989.59
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	Cc
Color	brown-yellow	yellow
Crystal size, mm	0.30x0.30x0.25	0.30 x 0.26 x 0.20
a /Å	12.680(3)	9.735(3)
b /Å	22.195(4)	32.238(9)
c /Å	15.194(3)	16.681(5)
β /°	104.74(3)	93.728(5)
V /Å^3	4135.3(14)	5224(3)
Z	4	2
D_{calc} /Mg/m^3	1.413	1.258
T /K	293(2)	293(2)
Refls. No.	36428	14652
Theta range	2.09-27.48	1.76-26.38
μ /mm^{-1}	0.792	0.616
F(000)	1808	2044
R, R_w	0.0493, 0.1243	0.0640, 0.1712
Goodness-of- fit	0.857	1.066
Flack's parameters		0.00(2)

under high vacuum. The crude product was purified by column chromatography on silica gel by using ethylacetate/methanol (80/20) as eluent. Yield: 0.94 g, 80 %; m.p. 114~115.5 °C.

^{1}H NMR (300 Hz, $CDCl_3$): 1.28 (t, J = 7 Hz, 6H), 3.24 (d, J = 22 Hz, 2H), 4.05 (m, 4H), 7.34 (m, 1H), 7.45 (m, 2H), 7.77 (d, J = 8 Hz, 1H), 7.88 (m, 2H), 8.12 (d, J = 8 Hz, 2H), 8.38 (d, J = 8 Hz, 1H), 8.64 (d, J = 8 Hz, 1H), 8.70 (d, J = 8 Hz, 1H).

Syntheses of [$Cu_2L_2(PPh_3)_2$](BF_4)$_2$ (1)

A mixture of equal mole of [$Cu(CH_3CN)_4$](BF_4) and L (0.5 mmol) in 30 mL dichloromethane was stirred for 1 hour, then equal mole of PPh_3 was added and reacted for additional 2 hours. The resulting yellow reaction mixture was concentrated in vacuum, and the crude product was precipitated by adding diethyl ether. The yellow single crystals were obtained from the solution of dichloromethane by vapor diffusion with diethyl ether. Yield: 82 %. Anal. Calc. for $C_{39}H_{38}BCuF_4N_2O_3P_2$ (795.04): C, 58.92; H, 4.82; N, 3.52. Found: C, 59.05; H, 4.96; N, 3.48 %.

Synthesis of [Cu(L)(dppeo)] (BF_4) (2)

The preparation of **2** was similar to that of **1**, except deepo was used in place of PPh_3. Yellow solid, yield: 89 %. Anal. Calc. for $C_{47}H_{47}BCuF_4N_2O_4P_3$ (947.14): C, 59.55; H, 4.96; N, 2.96. Found: C, 59.48; H, 5.01; N, 3.02.

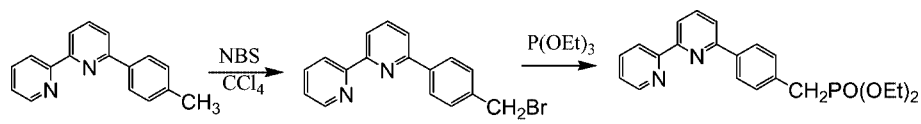
X-ray crystallography

Crystals of complexes **1** and **2** were obtained by vapor diffusion of diethyl ether into CH_2Cl_2 solution. Crystal data and details of data collection as well as refinement are summarized in Table 1. Diffraction data were collected at room temperature with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) on a Rigaku R-AXIS RAPID IP X-ray diffractometer for **1** and on a Bruker SMART CCD area detector for **2**. Diffracted data were corrected for absorption correction using the ABSCOR [13] program (**1**) or SADABS [14] program (**2**). The structures were solved by direct methods using the program SHELXS 97 [15] and refined by full-matrix least squares on F^2 using the SHELXL 97 [16] program package. The non-hydrogen atoms were refined anisotropically. CCDC 227448 (**1**) and 605459 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via **http://www.ccdc.cam.ac.uk/conts/retrieving.html** (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

Result and Discussion

Scheme 1 shows the details of the synthetic strategy adopted for the synthesis of the key ligand 6-(4-diethylmethylphosphonatephenyl)-2,2′-bipyridine (L) with good yield. Complexes **1** and **2** were prepared by reaction of equimolar quantities of [$Cu(CH_3CN)_4$](BF_4), ligand L and auxiliary ligand PPh_3 for **1** or dppeo for **2** in dichloromethane. Both complexes are colored solids (brown-yellow for **1** and yellow for **2**) and soluble in organic solvents such as dichloromethane, chloroform and acetonitrile. They are stable in air and moisture.

