Formation of Hexagonal Coordination Complexes

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The synthesis of the ligand 1,3-bis(3′-pyridylethynyl)benzene and the coordination complex formed with copper(II) acetate is described. The complex is hexagonal with two ligands bridged by paddlewheel-shaped dimeric copper(II) acetate moieties. The complexes are packed in such a way that the benzene rings from two separate complexes penetrate into the central cavity.

Introduction

The synthesis of porous solids is a research area of current interest.[1−4] For example solids that contain channel-like void spaces are attractive goals with potential applications in molecular adsorption, ion exchange, and also heterogeneous catalysis. Hexagonal channels and cavities are often found in nature, and several approaches to the synthesis of hexagonal channels have been reported. Moore, for example, reported the formation of a purely organic porous solid with wide channels based on the π-stacking and hydrogen bonding of a planar hexagonal macrocycle comprising six phenols linked by *meta*-ethynyl groups.[5] Robson reported a coordination chemistry approach and characterized a large hexagonal complex on self-assembly of 2,4,6-tris(4′-pyridyl)-1,3,5-triazine with copper(II) acetate.[6] That coordination network did not contain channels because of the offset packing of adjacent sheets of the coordination network. In this report we describe a different coordination chemistry approach to the preparation of hexagonal channels.

Results and Discussion

As ligand we chose to prepare the bidentate ligand 1,3-bis(3′-pyridylethynyl)benzene, **1**, and to self-assemble this with metals that favor linear coordination as shown in Equation (1). Sonagashira coupling[7] of 3-bromopyridine with 1,3-diethynylbenzene yielded the ligand **1** in good yield as shown in Equation (2).[8] We then allowed the ligand **1** to self assemble with copper(II) acetate in acetonitrile solution and obtained green diamond-shaped crystals.[9] Elemental analysis of the bulk solid indicated that a 1:2 ligand/Cu^{II} complex was formed. Single-crystal X-ray analysis revealed this to be a hexagonal 2:4 coordination complex as shown in Figure 1.[10]

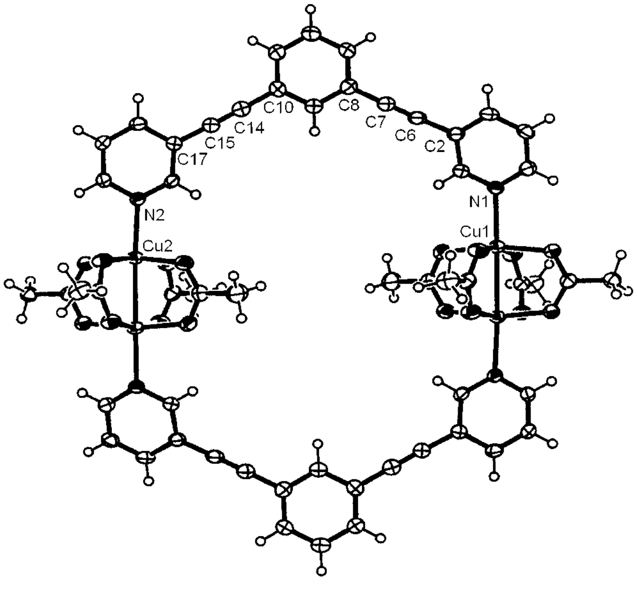
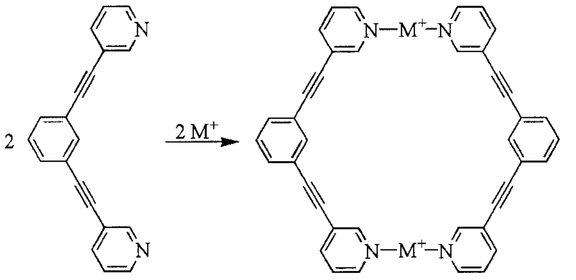


Figure 1. Ortep view of the 2:4 complex formed between **1** and copper(II) acetate; ellipsoids drawn at the 50% probability level



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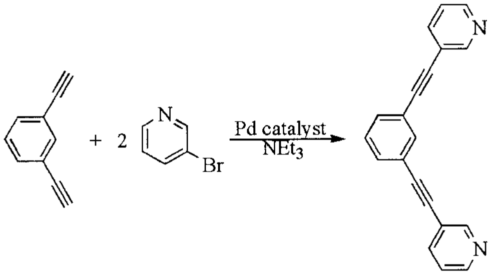

(2)

The complex between two ligands and two copper(II) acetate dimeric units forms a slightly irregular hexagon as shown in Figure 1. The copper(II) acetate linkage gives longer sides with a N(1)−N(2) distance of 6.957 Å, while the C(2)−C(8) and C(10)−C(17) distances are 4.067 and 4.065 Å, respectively. The copper acetate paddlewheel forms an almost linear connection between the pair of ligand molecules with nitrogen−copper−copper angles of 174.82(6) and 177.43(7)°. The copper−nitrogen bond lengths of 2.185(2) and 2.175(2) Å and the copper−copper bond length of 2.6053(5) Å are normal. The copper−oxygen bond lengths range from 1.959(2) Å to 1.987(2) Å, and the oxygen−copper−oxygen bond angles on each side of the paddlewheel range from 87.56(9) to 92.32(9)°. The alkynes are undistorted with normal triple bond lengths of 1.190(4) and 1.191(4) Å and angles about the sp C atoms between 177.3(4) and 179.3(4)°. The pyridyl rings are slightly twisted with respect to the central benzene ring with torsional angles of approximately 28 and 13°.

