

Three unique coordination geometries involving 1,2-dimethoxy-4,5-bis(2-pyridylethynyl)benzene

Jeffrey E. Fiscus,^a Sandra Shotwell,^a Ralph C. Layland,^b Mark D. Smith,^a Hans-Conrad zur Loye^{*a} and Uwe H. F. Bunz^{*a}

^a Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208, USA. E-mail: zurloye@sc.edu; bunz@mail.chem.sc.edu

^b Division of Biological and Physical Sciences, Lander University, Greenwood, South Carolina, USA

Received (in Columbia, MO, USA) 14th September 2001, Accepted 30th October 2001
First published as an Advance Article on the web 3rd December 2001

Reaction of the new ligand 1,2-dimethoxy-4,5-bis(2-pyridylethynyl)benzene with different metal centers under similar reaction conditions led to three distinct structure formation processes: molecular ring closure, dimerization, and polymer formation.

In synthetic, covalent organic chemistry the notion of conformers, oligomers and polymers are distinctly separated and irreconcilable. In supramolecular synthesis on the other hand this conception is less stringent. The utilized building blocks and the variety of binding forces that hold supramolecular assemblies together by arranging organic modules in the solid state makes the border of the very notions of conformers, cycles, and polymers more permeable. Here we wish to demonstrate that one organic module 1,2-dimethoxy-4,5-bis(2-pyridylethynyl)benzene **1** can form a supramolecular cycle, a dimer and polymer utilizing different inorganic connectors Cu(OAc)₂, CoCl₂ and [Rh(OAc)₂]₂.

Single crystals suitable for X-ray diffraction† of Cu(1)-(OAc)₂·CH₃OH **2** were obtained by layering a methanol solution (1 mL) of Cu(OAc)₂·H₂O (2.0 mg, 0.01 mmol) over a dichloromethane solution (1 mL) of **1** (6.7 mg, 0.02 mmol), with a layer of pure methanol separating them (20% yield). Crystals of [Co(**1**)Cl₂]₂ **3** were prepared similarly, substituting CoCl₂·6H₂O for Cu(OAc)₂·H₂O and ethanol for methanol (68% yield).‡ Crystals of *catena*-poly{[Rh(OAc)₂]₂**1**·CH₂Cl₂} **4** were prepared similarly to **2** except that [Rh(OAc)₂]₂ was substituted for Cu(OAc)₂·H₂O (maintaining the ligand to metal ratio) and ethanol was substituted for methanol (40% yield). These three systems each form a distinctly different structure and between them, demonstrate the importance of the free rotation of the pyridyl rings around the carbon–carbon bonds for facilitating the formation of the three structure types.

Compound **2** demonstrates the preference of Cu²⁺ for square planar coordination with copper positioned snugly between the two pyridyl rings. The resulting N–Cu–N (Cu–N 2.01 Å, N–Cu–N 172.98°) bonds close an eleven membered, triangular ring (Fig. 1), which is nearly identical to the structures reported by Bosch and Barnes for 1,2-bis(2-pyridylethynyl)benzene.² The square planar coordination of copper is completed by two *trans* oxygens from separate acetate groups.

Compound **3** contains Co²⁺, which is found in typical tetrahedral coordination.³ This tetrahedral preference, apparently, cannot be conveniently satisfied through a ring closure that would require a rotation of the pyridyl rings away from the 180° angle found in the copper complex. The result of such a rotation would be an elongated Co–N bond. Instead, the pyridyl rings rotate away from each other by 128° and bind to separate cobalt atoms with bond lengths of 2.03 Å, which is typical for Co–N bonds. The tetrahedral coordination in each case is completed by two chlorine atoms. The overall structure (Fig. 2) consists of two molecules of **1** bridging two cobalt atoms. An inversion center is located in the middle of the dimer.

