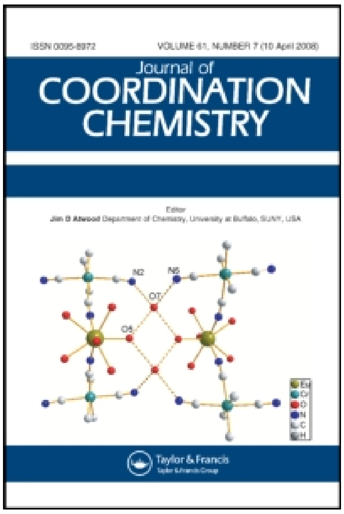

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# Ligand Flexibility and Dual Complexation Modes on Reaction of 1,2- bis (2'-pyridylethynyl)Benzene with Copper(I) Halides

Eric Bosch[a]; Charles L. Barnes[b]
[a] Department of Chemistry, Southwest Missouri State University, Springfield, Missouri [b] Department of Chemistry, University of Missouri, Columbia, Missouri

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# LIGAND FLEXIBILITY AND DUAL COMPLEXATION MODES ON REACTION OF 1,2-BIS(2′-PYRIDYLETHYNYL)BENZENE WITH COPPER(I) HALIDES

ERIC BOSCH[a,]* and CHARLES L. BARNES[b]

[a]*Department of Chemistry, Southwest Missouri State University, Springfield, Missouri 65804;*
[b]*Department of Chemistry, University of Missouri, Columbia, Missouri 65211*

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The reaction of the bidentate ligand 1,2-bis(2′-pyridylethynyl)benzene with copper(I) halides reveals the rich coordination chemistry of the ligand. The reaction with copper(I) iodide yields a linear 1D coordination polymer. The polymer features a series of rhomboid $CuI_2Cu$ centers bridged by two of the bipyridyl ligands. A tetramer is formed with copper(I) bromide where the ligand adopts two distinct conformations. One pair of ligands bridges two rhomboid $CuBr_2Cu$ centers and the second pair of ligands end-caps the two copper centers. The end capping ligands in the copper(I) bromide structure have pyridyl rings flexed with torsional angles of 11 and 28° with respect to the central benzene ring. A 2 : 4 complex is formed on reaction with copper(I) chloride. In this structure both pyridyls complex the same copper atom and are twisted out of planarity with the benzene ring with one alkyne coordinated to the second copper atom.

*Keywords:* Ligand flexibility; Bidentate; *Trans*-coordinating; Copper(I) halide; Coordination polymer

## INTRODUCTION

Crystal engineering of metal coordination supramolecules is a topical area of research [1] driven by the wide range of potential applications including molecular electronics [2] and magnetic and optical devices [3] as well as zeolite mimics [4] and novel catalysts [5]. The coordination characteristics of a variety of ligands and metal cations had earlier been determined in simple molecular complexes and this knowledge has been applied to the logical synthesis of novel 1D, 2D and 3D coordination polymers [1]. The bidentate pyridines and *N*-heterocycles used for 1D polymer formation generally have two *N*-atoms oriented in opposite directions as typified by 4,4′-dipyridine [6]. In contrast we, and others, recently described the synthesis and novel chelation characteristics of a simple dipyridyl ligand, 1,2-bis(2′-pyridylethynyl)benzene, **1** [7,8,9]. The 1:1 complexes

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*Corresponding author. Tel.: (417) 836-4277 (office); 836-4255 (lab.). Fax: (417) 836-5507. E-mail: erb625f@smsu.edu

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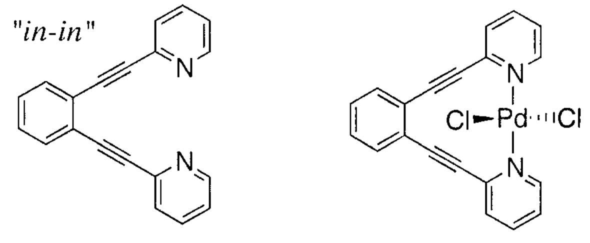


**1** $\mathbf{1} \cdot PdCl_2$

FIGURE 1 Ligand **1** in the "*in–in*" conformation alongwith the 1 : 1 complex with palladium (II) dichloride.

