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A Mixed-Ligand Coordination Polymer from the in Situ, Cu(I)-Mediated Isomerization of Bis(4-pyridyl)ethylene

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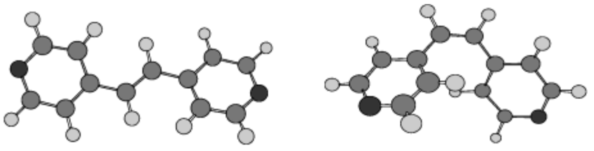
Reaction of $[Cu(PPh_3)_2(MeCN)_2]PF_6$ and *trans*-1,2-bis(4-pyridyl)ethylene (bpe) results in the trans–cis isomerization of the bpe and subsequent formation of a mixed-isomer linear coordination polymer over the course of several days or weeks depending on solvent. The one unique copper atom in the structure is coordinated to two bridging *cis*-bpe ligands, one bridging *trans*-bpe ligand, and one terminal triphenylphoshine ligand to create [Cu(*trans*-bpe)$_{0.5}$(*cis*-bpe)(PPh$_3$)]$^{+}_{\infty}$ zigzag chains. The reaction requires both visible light and Cu(I), and the crystallization of this particular coordination polymer is insensitive to the ratio of trans:cis isomers in solution, occurring both from trans-rich and cis-rich solutions.

The rational design of extended solids in which metal cations are linked together with organic ligands has sparked a great deal of excitement, due to the possibility of targeting structures possessing particular properties. Microporous,[1] magnetically ordered,[2] and nonlinearly optically active[3] solids are a few characteristics of "coordination polymers" that have been recently synthesized and characterized. In order to achieve predictability of structures resulting from molecular building blocks, a certain degree of structural rigidity is required. In fact, by using flexible ligands like 1,2-bis(4-pyridyl)ethane different ligand conformations can be incorporated into several different "supramolecular isomers" where structure prediction becomes very difficult indeed. Alternatively, *trans*-1,2-bis(4-pyridyl)ethylene, **1** (Chart 1), has been used as a rigid-rod linker in the construction of extended networks containing Cu(II),[5] Co(II),[5a] and Cu(I),[6] as well as Re-coordinated **1** in molecular rectangles.[7]

Chart 1. Optimized[4] Structures of *trans*-bpe, **1**, and *cis*-bpe, **2**



1 **2**

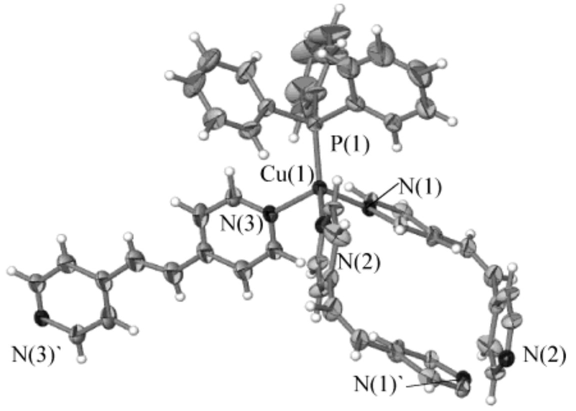


Figure 1. ORTEP drawing of the Cu(I) coordination sphere in **3**, showing all non-hydrogen atoms as 40% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Cu(1)−N(1) = 2.06(1), Cu(1)−N(2) = 2.08(1), Cu(1)−N(3) = 2.09(1), N(1)−Cu(1)−N(2) = 101.0(1), N(2)−Cu(1)−N(3) = 100.3(1), N(1)−Cu(1)−N(2) = 101.3(1).

The conformational rigidity of **1** and other substituted ethylenes and azobenzenes, arises from the large rotational barriers (40−45 kcal/mol) for the ground-state trans−cis isomerization due primarily to the loss of double-bond character in the transition state. However, rotational barriers in electronically excited states are often substantially lower, and the isomerizations can proceed efficiently under the proper illumination, ca. $\lambda \leq 340$.[8] Here we report the reaction of Cu(I) and **1** *under visible illumination* that results in the

