A Polymeric Structure Containing Cu_2Cl_2 Units Bridged by 4,4′-Bipyridine: $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}4,4'\text{-bipyridine})$

Jian Lu, Gerardo Crisci, Tianyan Niu, and Allan J. Jacobson*

Department of Chemistry, University of Houston,
Houston, Texas 77201-5641

Received May 9, 1997

Introduction

In a recent publication, Henary *et al.* reported the synthesis and structure of a new mixed-ligand Cu(I) polymer, $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyrazine})$.[1] The polymer contains dimers in which two copper (I) ions are bridged by two chloride ions. Each copper atom is coordinated to one PPh_3 ligand. The tetrahedral coordination about each copper atom is completed by pyrazine ligands that bridge the dimers to form an infinite chain. We and others have studied the synthesis and structures of coordination polymers in which ligands such as pyrazine and 4,4′-bipyridine are used to bridge adjacent metal metal centers to form one-, two-, and three-dimensional polymer structures. Some recent examples are reviewed in a recent paper by Lu *et al.*[2] In the course of our studies, we have synthesized a new one-dimensional Cu(I) polymer that is closely related to the compound described by Henary *et al.* but where the bridging pyrazine ligand is replaced by 4,4′-bipyridine. The synthesis and crystal structure of $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}4,4'\text{-bipyridine})$ are described in this note.

Experimental Section

Materials. $CuCl(PPh_3)_3$, CH_2Cl_2, 4,4′-bipyridine, THF, and diethyl ether were obtained from Aldrich and were used without further purification.

Synthesis. $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}4,4'\text{-bipyridine})$ was prepared by two different methods: In a typical preparation, a solution of $CuCl(PPh_3)_3$ (0.22 g, 0.25 mmol) in CH_2Cl_2 (10 mL) was placed in a tube to which was added a buffer layer of THF/CH_2Cl_2 (10 mL) Finally, a solution of 4,4′-bipyridine (0.19 g, 1.20 mmol) in THF (10 mL) was added to form a third layer. Yellow block crystals were formed on interdiffusion of the reactants in about 1 week. One suitable crystal was chosen for single-crystal X-ray diffraction. Polycrystalline $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2$ (μ-4,4′-bipyridine) was obtained by a direct ligand exchange reaction of $CuCl(PPh_3)_3$ in excess 4,4′-bipyridine at ∼80 °C. The product was recovered in the form of a yellow powder on removal of the excess 4,4′-bipyridine and triphenylphosphine by washing with ether.

Characterization. Powders were characterized by X-ray diffraction using a Scintag XDS 2000 automatic diffractometer ($\theta-\theta$ geometry, flat plate sample, Cu Kα radiation, $\lambda = 1.541\ 78$ Å). IR spectra were obtained using a Galaxy FTIR 5000 spectrometer (KBr, cm^{-1}): 3049 (m), 1599 (s), 1479 (s), 1428 (s), 1408 (s), 1215 (m), 1093 (s), 810 (s), 750 (s), 698 (s), 518 (s), 510 (s). Thermogravimetric analysis was carried out by using a TA Instruments thermal analyzer in N_2 at a heating rate of 10 °C min^{-1}.

X-ray Crystallography. Crystal parameters and details of the data collection and refinement are given in Table 1 (for full details see the Supporting Information). A suitable crystal was mounted with epoxy glue on the tip of a glass fiber and transferred to a Enraf Nonius CAD4 four-circle diffractometer. Data were collected using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The unit cell parameters were determined by least-squares refinement of 25 reflections. Data were collected using the $\omega-2\theta$ scan method to a maximum 2θ of 50°. Orientation and intensity changes were monitored with three standard reflections. All data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ scans was applied. The structure was solved in the triclinic space group $P\bar{1}$ by direct methods and standard difference Fourier techniques (SHELXS-86 and SHELXL-93 programs[3,4]). Selected bond lengths and angles are given in Table 2.

Table 1. Crystallographic Data for $Cu_2(\mu\text{-}Cl)_2(PPh_3)_2(\mu\text{-}4,4'\text{-bipyridine})$

chem formula $C_{23}H_{19}ClCuNP$	fw 439.35
$a = 9.080(2)$ Å	space group $P\bar{1}$ (No. 2)
$b = 9.295(2)$ Å	$T = 25$ °C
$c = 13.086(2)$ Å	$\lambda = 0.710\ 73$ Å
$\alpha = 105.64(1)°$	ρ(calcd) = 1.443 g cm^{-3}
$\beta = 105.30(1)°$	$\mu = 12.98\ cm^{-1}$
$\gamma = 94.91(2)°$	$R_1{}^a = 0.0514$
$V = 1011(3)$ Å^3	$wR_2{}^b = 0.1516$
$Z = 2$	