The polymeric structure of **4** (Fig. 3) results from the linear coordination preference of [Rh(OAc)₂]₂. The structure consists

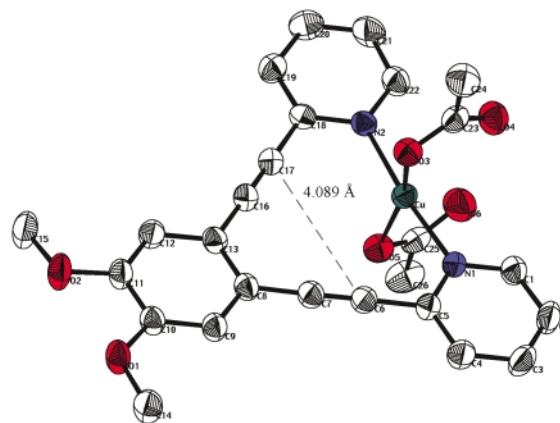


Fig. 1 A single molecule of **2**. The hydrogen atoms and methanol group have been omitted for clarity.

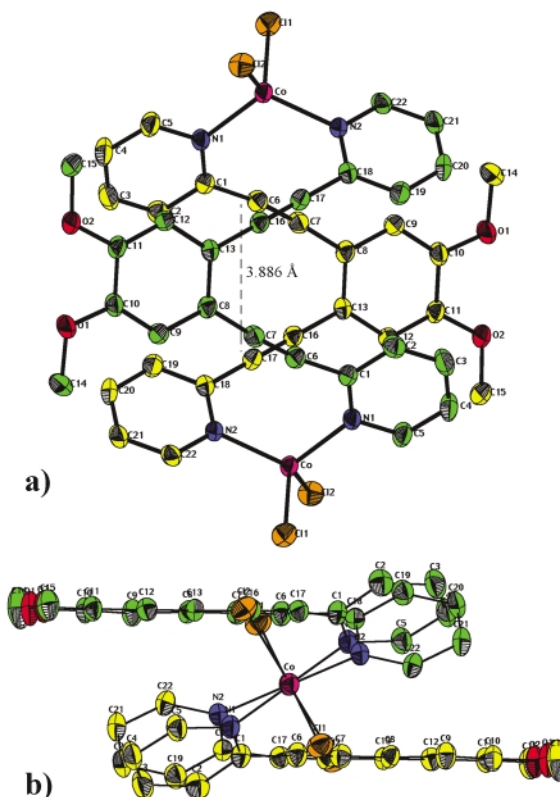


Fig. 2 Hydrogen atoms have been omitted for clarity. (a) a view of **3** from above showing the tetrahedral coordination of cobalt; (b) a view of **3** from the side showing the opposing orientations of **1** and the rotation of the pyridyl rings.

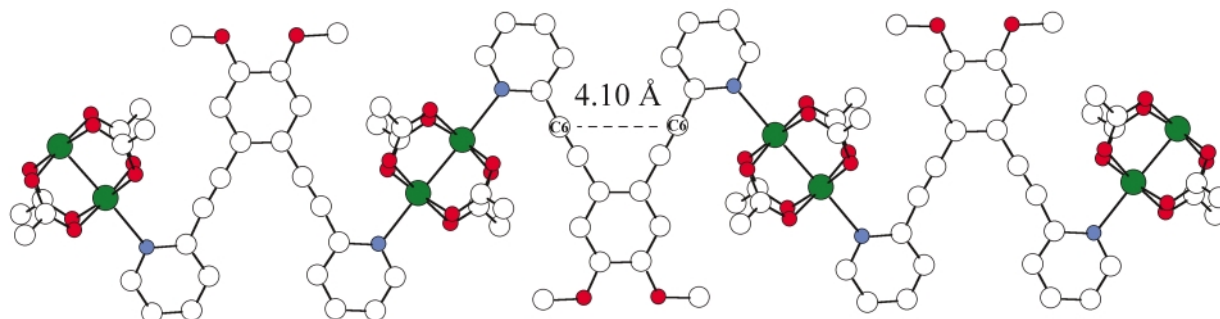


Fig. 3 A view of **4** showing the connectivity of **1** and the rhodium dimer. Hydrogens have been omitted for clarity.

of two acetate-bridged rhodium atoms that connect to the pyridyl rings of two separate molecules of **1** and mimics a conjugated organic polymer. The rhodium is six-coordinate with four equatorial oxygens from the acetate groups, one axial rhodium from the other half of the dimer and one nitrogen belonging to the pyridyl group on the ligand.

