

Communications to the Editor

A Two-Dimensional Geomimetic Coordination Polymer Containing Pentagonal Cavities

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One-step, self-assembly of metal cations and multitopic ligands¹ into one-, two-, and three-dimensional networks has spawned an explosion of “coordination solids” in recent years.² Equipped with the knowledge of both the metal’s coordination preferences and ligand geometry, chemists have succeeded in producing “molecular minerals” of several three-dimensional (3D) structure types including, PtS,³ NbO,⁴ rutile,⁵ and quartz.⁶ In this paper, we show that by employing the correct combination of bridging and terminal ligands, a novel two-dimensional (2D) coordination network can be formed, which possesses a structural motif never before seen in coordination polymers, but one that is closely related to *nekoite*, a naturally occurring sheet silicate mineral.

Our inspiration for designing coordination polymers using this building-block approach is drawn from silicate crystal chemistry. In terms of structural diversity silicate minerals are an attractive class of target compounds; identical building blocks (corner-shared SiO₄ tetrahedra) condense in a multitude of ways creating a vast array of structure types, including single and double chains, sheets, and numerous 3D frameworks. We recently reported the structures of two 3D coordination networks, and several 1D chains based on Cu(I) centers linked by four⁷ and two⁸ bent, bridging ligands, respectfully, which have mineral analogues. Although many layered coordination polymers have been reported, typically octahedral (four equatorial bridging ligands, two axial terminal ligands or anions)⁹ or square-planar complexes¹⁰ are linked into

grids; none have been fashioned from the building blocks of layered silicates. The *phyllosilicates* are layered crystalline minerals in which each *tetrahedral* silicon atom is coordinated by three bridging oxygen atoms and one terminal ligand (usually hydroxide, but occasionally halide or terminal oxygen).¹¹ Here we communicate the synthesis and crystal structure of a new coordination polymer, which combines both bridging and terminal ligands *on the same metal center* to form a porous 2D extended lattice. The defining structural units are the fused *pentagons* that comprise the layers, a motif never before seen in coordination polymers.

Layering of THF onto CHCl₃ solutions containing [Cu(PPh₃)₂(MeCN)₂]BF₄ and 4,4'-bipy¹² affords yellow, platelike prismatic crystals of [Cu(4,4'-bipyridine)_{1.5}(PPh₃)₃]BF₄·(THF)_{1.33}(CHCl₃)_{0.33}, **1**, after 1 day, which were suitable for single-crystal X-ray diffraction.¹³ The asymmetric unit contains three crystallographically unique copper atoms, although all are coordinated to three 4,4'-bipyridine (bipy) ligands and one triphenylphosphine (PPh₃). There are slight differences in Cu–N bond lengths between the copper atoms and all of the N–Cu–N angles are compressed from the tetrahedral angle due to the steric bulk of the phosphine ligand. The linear bipyridine ligands bridge Cu(I) centers, as has been observed in dozens of metal–bipy coordination polymers,¹⁴ but the *connectivity* of the building blocks in **1** is unprecedented. As shown in Figure 1, five copper atoms (corners) and five bipy ligands (sides) assemble into a nearly regular *pentagon*, with narrow ranges of Cu–Cu distances (11.18–11.22 Å) and Cu–Cu–Cu angles (103–108°) around the circumference of the five-membered rings.

To each Cu(I) center is coordinated a third bridging bipy ligand (not shown in Figure 1). These connections fuse the pentagons into corrugated ribbons, which are themselves laterally extended through large elliptical eight-membered rings, as shown in Figure 2a. The cavity center-to-center distances are ca. 23 and 13 Å, for the eight-membered rings and pentagonal rings, respectively, within which are contained the solvated THF and CHCl₃ molecules as well as the necessary charge-balancing, but nonco-

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(12) To [Cu(PPh₃)₂(MeCN)₂]BF₄ (110 mg in 3 mL of CHCl₃) as synthesized previously (Green, J.; Sinn, E.; Woodward, S.; Butcher, R. *Polyhedron* **1993**, *12*, 991) was added 60 mg 4,4'-bipyridine in 3 mL of CHCl₃. Approximately 4 mL of THF was carefully added to the top of the solution and allowed to diffuse at room-temperature overnight.

(13) Diffraction data for **1** were collected at –100 °C using a Siemens SMART system equipped with a CCD area detector on a yellow plate (0.4 × 0.2 × 0.05 mm) of [Cu(4,4'-bipyridine)_{1.5}(PPh₃)₃]BF₄·solvent. The SHELXTL program suite (Sheldrick, G. SHELXS and SHELXL, University of Göttingen, Germany, and Barbour, L. RES2INS, University of Missouri—Columbia, **1998**) was used for the initial solution and subsequent least-squares refinements. Monoclinic, space group: *P*2₁/*c*, *a* = 26.201(1) Å, *b* = 23.579(1) Å, *c* = 19.075(1) Å, β = 94.479(1)°, *Z* = 12, *V* = 11748(1) Å³, Final *R*₁ = 0.0896 for 16213 unique reflections, 1303 parameters, and 15 restraints: final restrained GOF = 1.045. There are four THF molecules and one CHCl₃ molecule per asymmetric unit (which contains three copper atoms); therefore, the stoichiometries are given as fractions per copper atom in the formula of the title compound. Upon exposure to air, the crystals rapidly become opaque and lose their single-crystal diffracting capability but remain yellow, indicating a loss of solvent, but not oxidation of the Cu(I). Full descriptions of the crystal structure solution and refinement details are provided as Supporting Information.