of **1** with silver(I) triflate and palladium dichloride demonstrated the *trans* chelation of the metal center as shown in Fig. 1. We are interested in exploring the complexation characteristics of **1**, and related ligands, with metals having other preferred coordination geometries and now describe the formation of a 1D coordination polymer, a tetramer and a 4 : 2 complex on reaction of **1** with copper(I) iodide, copper(I) bromide and copper(I) chloride, respectively, that demonstrate the rich coordination chemistry of this relatively simple ligand. Interestingly, Kawano and coworkers have recently demonstrated that the palladium and copper complexes of related ligands are effective catalysts [9].

## EXPERIMENTAL

### Synthesis

The preparation of ligand **1** was described earlier [7].

*Reaction of 1 with CuI.* Copper(I) iodide (20.0 mg, 0.105 mmol) and **1** (30.0 mg, 0.107 mmol) were placed in a vial and acetonitrile (7 mL) added. The vial was capped and the slurry stirred with gentle heating until a homogeneous yellow solution was formed. The vial was stored in the dark and canary yellow crystals were harvested after 3 days (29.9 mg, 60%). A second crop of yellow crystals was obtained by allowing the acetonitrile to evaporate to approximately one half of the initial volume (12.1 mg, 24%). Elemental analysis of the yellow crystals indicated that a 1 : 1 complex, **2**, was formed. Mp 198°C (dec.). IR (KBr) 2223 $cm^{-1}$; $\lambda_{max}$ (diffuse reflectance, 2% in $SiO_2$) 460 nm. Anal. Calcd. for $[C_{20}H_{12}CuIN_2]_n$: C, 51.03; H, 2.57; N, 5.96. Found: C, 51.04; H, 2.65; N, 5.94.

*Reaction of 1 with CuBr.* The reaction of CuBr with **1** was performed in a screw-cap vial as described for CuI. A bright yellow solution was formed in warm acetonitrile or nitromethane. Argon was bubbled through the homogeneous solution for 10 min and the vial then sealed tightly [if this step was omitted the solution turned green/brown after 12 h]. Orange rhomboid-shaped crystals began to form after several hours. After 2 days the orange crystals (47%) were separated and washed with dichloromethane. Elemental analysis indicated that a 1 : 1 complex, **3**, was formed. Mp 185° C (dec.). IR (KBr) 2224 $cm^{-1}$; $\lambda_{max}$ (diffuse reflectance, 2% in $SiO_2$) 530 nm. Anal. Calcd. for $C_{80}H_{48}Br_4Cu_4N_8$: C, 56.69; H, 2.85; N, 6.61. Found: C, 56.48; H, 2.85; N, 6.77.

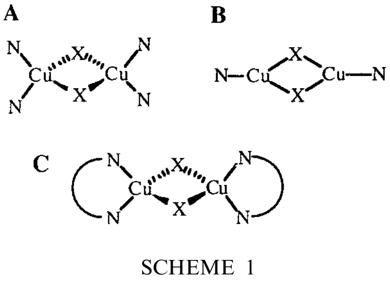
*Reaction of **1** with CuCl.* The reaction of **1** with CuCl in nitromethane was performed in a screw-cap vial as described for CuBr with argon bubbled through the mixture for 10 min before the vial was sealed. After 3 days orange hexagonal crystals of **4** formed. IR (KBr) 2220 and 2070 cm$^{-1}$. Anal. Calcd. for $C_{40}H_{24}Cl_4Cu_4N_4$: C, 50.22; H, 2.53; N, 5.86. Found: C, 50.22; H, 2.56; N, 5.89.