Tetrakis(carboxylato)rhodium compounds were first discovered in 1960,⁴ but it was not until 1981 that the first polymeric species containing such a rhodium dimer was synthesized.⁵ A survey of the CSD indicates that **1** is the largest ligand yet used in such a polymeric species. The polymeric structure is charge balanced, eliminating the need for counter ions competing for binding sites. This leads to higher site symmetry and makes such rhodium dimers attractive building blocks for coordination polymers.⁶ Because of its length, the dirhodium moiety cannot fit between the pyridyl rings and achieve ring closure, as in **2**, despite the favorable linear arrangement of the binding sites. Consequently, the pyridyl rings rotate outward by 180° to form a polymer chain with the rhodium dimer bridging adjacent ligands in a zig-zag fashion. This polymer is a supramolecular analogue of the hitherto unknown *ortho*-PPE⁷ and as such is a fascinating structure. The Rh–N distance within the polymer is 2.25 Å, typical for Rh–N bonds in such systems.^{5,8–10}

One interesting aspect of these structures are the carbon–carbon separations between the alkyne groups on the ligand **1** which, if close enough, could potentially be crosslinked in a Bergman reaction.¹¹ In **2**, the closed ring conformation results in a C6...C17 separation of 4.089 Å. This is almost the same as the C6...C6 distance of 4.100 Å in **4**, which should represent an unstrained system. By comparison, in **3**, the C6...C17 distance within the same molecule of **1** is 3.886 Å, while the alkyne groups on separate ligands are only 3.548 Å apart (within the range for π – π interactions). This suggests that the copper cation fits between the pyridyl rings without inducing any strain, while in **3**, the dimer formation strains the ligand, bending the pyridyl ligands towards one another, which effects a shorter C6...C17 distance.

These three structures demonstrate the diversity, which can be achieved using **1** that is made possible by the ability of the ligand to distort itself to the preferred coordination environment of the metal center. While one may expect a slight bending of the pyridylethynyl legs either towards or away from each other, these three structures show that rotation of the pyridyl ring around the ethynyl linkage seems more favorable.

Financial support was provided in part by the National Science Foundation through Grants DMR:9873570 and CHE:9814118 and in part by the South Carolina Commission on Higher Education through Grant CHE:R00-U25. The Bruker CCD Single Crystal Diffractometer was purchased using funds

provided by the NSF Instrumentation for Materials Research Program through Grant DMR:9975623.

Notes and references

† *Synthesis* of the ligand **1**: under nitrogen, 1,2-dimethoxy-4,5-diiodobenzene (2.00 g, 5.28 mmol),¹² 2-ethynylpyridine (1.09 g, 10.6 mmol),¹³ (Ph₃P)₂PdCl₂ (50 mg, 71 μmol), CuI (50 mg, 263 μmol) and piperidine (15 mL) are placed in a Schlenk flask and stirred for 24 h at ambient temperature. Aqueous workup followed by chromatography with EtOAc–hexanes (1:9) furnishes the ligand in 22% yield (395 mg) as a colorless powder (mp 154 °C). Spectroscopic data: IR, ν/cm^{-1} 2200 (m), 1590 (w), 1570 (s), 1550 (w), 1510 (s), 1460 (m), 1450 (m), 1435 (w), 1425 (w) 1415 (w), 1360 (s). ¹H NMR (CD₃CN), δ 3.90 (s, 6H, OCH₃), 7.24 (s, 2H, aryl-H), 7.38 (ddd, 2H, pyridyl-H), 7.77 (dt, 2H, pyridyl-H), 7.82 (td, 2H, pyridyl-H), 8.65 (d, 2H, pyridyl-H). ¹³C NMR (CDCl₃), δ 150.28, 149.812, 143.83, 136.38, 127.54, 122.92, 118.65, 114.67, 91.94, 88.33, 56.34. MS EI, *m/z* 340 (100%, M⁺), 341 (25%, M⁺), 342 (5%, M⁺), 325 (M⁺ – CH₃, 15%), 309 (M⁺ – OCH₃, 4%), 263 (M⁺ – pyridine, 97%).