Unfortunately, the hexagonal complexes do not stack on top of each other to form porous materials − instead individual complexes stack in an offset manner with the end of two complexes partially penetrating the central cavity of a third complex. This is shown in Figure 2.

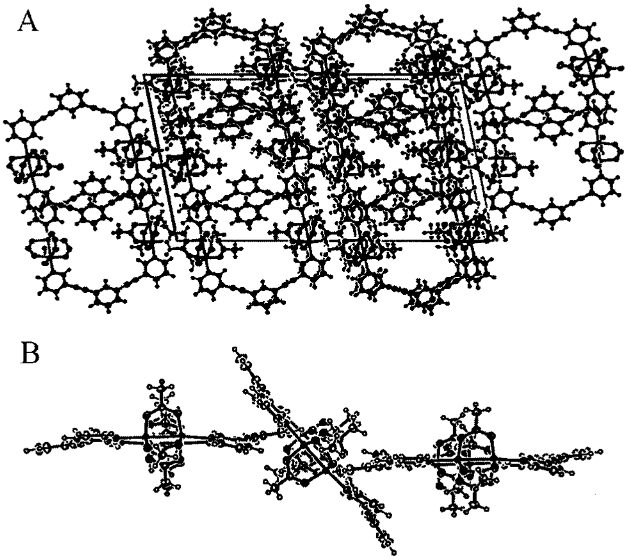

Figure 2. **A:** The packing in the unit cell viewed along the a axis; **B:** view showing the partial penetration of two complexes into a central tilted complex.

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[8] 1,3-Diethynylbenzene (1.26 g, 10 mmol) was added with the aid of a syringe to a mixture of 3-bromopyridine (3.26 g, 20.6 mmol), bis(triphenylphosphane)palladium(II) dichloride (150 mg), CuI (15 mng), and triphenylphosphane (150 mg) in diethylamine (25 mL). Nitrogen was bubbled though the mixture for 10 minutes, and the reaction was heated to 60 °C under nitrogen for 16 h. The crude product was purified, by precipitation from ethyl acetate with hexanes, as a white powder in 64% yield (1.02 g). ^{1}H NMR (CDCl$_3$): δ = 7.38−7.26 (m, 3 H, ArH), 7.56−7.52 (m, 2 H, ArH), 7.75 (t, J = 1.5 Hz, 1 H, ArH), 7.81 (td, J = 1.8, 8.0 Hz, 2 H, ArH), 8.57 (dd, J = 1.8, 5.2 Hz, 2 H, ArH), 8.78 (dd, J = 0.8, 2.0 Hz, 2 H, ArH) ppm. ^{13}C NMR: δ = 86.7, 91.5, 120.1, 123.0, 128.6, 131.8, 134.7, 138.4, 148.7, 152.3 ppm. $C_{20}H_{12}N_2$ (280.32): calcd. C 85.71, H 4.29, N 10.00; found C 85.55, H 4.32, N 9.90.

[9] A mixture of acetonitrile (2 mL) and dichloromethane (2 mL) was layered over a solution of 1,3-bis(3′-pyridylethynyl)benzene (11.0 mg, 0.04 mmol) in dichloromethane (2 mL). A solution of copper(II) acetate monohydrate (16.0 mg, 0.08 mmol) in acetonitrile (2 mL) was carefully layered over that. The vial was capped and placed in the dark. Green diamond-shaped crystals formed after 2 days (14.7 mg, 59%). m.p. 222 °C. $C_{28}H_{24}N_2Cu_2O_8$ (643.6): calcd. C 52.25, H 3.76, N 4.35; found C 52.32, H 3.68, N 4.37.

[10] Crystal size 0.40 × 0.25 × 0.05 mm, $C_{28}H_{24}Cu_2N_2O_8$, mol. mass 643.57; monoclinic, $C2/c$, a = 36.5577(17) Å, b = 7.8999(4) Å, c = 21.4256(11) Å; β = 100.3440(10)°; V = 6087.2(5) Å^3; Z = 8; ρ (calculated) = 1.404 Mg/m^3; reflections collected = 21246 (6700 unique); F(000) = 2624; Absorption coefficient = 1.445 mm^{-1}; 1.93 < θ < 27.14 ; max. and min. transmission = 0.93 and 0.59; final R indices [$I > 2\sigma(I)$], $R1$ = 0.0440, $wR2$ = 0.1005; largest diff. peak and hole = 0.660 and −0.382 e·Å^{-3}. CCDC-246104 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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