### *X-ray Data Collection, Structure Solution, and Refinement*

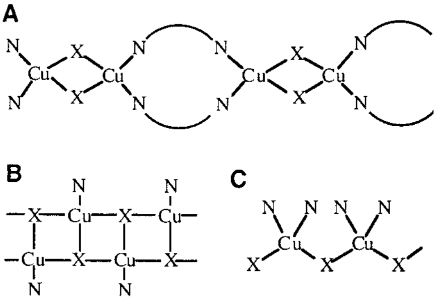
Yellow crystals of **2** grown directly from an equimolar acetonitrile solution of **1** and copper iodide were suitable for X-ray analysis. A yellow rod-shaped crystal of dimensions 0.45 × 0.25 × 0.20 mm was selected. Crystals of **3** (0.25 × 0.25 × 0.10 mm) and **4** (0.40 × 0.20 × 0.20 mm) were similarly culled from the group of crystals directly grown from acetonitrile and nitromethane solutions respectively. The X-ray data for **2**, **3** and **4** were collected on a Siemens CCD area detector-equipped diffractometer with MoK$\alpha$ radiation. The structures were solved using SHELXS-97 and refined using SHELXL-97 [10]. Hydrogen atoms were included in the calculated positions. **2** was shown to be a linear 1D coordination polymer, **3** a tetramer and **4** a 4 : 2 complex. Ortep 3 was used to prepare the figures [11].

## RESULTS AND DISCUSSION

Copper(I) halide complexes with *N*-donor ligands favor *pseudo*-tetrahedral or trigonal geometry shown as A and B in Scheme 1. A search of the Cambridge Structural Database revealed that a variety of unhindered monodentate *N*-donor ligands [12] formed 4 : 2 complexes with copper(I) iodide wherein each copper has *pseudo*-tetrahedral geometry completed with two *N*-donor ligands and the two bridging iodides as shown in Scheme 1A. In contrast, the hindered pyridines, 2,6-dimethylpyridine [13] and 1,2,3,4,5,6,7,8-octahydroacridine [14], form dimeric complexes with trigonal geometry about the copper as shown in Scheme 1B. Indeed 2,2,6,6-tetramethylpiperidine forms a similar complex [15]. The prototypical *cis*-coordinating ligands 2,2′-bipyridine [16] and 1,10-phenanthroline [17] both form dimeric complexes with copper(I) iodide with central $CuI_2Cu$ core and one ligand completing the coordination about each copper atom as in Scheme 1C. A variety of other more flexible *cis*-coordinating bidentate ligands, including *N*,*N*,*N*′,*N*′-tetramethylethylenediamine [18] and *N*,*N*-bis(2-pyridyl) amine [19], form similar dimeric complexes with tetrahedral coordination about copper as shown in Scheme 2A.



SCHEME 1



SCHEME 2

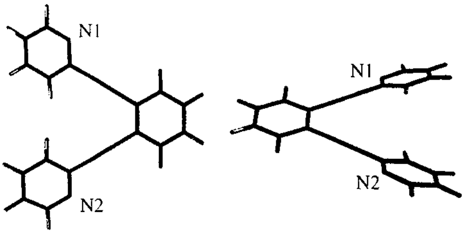


FIGURE 2 Two views of the minimized structure of the ligand **1**.

In addition it should be noted that a varaiety of coordination networks have been formed with nitrogen-based donor ligands in which the copper atoms have *pseudo*-tetrahedral geometry [20]. Thus the rhombic CuX$_2$Cu connecting spacer has been characterized in several 1D polymers in which bidentate ligands bridge the CuX$_2$Cu units as shown in Scheme 2A [21,22]. The copper halides may also form the "stair-" or "ladder-like" arrangement shown in Scheme 2B [12(b),23] or infinite chains as shown in Scheme 2C [23(b),24].

The spacing between the nitrogen atoms in **1** with the "*in–in*" conformation of the pyridyl rings is ideally suited for *trans*-coordination of metal cations as shown in Fig. 1 and clearly is not optimal for *cis*-coordination [7]. It is, however, interesting to note that the minimized structure of the ligand has the nonplanar "*out–out*" conformation shown in Fig. 2 [25].

