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Two Types of New Polymeric Copper(I) Complexes of Pyrazinecarboxamide Having Channel and Helical Structures

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Introduction

The development of new synthetic strategies for the self-assembly of infinite molecular components with specific network topologies is of current interest.[1] Pyrazine and substituted pyrazines have long been known to act as *exo*-bidentate ligands to linearly bridge metal ions, generating oligomeric and polymeric metal complexes with infinite-chain and pleated-sheet structures,[2] double and triple interpenetrating frameworks[3] and interwoven honeycomb architecture.[4] We are exploring ways to modify the substituents to tailor the copper/pyrazine and silver/pyrazine polymer structures as to mode of polymerization, dimensionality, and the framework,[5−8] Scheme 1. Here we report copper(I) coordination polymers with the tridentate ligand 2-pyrazinecarboxamide (pzca). We have found that it is possible to use this simple molecular building block to generate unusual hexanuclear circular arrays of ligand-bridged Cu(I) ions. Depending upon whether the counterion is perchlorate or tetrafluoroborate, these arrays assemble respectively as a channel structure or as a single cyclic helix.

Experimental Section

Reduction of an acetone solution (5 mL) of copper(II) perchlorate hexahydrate (0.015 mM, 5.6 mg) by copper metal sheets under an ethylene atmosphere afforded a colorless copper(I) solution, to which pzca (0.03 mM, 3.7 mg) was added. The solution was stirred and filtered, and the filtrate was allowed to stand in a 7 mm diameter glass tube for 2 days in a thermobottle at 50 °C, initially yielding deep red columnar crystals of $[Cu_2(pzca)_3](ClO_4)_2(Me_2CO)_2$ (**1**) (yield 42%). Anal. Calcd for $C_{21}H_{27}Cu_2Cl_2N_9O_{13}$: C, 31.08; H, 3.35; N,15.53. Found: C, 31.02; H, 3,17; N, 15.24. Although acetone molecules act as guests in the channel structure (see Results and Discussion), they were not observed in the IR spectrum and X-ray analysis indicated that they were lost after the crystals were exposed to argon for 3 days. A similar reaction was carried out in thermostat at 55 °C using $Cu(BF_4)_2 \cdot 6H_2O$ in place of $Cu(ClO_4)_2 \cdot 6H_2O$, and red brick-shaped crystals of $[Cu(pzca)(Me_2CO)_{0.5}](BF_4)$ (**2**) were formed at the interface (yield 37%). Anal. Calcd for $C_{6.5}H_8CuF_4N_3O_{1.5}B$: C, 25.81; H, 2.67; N,13.89. Found: C, 25.67; H, 2.41; N, 13.52. The infrared spectra of both **1** and **2** exhibit a shift of the C═O stretching band from 1714 cm^{-1} for the free pzca to 1705 cm^{-1}. Upon coordination, the stretching frequency of C═N at 1612 cm^{-1} for the ligand is observed at 1620 and 1630 cm^{-1} for **1** and **2**, respectively.

Scheme 1

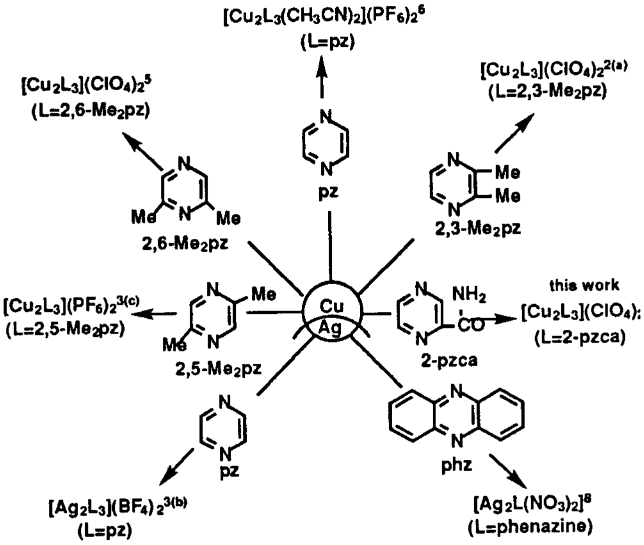

Table 1. Crystallographic Data for $[Cu_2(pzca)_3](ClO_4)_2(Me_2CO)_2$ (**1**) and $[Cu(pzca)(Me_2CO)_{0.5}](BF_4)$ (**2**)

	1	**2**
empirical formula	$C_{21}H_{27}Cl_2Cu_2N_9O_{13}$	$C_{13}H_{16}Cu_2N_6F_8B_2O_3$
fw	811.49	605.01
space group	$P2_1/a$	$Fdd2$
a, Å	10.979(7)	21.460(5)
b, Å	20.291(4)	24.199(1)
c, Å	14.715(6)	8.449(3)
β, deg	91.07(4)	
V, Å^3	3277(2)	4387(1)
Z	4	8
ρ_{calc}, g cm^{-3}	1.632	1.832
T, K	296	296
μ(Mo Kα), cm^{-1}	15.34	20.35
R[a]	0.067	0.043
R_w[b]	0.075	0.047

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$.