[a] $R = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR_2 = [\sum w(F_0{}^2 - F_c{}^2)^2/\sum w(F_0{}^2)^2]^{1/2}$, $w = [\sigma^2(F_0)^2 + (0.1(\max(0,F_0{}^2) + 2F_c{}^2)/3)^2]^{-1}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

Cu−N	2.057(3)	N−Cu−P	119.63(9)
Cu−P	2.199(1)	N−Cu−Cl	100.89(10)
Cu−Cl	2.398(1)	P−Cu−Cl	117.92(4)
Cu−Cl	2.434(1)	N−Cu−Cl	99.79(9)
Cu−Cu	2.997(1)	P−Cu−Cl	112.55(4)
P−C(11)	1.822(4)	Cl−Cu−Cl	103.35(3)
P−C(21)	1.827(4)		
P−C(31)	1.830(4)		

Results and Discussion

The compound $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}4,4'\text{-bipyridine})$ is formed by reaction of $CuCl(PPh_3)_3$ with excess 4,4′-bipyridine in THF solution. The same product is obtained in polycrystalline form by a direct ligand exchange reaction in excess 4,4′-bipyridine. This was confirmed by IR spectroscopy and by comparison of the powder X-ray diffraction pattern with a pattern simulated from the structural parameters determined by single-crystal X-ray diffraction. Even the reaction at higher temperature (∼115 °C) did not lead to replacement of all of the triphenylphosphine groups and to the formation of CuCl(4,4′-bipyridine). The latter phase was obtained by Yaghi and Li from the reaction of CuCl with 4,4′-bipyridine in acetonitrile.[5]

Thermogravimetric analysis indicated the onset of decomposition at 190 °C and loss of bipyridine and triphenylphosphine. There was no evidence for the formation of an intermediate compound by selective loss of either bipyridine or triphenylphosphine.

A fragment of the crystal structure of $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}4,4'\text{-bipyridine})$ is shown in Figure 1, and the packing arrangement is shown in Figure 2. The structure consists of $(PPh_3)_2Cu_2Cl_2$ units that are bridged by 4,4′-bipyridine ligands to form infinite chains. Triphenylphosphine ligands complete the coordination around the copper atoms. The chains travel along the [110] axis and are stacked perpendicular to this direction. The Cu_2Cl_2 dimer has an inversion center between the two copper atoms, and there is also an inversion center in the bipyridine unit that bridges the dimers forming the infinite chain.

The structures of $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}4,4'\text{-bipyridine})$ and the previously reported $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyrazine})$ are analo-

---

* Author to whom correspondence should be addressed.

(1) Henary, M.; Wootton, J. L.; Khan, S. I.; Zink, J. I. *Inorg. Chem.* **1997**, *36*, 796.

(2) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923.

(3) Sheldrick, G. M. *SHELXS-86 User Guide*; University of Gottingen: Gottingen, Germany, 1986.

(4) Sheldrick, G. M. *SHELXL-93: Program for crystal structure refinement*; University of Gottingen: Gottingen, Germany, 1993.

(5) Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207.

S0020-1669(97)00550-8 CCC: $14.00

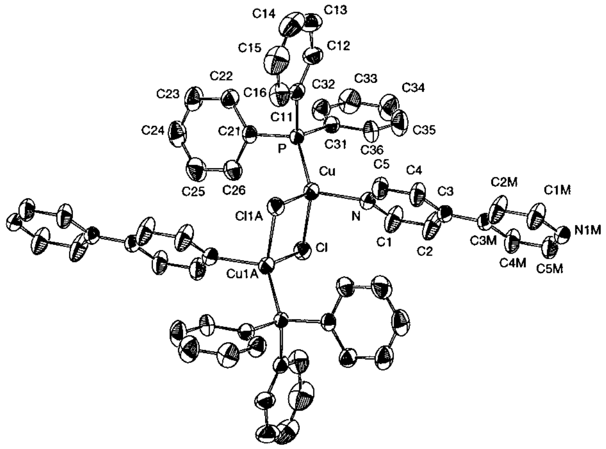

Figure 1. One unit of the $Cu_2Cl_2(PPh_3)_2$(4,4′-bipyridine) polymer.