Although the stoichiometry of ligand **1** to CuX within the products formed from copper iodide and copper bromide is identical, the structures are significantly different. The structure of **2** is a linear 1D polymer as shown in Fig. 3. The repeating unit of the 1D polymer, **2**, is shown in Fig. 4 with the atoms in the asymmetric unit labeled. The repeating unit comprises two bridging ligands and two copper iodide moieties that combine to form iodide-bridged rhomboid interconnecting units. Each copper atom adopts a distorted tetrahedral geometry and is bound to one pyridine from each of the two bridging ligands and to two bridging iodides. The angles about the copper atoms are 116.409(10), 117.01(7), 111.50(5), 105.26(5), 107.37(5) and 99.05(5)° for I(1)–Cu(1)–I(1)#1, N(1)–Cu(1)–N(2), N(1)–Cu(1)–I(1), N(1)–Cu(1)–I(1)#1, N(2)–Cu(1)–I(1) and N(2)–Cu(1)–I(1)#1, respectively. Considering the CuI$_2$Cu moiety the Cu(1)–I(1)–Cu(1)#1 angle is 63.591(11)° and the copper centers are separated by 2.8205(5) Å. This close Cu–Cu contact has been noted in a variety of complexes containing the

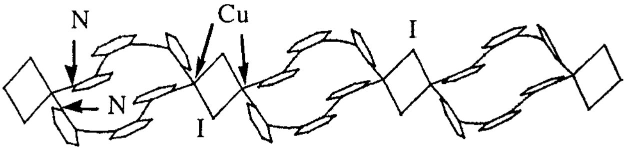


FIGURE 3 Stick representation of the 1D polymer formed between the ligand **1** and copper(I) iodide [10].

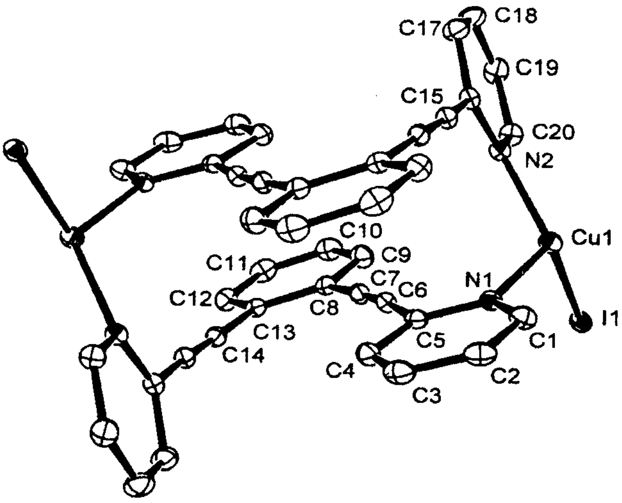


FIGURE 4 Ortep plot of the repeating unit in the copper iodide coordination polymer with thermal ellipsoids drawn at 30% probability and hydrogen atoms omitted for clarity.

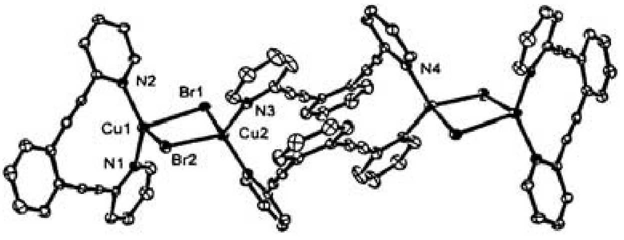


FIGURE 5 Ortep plot of the tetramer isolated from reaction of copper(I) bromide with ligand **1**. Thermal ellipsoids drawn at 30% probability and hydrogen atoms omitted for clarity.

$CuI_2Cu$ unit where Cu–Cu distances in the range 2.6–3.1 Å have been reported [26]. Each bridging dipyridyl ligand has one pyridyl ring essentially coplanar with the benzene ring, with a torsional angle of approximately 3°, while the second pyridyl ring makes a dihedral angle of approximately 89° with the benzene ring as shown in Fig. 4. The relatively inflexible nature of the bridging ligand prevents the pyridyls from attaining a more favorable coordination position and coordination to the pyridyl rings is not optimal. For example the copper atom, Cu(1), lies an unusual 17° below the plane of the twisted pyridine, N(2), and 6° below the plane of coplanar pyridine, N(1). In addition, both alkynyl groups are bent with the alkyne [C(14)–C(15)] bent by approximately 6.4° and alkyne C(6)–C(7) bent by 4°.