Crystal data for **1** and **2** are given in Table 1. Red columnar crystals, of dimensions 0.10 × 0.10 × 0.10 mm and 0.20 × 0.15 × 0.10 mm for **1** and **2**, respectively, were mounted in a glass capillary, and room-temperature intensity data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation in the $\omega-2\theta$ scanning mode. Each structure was determined by direct methods (MITHRIL)[9] and refined by full matrix least-squares minimization of

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(1) (a) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992; Chapter 19. (b) Mann, S. *J. Chem. Soc., Dalton Trans.* **1993**, 1. (c) Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807. (d) Iwamoto, T. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1991; Vol. 5, Chapter 6, pp 177−212.

(2) (a) Turnbull, M. M.; Pon, G.; Willett, R. D. *Polyhedron* **1991**, *10*, 1835. (b) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1989**, *67*, 1964. (c) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1990**, *68*, 1901. (d) Jung, O.-S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 2229.

(3) (a) Soma, T.; Yuge, H.; Iwamoto, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1665. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562. (c) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Inorg. Chem.* **1993**, *32*, 1607.

(4) MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325.

(5) Kitagawa, S.; Kawata, S.; Kondo, M.; Nozaka, Y.; Munakata, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3387.

(6) Kitagawa, S.; Munakata, M.; Tanimura, T. *Inorg. Chem.* **1992**, *31*, 1714.

(7) Kawata, S.; Kitagawa, S.; Kondo, M.; Furuchi, I.; Munakata, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1759.

(8) Kuroda-Sowa, T.; Munakata, M.; Matsuda, H.; Akiyama, S.; Maekawa, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2201.

(9) Gilmore, C. J. MITHRIL, an integrated direct method computer program. *J. Appl. Crystallogr.* **1984**, *17*, 42.