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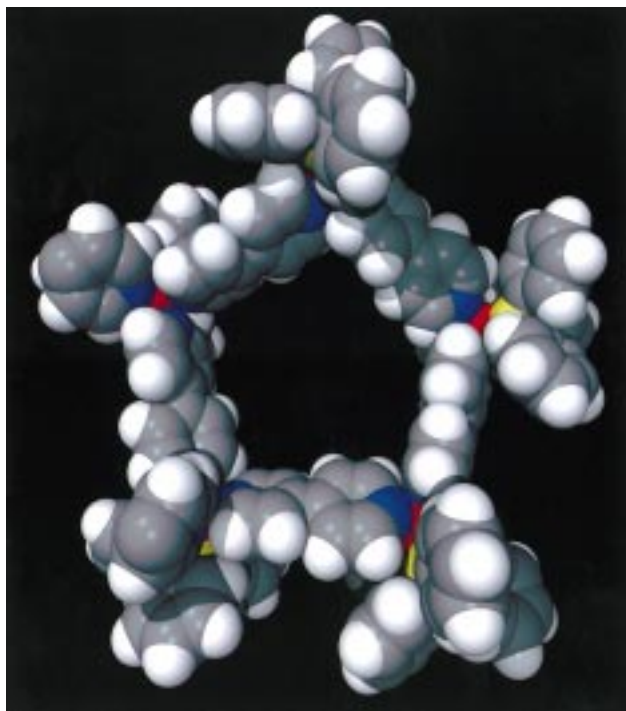


Figure 1. Space-filling representation of the pentagonal structure in **1**. Each of the copper atoms at the corners has an additional coordinated bipy (only one of the rings is shown) that bridge to other copper atoms. Cu, red; N, blue; P, yellow; C, gray; H, white.

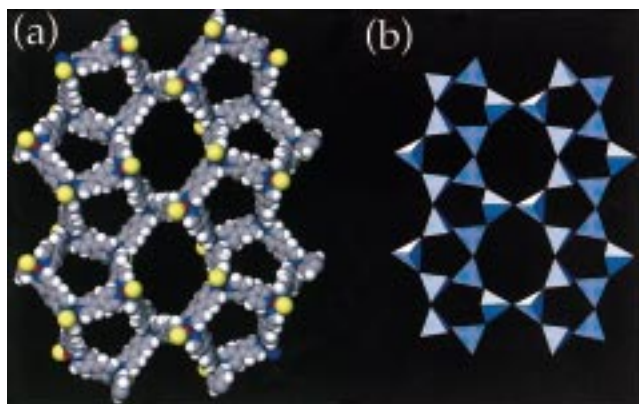


Figure 2. Comparison of the space-filling representation of the layered framework of **1**, (a), with the polyhedral representation of the silicate network in nekoite, $\text{Ca}_3\text{Si}_6\text{O}_{15}\cdot 7\text{H}_2\text{O}$, (b). Color scheme in 2a is identical to Figure 1, and the phenyl rings of the PPh_3 ligands in (a) are omitted for clarity.

ordinating BF_4^- anions. Although **1** represents a novel, very complex coordination motif, silicate crystal chemistry provides a geological analogue. Figure 2b displays the polyhedral representation of the Si–O network of the mineral *nekoite*, a hydrated sheet silicate, which also contains ribbons of fused pentagons

connected through elliptical eight-membered rings.¹⁵ A subtle orientational difference between the tetrahedra lining the eight-membered rings arises from an inversion center in **1** that is absent in the chiral silicate. Nevertheless, the *connectivity* of the tetrahedral networks is identical, and the similarity between these very complex structures—having quite different chemical compositions—is remarkable.

We emphasize that the geometrical influence of the terminal PPh_3 group is vital to the formation of the novel structure. In stoichiometrically equivalent frameworks (metal:ligand = 1:1.5) having other coordination geometries (octahedral, T-shaped, or square-planar) very different structures are obtained including ladders,¹⁶ 3D nets,¹⁷ and bilayers.¹⁸ Stang et al. discussed the fact that bidentate tetrahedral corners linked with linear ligands have the correct geometry to form isolated pentagons and further hypothesized the construction of an isolated, closed dodecahedron from tridentate metal centers (with “tetrahedral bond angles” and linear bridging ligands).¹⁹ Under our crystallization conditions, the pentagons are formed, but instead of forming a closed-shell polyhedron with all terminal PPh_3 groups pointed “out”, each pentagon has two “up” and three “down” phosphines (or vice versa), forming the extended sheet structure.

The layers lie slightly offset from one another, to accommodate a PPh_3 group from the layer above and below to partially occupy the large elliptical voids. Interestingly, the resulting zigzag pentagonal channels include all three “guest” species, chloroform, THF, and BF_4^- anions, but the constricted eight-membered ring channels contain *only* THF and anions. Natural clays often display varying degrees of hydration, with the well-known lattice swelling. We envision the solvent molecules and noncoordinated anions as possibly analogous weakly coordinated interlayer species. These weak interactions, coupled with the molecular segregation described above, and the juxtaposition of the phosphine ligands lining the “walls” of only the eight-membered ring channels, bodes well for further chemical functionalization by incorporating readily available PR_3 derivatives.

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Supporting Information Available: Numbered ORTEP diagrams, tables of crystallographic data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen positions for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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