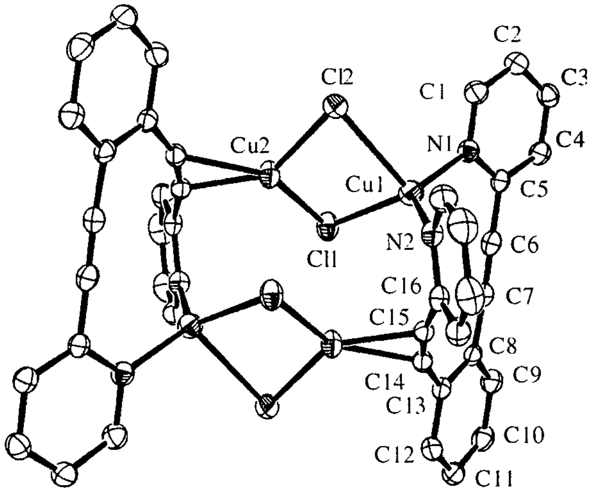


FIGURE 6 Complex formed on reaction of **1** with copper(I) chloride. Thermal ellipsoids drawn at 50% and hydrogen atoms omitted for clarity.

In contrast the complex with copper(I) bromide, **3**, is a tetramer shown in Fig. 5. This complex is a rare example of one ligand adopting *two different coordination modes* within a single complex. Thus, the tetramer has two rhomboid $CuBr_2Cu$ connecting linkages that are bridged by two ligands with a similar orientation to the bridging ligand in the copper(I) iodide polymer (compare Figs. 4 and 5). Within these bridging ligands the pyridyl rings are twisted out of coplanarity with the central benzene ring by angles of approximately 13 and 76° and make an N(1)–Cu(1)–N(2) angle of 133.96°. Interestingly the two $Cu_2Br_2$ units are end-capped by a flexed ligand that coordinates in a bidentate fashion to the copper centers. These pyridyl rings of the end capping ligand make torsional angles of only 11 and 28° with the central benzene ring. Interestingly the tetrahedral coordination about the inner copper, Cu(2), is less distorted than that about the outer copper, Cu(1): thus the angles about Cu(1) are in the range 95.294(16) to 133.97(10)° and between 101.390(17) and 118.95(10)° about Cu(2).

A third structure was obtained on reaction of ligand **1** with copper(I) chloride. In the complex with copper chloride (Fig. 6) the ligand adopts a slightly twisted conformation similar to the "end-capping" conformation in the copper bromide complex. Within the complex the copper chloride exists as the $(CuCl)_2$ dimeric unit; however, only one copper, Cu(1), is bound to both pyridyls of the twisted ligand. This copper has distorted tetrahedral geometry with angles ranging from 91.29(2) for Cl(1)–Cu(1)–Cl(2) to 128.39(8) for N(1)–Cu(1)–N(2). The second copper, Cu(2), is $\pi$-bound to an alkyne from the second ligand. The bond length of the bound alkyne, C(15)–C(16), at 1.219(4) Å is slightly longer than the unbound alkyne, C(6)–C(7), that is 1.200(4) Å. This is accompanied by a loss of linearity with angles of 161.5(3) and 168.5(3)° for C(13)–C(14)–C(15) and C(14)–C(15)–C(16), respectively. This weakening of the triple bond is reflected in the infrared spectrum that has two alkynyl stretching frequencies: $2220\,cm^{-1}$ for the unbound alkyne and $2069\,cm^{-1}$ for the bound alkyne. The slight elongation of the alkyne on complexation to copper and the copper–alkyne distance

Cu(2)–C(14) and Cu(2)–C(15) of 2.010(2) and 2.039 Å are within the range reported for similar $\pi$-complexes [28].

In conclusion we have shown that the ligand initially designed to be *trans*-coordinating may also coordinate metal centers favoring tetrahedral geometry by adopting higher-energy nonplanar conformations. This flexibility coupled with our earlier results and those reported by Bunz *et al.* [8], demonstrate that ligand **1** has a rich coordination chemistry and is a versatile bidentate ligand with potential uses in transition metal catalyzed reactions.

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## *Supporting Information Available*

X-ray crystallographic files in CIF format for **2**, **3** and **4**.

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