S0020-1669(97)00427-8 CCC: $14.00

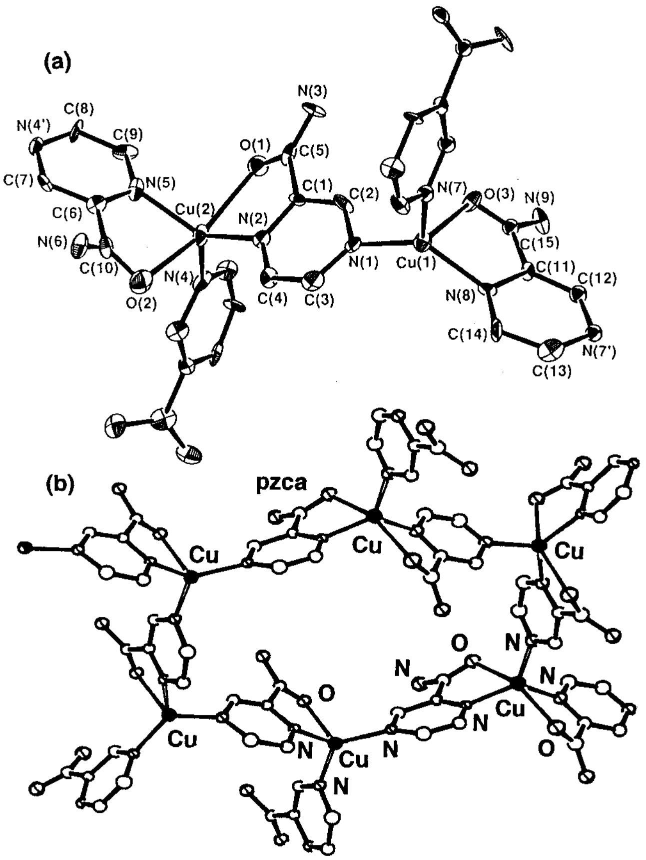

Figure 1. Local coordination around the copper atoms in **1**: (a) atom-numbering scheme; (b) hexagonal array of copper atoms connected by the ligand. Cu(1)−N(1) = 1.98(2), Cu(1)−N(7) = 1.97(2), Cu(1)−N(8) = 1.99(2), Cu(1)−O(3) = 2.23(2), Cu(2)−N(2) = 2.01(2), Cu(2)−N(4) = 1.97(2), Cu(2)−N(5) = 2.00(2), Cu(2)−O(1) = 2.40(2), Cu(2)−O(2) = 2.46(2) Å, O(3)−Cu(1)−N(1) = 99.5(8), O(3)−Cu(1)−N(7) = 105.5(8), O(3)−Cu(1)−N(8) = 77.7(8), N(1)−Cu(1)−N(7) = 115.2(8), N(1)−Cu(1)−N(8) = 131.0(8), N(7)−Cu(1)−N(8) = 112.5(9), O(1)−Cu(2)−O(2) = 155.7(6), O(1)−Cu(2)−N(2) = 76.5(8), O(1)−Cu(2)−N(4) = 100.6(9),O(1)−Cu(2)−N(5) = 95(1), O(2)−Cu(2)−N(2) = 92.1(8), O(2)−Cu(2)−N(4) = 104(1),O(2)−Cu(2)−N(5) = 76(1), N(2)−Cu(2)−N(4) = 118.1(9), N(2)−Cu(2)−N(5) = 129.5(9), N(4)−Cu(2)−N(5) = 112.4(9)°.

$\sum w(|F_o| - F_c|)^2$ with anisotropic thermal parameters for all the non-hydrogen atoms. All of the calculations were performed using the TEXSAN package[10] on a micro VAX computer.

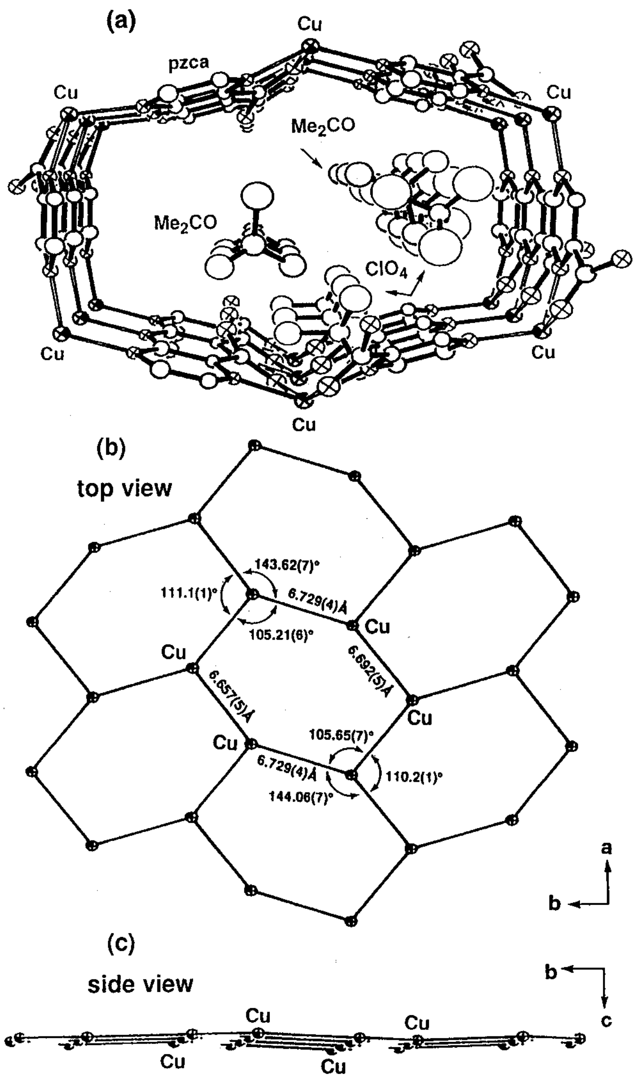

Figure 2. (a) The hexagonal motif in **1** extending along the *c* axis to give hexagonal channels with pores open to accommodate ClO_4^- ions and acetone molecules. (b) Top and (c) side views of the 2D sheet network of **1**, where only copper atoms are shown.