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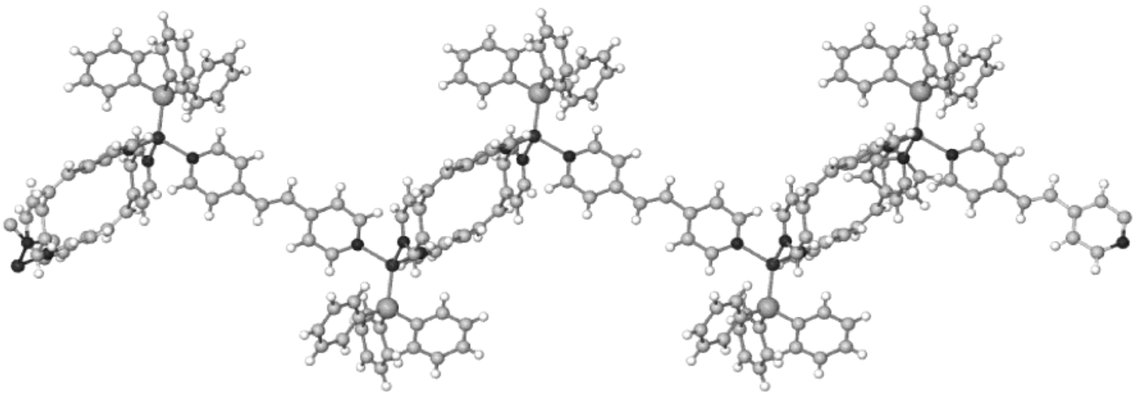

Figure 2. Ball-and-stick drawing of the [Cu(*trans*-bpe)$_{0.5}$(*cis*-bpe)(PPh$_3$)]$^+_\infty$ zigzag chains in **3**.

crystallization of Cu(*trans*-bpe)$_{0.5}$(cis-bpe)PPh$_3$]PF$_6$, a linear coordination polymer containing *both* isomers of bpe. The absorption of the Cu(I)−*trans*-bpe complex tails into the visible region, allowing the photolytic isomerization to proceed under ambient illumination. Though we can certainly not claim rational design, this kind of in situ transformation may be an exploitable avenue for inorganic crystal engineering or even directed/catalyzed small-molecule organic synthesis.

Reaction of [Cu(MeCN)$_2$(PPh$_3$)$_2$]PF$_6$ with **1** in a 12:12:1 mixture of CH$_2$Cl$_2$ or CHCl$_3$, toluene, and MeCN affords yellow prismatic crystals.[9] Remarkably, X-ray diffraction analysis of these crystals[10] reveals that not only one molecule of **1** but also two molecules of **2** are coordinated to the one unique copper center! Figure 1 displays the distorted tetrahedral geometry typical for Cu(I), with one PPh$_3$ completing the metal coordination sphere.[11] Cu−N bond lengths and angles are consistent with similar compounds, though the N−Cu−N angles are all ~101° due to the steric influence of the PPh$_3$ ligand.

The *trans*-bpe links to another Cu(1), and the two cis isomers bridge *to the same* Cu(1), which results in linear polymeric structure of composition [Cu(*trans*-bpe)$_{0.5}$(*cis*-bpe)(PPh$_3$)]$^+_\infty$ as shown in Figure 2. The N−Cu−N angles between cis ligands are essentially identical to the angles between trans and cis. The structural motif is similar to several other linear chain structures, but the components are quite unique. The alternating cis and trans linkages result in two alternating Cu−Cu distances (9.46 Å between cis-connected, 13.6 Å between trans-connected) along the chain. The zigzag chains are stacked together in an offset arrangement, leaving room for the noncoordinating anions, as well as one CH$_2$Cl$_2$ and one toluene molecule (the latter disordered over two positions) per Cu atom to be incorporated into the structure, as shown in Figure 3.

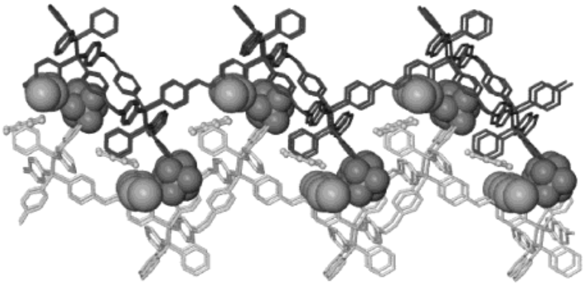

Figure 3. Packing diagram of **3** viewed down the *a*-axis. The chains are represented as monotone gray sticks, with the PF$_6^-$ anions and CH$_2$Cl$_2$ molecules shown as space-filling spheres. Both orientations of the disordered toluene molecules are shown as balls and sticks.