The single crystals of **1** and **2** suitable for X-ray analysis were obtained from their dichloromethane solution by vapor diffusion with diethyl ether. Their perspective views are shown in Figures 1 and 2, and selected bond distances and angles are summarized in Table 2. The molecular structure of **1** consists of two centrosymmetric dimeric units of [$CuL(PPh_3)$]$^+$, in which two symmetrically related copper(I) atoms are held together by O donor atoms of the tridentate ligands **L**. The Cu, O, P, C and N atoms form a twenty membered ring. The copper(I) adopts a distorted tetrahedral coordination structure with two nitrogen and one oxygen atoms from ligand **L** and one phosphorous atom from auxiliary ligand PPh_3. The angles around the copper atom range from 80.10(11)° for N1-Cu-N2 to 125.24(7)° for N(2)-Cu-P(1). The calculated long Cu-Cu(A) distance 8.503 Å reveals no Cu-Cu contact in complex **1**. The Cu-O distance (2.178(2) Å), Cu-N distance (2.052(3) Å and 2.116(3) Å) and Cu-P distance (2.1725(10) Å) are normal, and are within the values of reported related structures [8−9, 17−18]. It is noteworthy here that the ligand **L** behaves as tridentate donor with two N atoms adopting normal chelating mode and O bridging mode. The dihedral an-



3 **4** **L**

Scheme 1

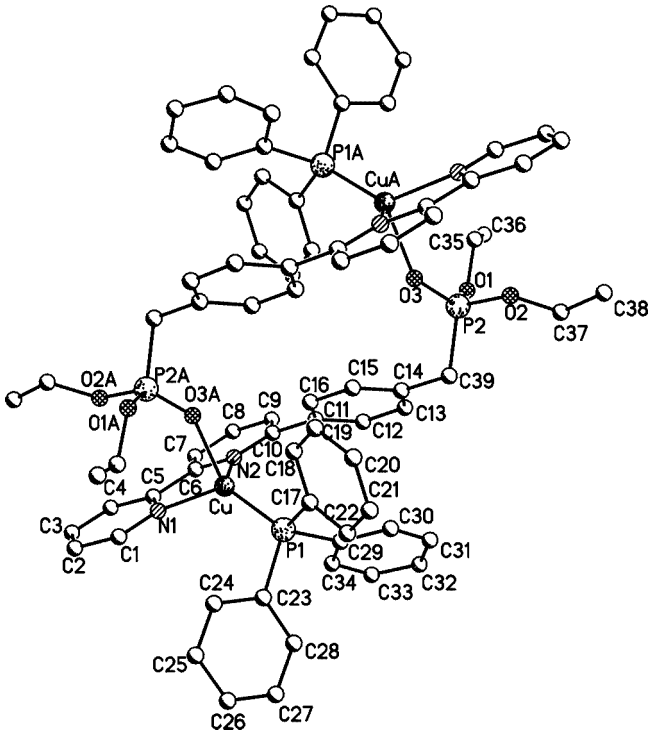


Figure 1 The cation structure of $[Cu_2L_2(PPh_3)_2](BF_4)_2$ (**1**), the hydrogen atoms are omitted for clarity

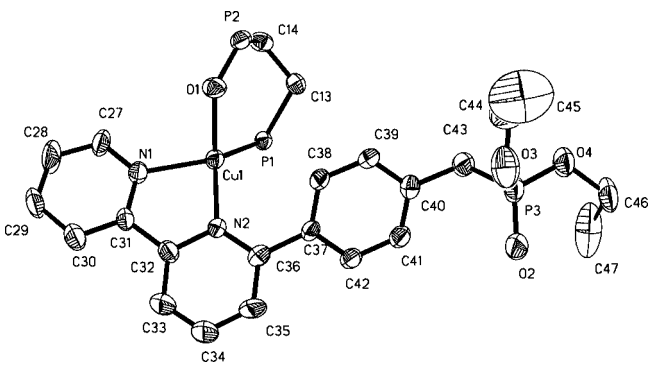


Figure 2 The cation structure of $[Cu(L)(dppeo)](BF_4)$ (**2**), the phenyl rings in dppeo (C1-C12 and C15 to C26) and all hydrogen atoms are omitted for clarity

gle between two pyridine rings is 4.1 (2)°, and the torsion angle between the pendant aromatic rings and adjacent pyridine fragments is 38.9 (2)°. These values compared with that of **2** indicates the centrosymmetric dimeric structure for complex **1** is favorable in structure.

