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Unprecedented Homochiral Olefin−Copper(I) 2D Coordination Polymer Grid Based on Chiral Ammonium Salts as Building Blocks

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Summary: 4-Vinylbenzylcinchonidinium chloride ([VB-N-CIN]Cl; ***1****), prepared from the corresponding cinchona alkaloid and 4-vinylbenzyl chloride in refluxing acetone and N,N-dimethylformamide, solvothermally reacts with* Cu^ICl *to afford the unprecedented 2D homochiral copper(I)−olefin coordination polymer* Cu_5Cl_6*(VB-N-CIN)*$_2$·C_2H_5OH *(***2***·EtOH) with a 2D layered network. A preliminary enantioseparation investigation shows that the 2D layered network in* ***2*** *is capable of selectively intercalating (R)-2-butanol.*

Chiral phase transfer catalysts (PTCs) have been increasingly used in organic synthesis because ion-pair-mediated reactions with high enantiomeric excess (ee) can occur under phase transfer conditions.[1] Among these catalysts, cinchona alkaloid derived quaternary ammonium salts have been excellent candidates in catalytic asymmetric synthesis and, thus, have received much attention recently. In particular, resin-bound cinchonidine and cinchonine have been employed as recoverable PTCs.[2] From a metal coordination polymer (MCP) point of view, these compounds give us a hint that MCP with PTC as building blocks will be useful in asymmetric catalysis and enantioseparation because MCP can mimic some properties of zeolites.[3,4] Supramolecular motifs based on MCP with PTC as chiral building blocks, to the best of our knowledge, have not been reported in the literature and remain largely unexplored.

Homochiral coordination polymers where all crystals have the same handedness can display the added advantage of offering applications in heterogeneous asymmetric catalysis and enantioselective separation.[4] We reported recently the first homochiral coordination polymer (or zeolite analogue) used for the resolution of a racemic mixture.[5a] Furthermore, we have been investigating coordination networks involving copper−olefin interactions[6] and successfully assembled the first homochiral copper−olefin networks with a 2D layered grid topology in which they failed to display any enantio-intercalation of racemic molecules.[6f] Thus, a successful access to an enantio-resolvable zeolite analogue composed of olefin−copper polymer has been a great challenge.[7] With this in mind, we noticed on that Cu^ICl easily forms an anion cluster with halide bridging linkers while the cluster can coordinate to the cationic ligand with an olefin moiety to form supramolecular arrays. One chiral quaternary ammonium salt candidate that fulfills these requirements is *N*-4-vinylbenzylcinchoninium chloride (I). This compound not only supplies a Cl anion as a bridging linker to bind with Cu(I) to form an anionic cluster but also contains a pyridyl group and two olefin moieties which are easily coordinated to Cu(I). The enantiopure chiral building block (VB-N-CIN, **1**), which is prepared from off-the-shelf cinchona and 4-vinylbenzyl chloride, ethanothermally reacts with Cu^ICl to give the novel homochiral 2D layered Cu_5Cl_6(VB-N-CIN)$_2$·C_2H_5OH (**2**·EtOH), in which an ethanol molecule is intercalated between the layers (Scheme 1).

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(1) O'Donnell, M. J.; Benett, W. D.; Wu, S. *J. Am. Chem. Soc.* **1989**, *111*, 2353. (b) Lygo, B.; Wainwright, P. G. *Tetrahedron Lett.* **1997**, *38*, 8595. (c) Corey, E. J.; Xu, F.; Noe, M. C. *J. Am. Chem. Soc.* **1997**, *119*, 12414. (d) Ooi, T.; Kaneda, M.; Marruoka, K. *J. Am. Chem. Soc.* **1999**, *121*, 6519.

(2) (a) Zhang, Z.; Wang, Y.; Zhen, W.; Hodge, P. *React. Funct. Polym.* **1999**, *41*, 37. (b) Chinchilla, R.; Mazon, P.; Najera, C. *Tetrahedron: Asymmetry* **2000**, *11*, 3277.

(3) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jin, Y.; Kim, K. *Nature* **2000**, *404*, 982. (b) Chin, J.; Lee, S. S.; Lee, K. J.; Park, S.; Kim, D. H. *Nature* **1999**, *401*, 254.