More fascinating than the structure are the synthetic requirements for generating the structure. Both Cu(I) and ambient illumination are necessary; the isomerization reaction does not occur in the dark,[12] or in the absence of Cu(I) in room light. If UV light (365 nm) is used, the solution becomes discolored, though a few poorly formed crystals of **3** are formed. When the reaction is carried out under a normal incandescent bulb fitted with a band-pass filter (420 ± 10 nm), high-quality single crystals are produced identical to those produced under unfiltered lab light within approximately the same time frame. Solution UV−vis spectroscopy shows that neither the free ligand nor the [Cu(MeCN)$_4$]$^+$ complex has any appreciable absorption at wavelengths longer than ca. 370 nm. However, addition of Cu(I) to CH$_2$Cl$_2$ solutions of **1** results in a significant red shift due to donation of the nitrogen lone pairs to the metal center, and a decrease in the M → L charge transfer energy; the solution and the resulting crystals are yellow. In a related reaction using Ag(I) and **1**, a photolytic, [2 + 2] cycloaddition reaction resulted in a new tetradentate ligand, but no evidence of **2** was reported.[13]

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(9) Specifically, 0.032 g of [Cu(MeCN)$_2$(PPh$_3$)$_2$]PF$_6$ (0.039 mmol) dissolved in 6 mL of CH$_2$Cl$_2$, 3 mL of toluene, and 0.5 mL of MeCN was added to 0.021 g of **1** (0.104 mmol), 6 mL of CH$_2$Cl$_2$, and 6 mL of toluene in a 20 dram screw-top vial. Yellow crystals were harvested from the bottom of the vial after 3 weeks in 60% yield based on Cu. When carried out with CHCl$_3$ replacing CH$_2$Cl$_2$, crystals are harvested in a few days, yielding yellow crystals of identical unit cell parameters.

(10) Crystal structure determination for compound **3**: crystal data, CuC$_{44}$H$_{40}$N$_3$P$_2$Cl$_6$F$_6$, $M = 921.2$ g/mol, monoclinic, space group $P2_1/c$, $a = 10.023(1)$ Å, $b = 18.794(2)$ Å, $c = 23.845(3)$ Å, $\beta = 98.927(2)°$, $V = 4437.2(10)$ Å^3, $T = 173$ K, $Z = 4$, μ(Mo Kα) = 0.744 mm^{-1}, 19860 reflections measured, 6368 unique ($R_{int} = 0.0377$). Full-matrix least-squares on F^2 refinements were used. The cis-bridging ligands were modeled as disordered over two positions (related by a ca. 20° twist) with 55:45 occupancy. In the figures, the higher occupied orientation only is shown. Further details of the refinements are provided in the Supporting Information. The final $R(F)$ was 0.0837 for $I > 2\sigma$ and 0.1163 for all observed data.

(11) Replacement of one, and only one, PPh$_3$ by 4,4-bipy on [Cu(MeCN)$_2$(PPh$_3$)$_2$]$^+$ has been previously observed. Keller, S. W.; Lopez, S. *J. Am. Chem. Soc.* **1999**, *121*, 6306.

(12) A few, poorly formed reddish crystals were collected from this reaction which contain no PPh$_3$, which we believe to be [Cu(bpe)$_2$]PF$_6$ that was previously reported in ref 5b.

Each of the components in the complex solvent mixture plays a key role. In our initial reactions with Cu(I) and **1** (without added MeCN), crystallization occurred rapidly, not allowing for any appreciable isomerization.[6d] With insufficient toluene, no crystals are formed in the light; however, crystallization of **3** can be initiated from these photolyzed solutions by simply adding more toluene. Crystallization can be accelerated dramatically if the less polar $CHCl_3$ replaces the CH_2Cl_2. Preliminary solution NMR studies indicate that the isomerization rates in $CHCl_3$ and CH_2Cl_2 (with and without toluene) are similar, leading to a cis-rich (4:1) photostationary state after about 48 h. Therefore, by controlling the solvent mixture, nucleation and crystal growth can be initiated from very different solution compositions. Specifically, crystallization occurs in $CHCl_3$ when the trans:cis ratio is approximately 4:1, but it can be significantly delayed in CH_2Cl_2, until the cis isomer is the dominant species when the crystals are formed. The surprising implication is that the resulting extended structure is essentially insensitive to the ratio of **1**:**2** in solution at the time the crystals initially appear.

Previous synthesis studies that report successful incorporation exclusively of **1** into Cu-coordination networks are consistent with this observation. Zubieta and co-workers conducted hydrothermal reactions in stainless steel pressure vessels (necessarily in the absence of light) and observed no evidence of any cis isomer.[5b] In another case,[6c] crystallization occurred in 4 h, not enough time to produce appreciable amounts of **2**. When the crystallizations did occur over several days, layered solvents were used,[12] with **1** and the metal salt *in separate solutions* so that very little of the Cu(I)−bpe complex was formed, limiting the amount of **2** in solution, again consistent with our hypothesis.

Current investigations center on density functional calculations of model complexes as well as time-resolved fluorescence spectroscopy to more fully characterize the role of metal coordination on the electronic structure of bpe, as well as quantify the quantum yields of the isomerization reactions.

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Supporting Information Available: Synthetic details, description of the X-ray structure solution and refinement, and tables of crystallographic details for **3**. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, crystallographic data (excluding calculated and observed structure factor tables) for **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 184154. Copies of the information can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

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