Results and Discussion

The fact that two very different compounds were obtained from the two similar syntheses indicates that the counteranions play an important role not only in obtaining large crystals suitable for X-ray analysis but also in regulating the coordination of solvent molecules to the metal ions. Figure 1 shows the local coordination around the copper atoms in **1**. Complex **1** contains noninteracting ClO_4^- anions and macrocations $[Cu_2(pzca)_3]^{2+}$ in which there are two crystallographically independent copper(I) ions. The Cu(1) ion involves a distorted trigonal pyramidal CuN_3O core, generated by the terminal pyrazine nitrogens of three different pzca molecules and an axial carboxamide oxygen. The geometry around the Cu(2) atom, however, is distorted trigonal bipyramidal with two, rather than one, carboxamide oxygens occupying the apical positions. Each pzca molecule exhibits a tridentate coordination mode bridging two metal centers. All the ligands are aligned so that their planes are parallel to the *c* axis. The copper atoms bind them into a hexagonal motif which extends throughout the structure along the *c* axis, giving apparently hexagonal channels with pores open (6.7 × 12.8 Å) to accommodate ClO_4^- ions and acetone molecules as guests in the crystal, Figure 2. Thus, such a channel structure, like the materials with microchannels and micropores, can also be viewed as composed of host frameworks.[11] The average Cu−Cu separation within the hexagon is 6.69 Å, preclusive of any direct metal−metal interactions. Although similar planar sheets composed of hexagonal Cu_6 motifs have been observed for the three-coordinate copper(I) polymer of 2,6-dimethylpyrazine and the four-coordinate copper(I) complex of pyrazine,[5,6] the present work describes the first example of mixed four- and five-coordinate copper(I) ions comprising such a hexagon. This is attributable to the fact that each pzca acts as a tridentate ligand linking two Cu(I) ions.

A crystallographic analysis of **2** reveals that the extended structure of the cation $[Cu(pzca)(Me_2CO)_{0.5}]^+$ is made up of the building-block unit shown in Figure 3: each metal atom is linked to two pzca ligands, forming a distorted trigonal plane, and axially bridged to another metal center by one acetone molecule with a Cu−O(2) distance of 2.423(9) Å. Acetone is commonly found as a molecule of solvation in complexes, and the occurrence of acetone as a ligand in copper(I) and

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(10) *TEXSAN-TEXRAY Structural Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.

(11) Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: New York, 1978.

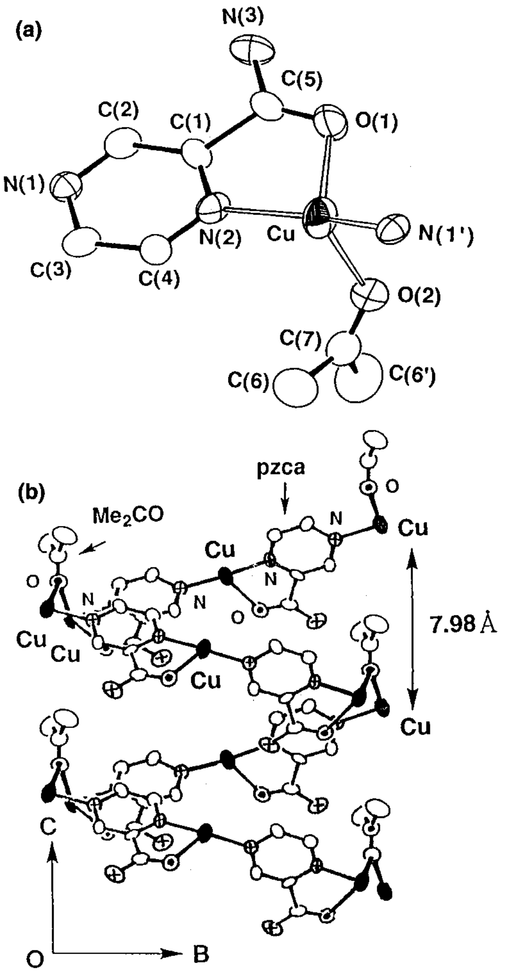

Figure 3. The local coordination around the copper atoms in **2**: (a) atom-numbering scheme; (b) a helix formed by six copper atoms, four pzca ligands, and two acetones. Cu−N(1) = 1.933(9), Cu−N(2) = 1.924(9), Cu−O(1) = 2.230(8), Cu−O(2) = 2.423(9) Å; O(1)−Cu−O(2) = 101.3(3), O(1)−Cu−N(1) = 114.5(4), O(1)−Cu−N(2) = 79.6(4), O(2)−Cu−N(1) = 102.4(3), O(2)−Cu−N(2) = 101.2(3), N(1)−Cu−N(2) = 149.2(4)°.