‡ *Crystal data* for **2**: C₂₇H₂₆CuN₂O₇, *M* = 554.04, triclinic, space group *P* $\bar{1}$, *a* = 8.2357(4), *b* = 12.5088(6), *c* = 13.3128(6) Å, α = 78.3000(10)°, β = 72.1170(10)°, γ = 76.6810(10)°, *U* = 1257.12(10) Å³, *T* = 293(2) K, *Z* = 2, λ = 0.71073 Å, 11656 reflections measured, 5144 unique (*R*_{int} = 0.0199) which were used in all calculations. *R*₁ = 0.0374 and *wR*₂ = 0.0922. For **3**: C₄₄H₃₂Cl₄Co₂N₄O₄, *M* = 940.40, monoclinic, space group *P*2₁/*n*, *a* = 8.5272(6), *b* = 18.3653(13), *c* = 13.3493(9) Å, β = 103.574(2)°, *U* = 2032.2(2) Å³, *T* = 190(2) K, *Z* = 2, λ = 0.71073 Å, 13541 reflections measured, 4156 unique (*R*_{int} = 0.0347) which were used in all calculations. *R*₁ = 0.0504 and *wR*₂ = 0.1107. For **4**: C₃₁H₃₀Cl₂N₂O₁₀Rh₂, *M* = 867.29, monoclinic, space group *C*2/*c*, *a* = 21.5985(13), *b* = 20.2480(12), *c* = 8.0207(5) Å, β = 103.2650(10)°, *U* = 3414.1(4) Å³, *T* = 190(2) K, *Z* = 4, λ = 0.71073 Å, 15208 reflections measured, 3504 unique (*R*_{int} = 0.0545) which were used in all calculations. *R*₁ = 0.0613 and *wR*₂ = 0.1222. CCDC reference numbers 173558–173560. See <http://www.rsc.org/suppdata/cc/b1/b109849g/> for crystallographic data in CIF or other electronic format.

- S. Shotwell and U. H. F. Bunz, manuscript in preparation.
- E. Bosch and C. L. Barnes, *Inorg. Chem.*, 2001, **40**, 3097.
- N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Reed Educational and Professional Publishing, Oxford, 2nd edn., p. 1129.
- I. I. Chernyaev, E. V. Shenderetskaya and A. A. Karyaguba, *Russ. J. Inorg. Chem.*, 1960, **5**, 559.
- F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1981, **20**, 600.
- F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, in press.
- R. H. Grubbs and D. Kratz, *Chem. Ber.*, 1993, **126**, 149.
- T. Niu, J. Lu, G. Crisci and A. J. Jacobson, *Polyhedron*, 1998, **17**, 4079.
- H. Kitamura, T. Ozawa, K. Jitsukawa, H. Masuda, Y. Aoyama and H. Einaga, *Inorg. Chem.*, 2000, **39**, 3294.
- F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1981, **20**, 584.
- R. G. Bergman, *Acc. Chem. Res.*, 1973, **6**, 25; T. Chandra, J. C. Huffman and J. M. Zaleski, *Inorg. Chem. Commun.*, 2001, **4**, 434.
- J. D. Kinder and W. J. Youngs, *Organometallics*, 1996, **15**, 460.
- D. E. Ames, D. Bull and C. Takundwa, *Synthesis*, 1981, 364.