When the auxiliary ligand PPh_3 changed into the hemilabile ligand dppeo which containing both soft donor tertiary phosphine and hard donor P=O, we only obtained the mononuclear complex **2**. The crystal structure of **2** consists discrete cations $[Cu(L)(dppeo)]^+$, tetrafluoroborate anions and solvent dichloromethane molecules. In **2**, both ligands **L** and dppeo act as a bidentate chelating donor. Chelating produces one five membered ring via Cu1-N1-C31-C32-N1 in a plain conformation, and six membered ring via Cu1-P1-C13-C14-P2-O1 in a chair conformation which is very similar to the reported six-membered chelate structure found in $[Cu(dppeo)_2](ClO_4)$ [19]. The center atom adopts distorted tetrahedron structure, and the bond angles and the bond distances around the copper atom are similar to those of **1**. In ligand **L**, the bipyridine units are almost co-planar with dihedral angles of 6.63°, and the torsion angle between the pendant aromatic rings and adjacent pyridine fragments is 40.53°. However the P=O group in ligand **L** is free, and the bond distance 1.436(8) Å (P3-O2) is shorter than that in complex **1** (1.465(2) Å, P2-O3). The tetrafluoroborate anions in **2** are disorder, and no specific interactions between the tetrafluoroborate anions and the cationic complex are observed.

Table 2 Selected bond distances /Å and angles /°:

		complex **1**	
Cu-N1	2.052(3)	Cu-P1	2.1725(10)
Cu-N2	2.116(3)	Cu-O3A [a]	2.178(2)
P2-O3	1.465(2)		
N1-Cu-N2	80.10(11)	N1-Cu-O3A	96.79(10)
N1-Cu-P1	130.47(8)	N2-Cu-O3A	99.01(9)
N2-Cu-P1	125.24(7)	P1-Cu-O3A	116.37(7)
		Complex **2**	
Cu1-N1	2.047(6)	Cu1-P1	2.164(2)
Cu1-N2	2.081(6)	Cu1-O1	2.172(5)
P2-O1	1.469(6)	P3-O2	1.436(8)
N1-Cu1-N2	81.1(2)	N1-Cu1-O1	96.1(3)
N1-Cu1-P1	134.1(2)	N2-Cu1-O1	115.7(2)
N2-Cu1-P1	125.8(2)	P1-Cu1-O1	101.6(2)

[a] Symmetry code: −x + 1,−y + 1,−z

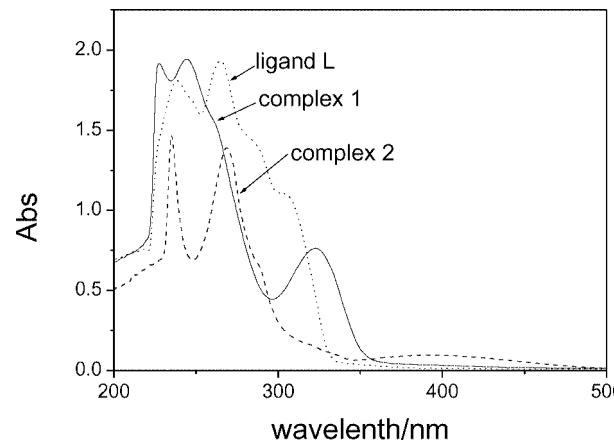


Figure 3 UV-Vis spectra of free ligand **L** (0.85×10^{-4} mol·L^{-1}), complex **1** (2.66×10^{-5} mol·L^{-1}) and complex **2** (4.95×10^{-5} mol·L^{-1}) in neat dichloromethane solution.

The UV-Vis absorption spectra for complexes **1** and **2** in dichloromethane are shown in Figure 3. For comparison, the spectra of free ligand L are also given. For complex **1**, it is no doubt that the bands at 244 nm (7.30×10^{-4} dm^3·mol^{-1}·cm^{-1}) and 260 nm (sh,

5.91×10^{-4} $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) are assigned to intraligand (IL $\pi \rightarrow \pi^*$) transitions of the ligand, which based on similarities with the absorptions of the free ligand. The band at 322 nm with large extinction coefficient (2.86×10^{-4} $dm^3 \cdot mol^{-1} \cdot cm^{-1}$), which only red-shift 18 nm when compared with band at 306 nm (sh) of the free ligand, and occur at a shorter wavelength when compared with analogous complexes such as $[Cu(bpy)(PPh_3)]^+$ and $[Cu(Phen)(PPh_3)]^+$ [20]. We tentative assign this band to a mixture transitions that involve IL transitions and metal-to-ligand charge-transfer (MLCT) transitions. For complex **2**, the low-energy broad absorption band with peak at 372 nm is characteristic for MLCT transition.

Conclusion

Binuclear complex $[Cu_2L_2(PPh_3)_2](BF_4)_2$ (**1**) and mononuclear copper(I) complex $[Cu(L)(dppeo)](BF_4)$ (**2**) with 6-(4-diethylmethylphosphonatephenyl)-2,2′-bipyridine (**L**) have been prepared and characterized. For binuclear complex **1,** two symmetrically related copper(I) atoms are held together by P=O donor atoms of the tridentate ligands **L**, while in complex **2**, both ligands **L** and dppeo behave as bidentate chelating ligands resulting mononuclear copper(I) complex.

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