copper(II) chemistry is very limited.[12,13] Each tridentate pzca molecule, as in **1**, links two metal centers, and all ligand groups extend approximately along the *c* axis, which gives rise to an infinite helical structure. The most remarkable feature of **2** is that the infinite helices generate a two-dimensionally extended hexagonal array of Cu atoms with a large cavity where the counteranions, BF_4^-, are placed. Figure 4 shows these features with a space-filling model of the cation illustrating the helical structure. Organic and inorganic polymers existing in helical structures are of great practical and theoretical interest.[14] Most previously reported single- and double-helical polynuclear copper(I) and silver(I) complexes based on oligopyridine or oligophenanthroline ligands are generated by the complexation of two ligands twisted around the tetrahedral metal ions lying on the helical axis.[15,16] The helical structure of **2** is unique in a sense that it is composed of a hexanuclear copper unit bridging two acetone and four pzca molecules. In this structure, the primary coordination involves pzca groups tridentately bridging two copper atoms, and the helical structure is further stabilized by secondary interactions between Cu atoms and the bridging acetone as a continuous strand. It demonstrates that assembled helical structures of copper(I) complexes with tridentate oligopyrazine ligands, rather than bidentate oligopyridine or oligophenanthroline ligands, can also be achieved by introducing a suitable spacer group like acetone between the metal-binding sites to match the metal ion stereochemical preference.[16] The conditions for self-assembly of the Cu(I)/pzca polymer derived from the detailed study of complex **2** might be able to be applied to different systems for the successful synthesis of many other helical coordination compounds.

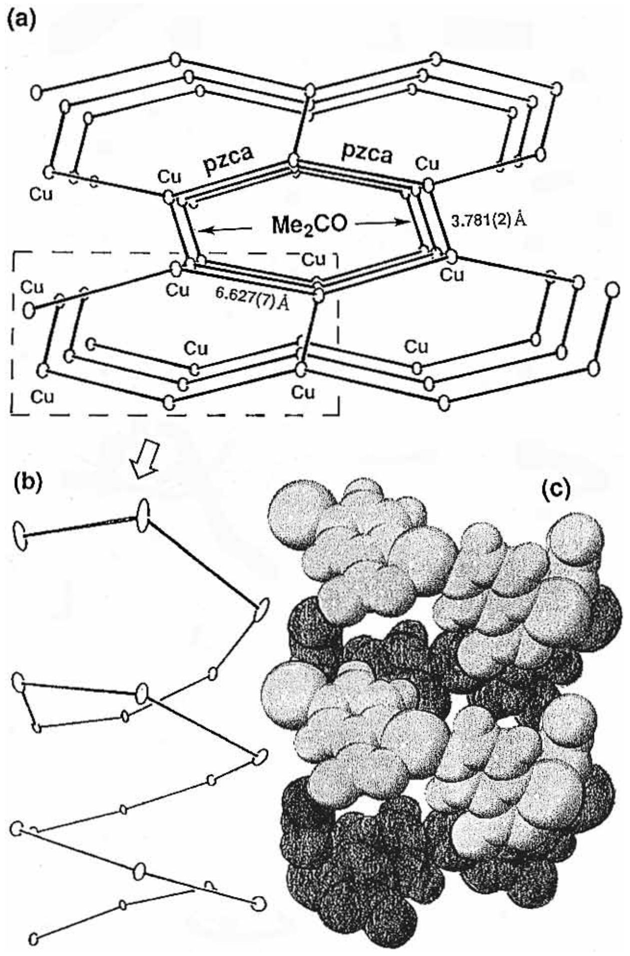

Figure 4. (a)The infinite helices in **2** generating an extended hexagonal array of Cu atoms with a large cavity. (b) The helical cyclic array, where only copper atoms are shown. (c) Space-filling model of **2**. BF_4^- ions are omitted for clarity.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and intramolecular bond lengths and angles for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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[12] Smith, G.; O'Reilly, E. J.; Kennard, C. H. L.; Mak, T. C. W.; Yip, W.-H. *Polyhedron* **1985**, *4*, 451.

[13] Munakata, M.; Kitagawa, S.; Emori, T. *J. Chem. Soc., Chem. Commun.* **1991**, 1244.

[14] (a) Garrett, T. M.; Koert, U.; Lehn, J.-M.; Rigault, A.; Meyer, D.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 557. (b) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995. (c) Ohta, N.; Masuda, H.; Yamauchi, O. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 531.

[15] Gelling, O. J.; van Bolhuis, F.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1991**, 917.

[16] (a) Piguet, C.; Bernardinelli, G.; Bocquet, B.; Quattropani, A.; Williams, A. F. *J. Am. Chem. Soc.* **1992**, *114*, 7440. (b) Rüttimann, S.; Piguet, C.; Bernardinelli, G.; Bocquet, B.; Williams, A. F. *J. Am. Chem. Soc.* **1992**, *114*, 4230.