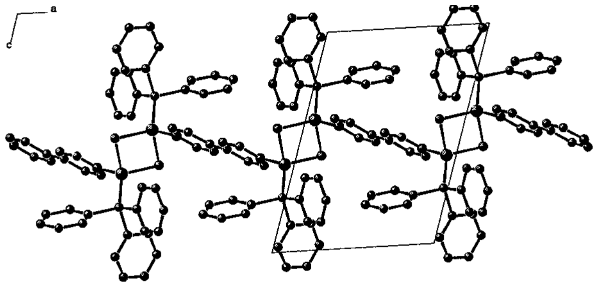

Figure 2. View of the $Cu_2Cl_2(PPh_3)_2$(4,4′-bipyridine) chain.

gous.[1] In the latter compound, pyrazine rather than 4,4′-bipyridine acts as the bridging ligand to form the infinite chains. The Cu−Cl bond distances in $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu$-4,4′-bipyridine) (2.398(1) and 2.434(1) Å) are similar to those observed in $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu$-pyrazine) (2.378(1) and 2.381(1) Å). The Cu−Cu (2.997(1) Å, bipy; 3.059(1) Å, pyr) and Cu−N (2.057(3) Å, bipy; 2.044(3) Å, pyr) are also similar. It is of interest to compare the structures of the chain structure polymers with the three-dimensional interpenetrated network formed by CuCl(4,4′-bipy).[5] The structure of CuCl(4,4′-bipy) has the same dimeric Cu_2Cl_2 unit, but in this structure, two 4,4′-bipyridine ligands are coordinated to each copper atom. The additional bridging ligands that replace the triphenylphosphine ligands in $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu$-4,4′-bipyridine) result in the formation of a three-dimensional network. We note that, in $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu$-4,4′-bipyridine), the pyridine rings are nearly coplanar (1° dihedral angle). In contrast, in CuCl(4,4′-bipy) the dihedral angles are 22 and 15.6°.[5]

Several other structures in which 4,4′-bipyridine ligands bridge copper ions have been reported in the literature. Examples of infinite linear[5−8] and zigzag[9] chain structures containing divalent copper in octahedral coordination are known. The compound $CuCl_2$(4,4′-bipyridine) forms a two-dimensional structure in which infinite chains of composition $[CuCl_{4/2}]$ are bridged by bipyridine ligands to form layers.[10]

A series of Cu(I) compounds with chain structures containing Cu_2Cl_2 dimers and with the general composition CuCl·L (where L = CH_3CN,[11] C_6H_5CN,[12] quinoline C_9H_7N,[13] pyridine[14]) have also been reported. Each of these compounds contains Cu_2Cl_2 dimers that are linked into an infinite chain by sharing the Cl atoms between dimers. Each chlorine atom is coordinated to three Cu(I) atoms and the tetrahedral coordination about Cu is completed by the ligand L. The chain composition can be expressed as $CuCl_{3/3}L$.

Finally, we note that an infinite zigzag chain was found in the pseudotetrahedral Mn(II) compound Mn(4,4′-bipyridine)-$\{N(SiMe_3)_2\}_2$ by Andruh *et al.*[15] $(PPh_3)_2Cu_2$ $(\mu\text{-}Cl)_2(\mu$-4,4′-bipyridine) can be considered the binuclear analog of the manganese compound.

Acknowledgment. We thank the National Science Foundation (Grant DMR-9214804) and the Robert A. Welch Foundation for support of this work.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the complex $(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu$-4,4′-bipyridine) is available on the Internet only. Access information is given on any current masthead page.

IC9705507

---

(6) Yu, K. B.; Gou, S. H.; You, X. Z.; Xu, Z. *Acta Crystallogr.* **1991**, *C47*, 2653.
(7) Gou, S. H.; You, X. Z.; Xu, Z.; Zhou, Z. Y.; Yu, K. B.; Yu, Y. P.; Zhu, D. L. *Acta Crystallogr.* **1991**, *C47*, 1303.
(8) Shi, S.; Xu, Y. *J. Struct. Chem.* **1985**, *4*, 38.
(9) Chen, C.; Xu, D., Xu, Y.; Cheng, C. *Acta Crystallogr.* **1992**, *C48*, 1231.
(10) Masciocchi, N.; Cairati, P.; Carlucci, L.; Mezza, G.; Ciani, G.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1996**, 2739.
(11) Jones, P. G. *Acta Crystallogr.* **1992**, *48C*, 1307.
(12) Massaux, M.; Le Bihan, M.-T. *Acta Crystallogr.* **1976**, *32B*, 1586.
(13) Healy, P. C.; Skelton, B. W.; Waters, F. W.; White, A. H. *Aust. J. Chem.* **1991**, *44*, 1049.
(14) Campbell, J. A.; Raston, C. L.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 1937.
(15) Andruh, M.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *Z. Naturforsch.* **1994**, *49b*, 31.