(4) (a) Mallouk, T. E.; Gavin, J. A. *Acc. Chem. Res.* **1998**, *31*, 209 and references therein. (b) Evans, O. R.; Ngo, H. L.; W. Lin, *J. Am. Chem. Soc.* **2001**, *123*, 10395. (c) Cui, Y.; Evans, O. R.; Ngo, H. L.; White, P. S.; Lin, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 1159. (d) Pschire, N. G.; Ciurtin, D. M.; Smith, M. D.; Bunz, U. H. F.; Zur Loye, H. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 583.

(5) (a) Xiong, R.-G.; You, X.-Z.; Abrahams, B. F.; Xue, Z.; Che, C.-M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4422. (b) Xiong, R.-G.; Zuo, J.-L.; You, X.-Z.; Fun, H.-K.; Raj, S. S. S. *New J. Chem.* **1999**, *23*, 1051. (c) Chen, Z.-F.; Zhang, J.; Xiong, R.-G.; You, X.-Z. *Inorg. Chem. Commun.* **2000**, *3*, 493. (d) Xie, Y.-R.; Xiong, R.-G.; Xue, X.; Chen, X.-T.; Xue, Z.; You, X.-Z. *Inorg. Chem.* **2002**, *41*, 3323.

(6) (a) Zhang, J.; Xiong, R.-G.; Zuo, J.-L.; You, X.-Z. *Chem. Commun.* **2000**, 1495. (b) Zhang, J.; Xiong, R.-G.; Zuo, J.-L.; Che, C.-M.; You, X.-Z. *J. Chem. Soc., Dalton Trans.* **2000**, 2898. (c) Zhang, J.; Xiong, R.-G.; Chen, X.-T.; Che, C.-M.; Xue, Z.; You, X.-Z. *Organometallics* **2001**, *20*, 4118. (d) Zhang, J.; Xiong, R.-G.; Chen, X.-T.; Xue, Z.; Peng, S.-M.; You, X.-Z. *Organometallics* **2002**, *21*, 225. (e) Xue, X.; Wang, X.-S.; Xiong, R.-G.; Abrahams, B. F.; You, X.-Z.; Che, C.-M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2944. (f) Qu, Z.-R.; Chen, Z.-F.; Zhang, J.; Xiong, R.-G.; Abrahams, B. F.; Xue, Z. *Organometallics* **2003**, *22*, 2814.

(7) (a) Cavallo, L.; Cucciolito, M. E.; De Martino, A.; Giordano, F.; Orabona, I.; Vitagliano, A. *Chem. Eur. J.* **2000**, *6*, 1127. (b) Fraysse, S.; von Zelewsky, A. *New J. Chem.* **2001**, *25*, 1374.

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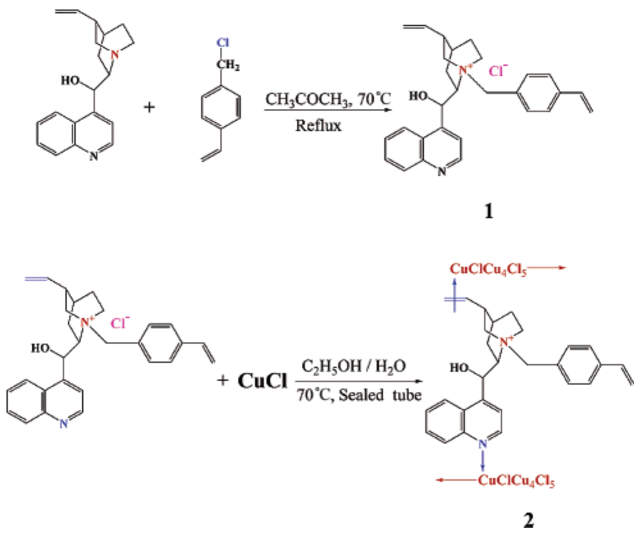
Scheme 1



Preliminary studies of a similar reaction of **1** and Cu^{I}Cl conducted in racemic 2-butanol indicate that (*R*)-2-butanol may be selectively intercalated between two chiral layers. Herein we report the synthesis, solid-state structures, and possible resolution ability of **2**, which represents, to our knowledge, the first example of a homochiral coordination polymer containing copper−olefin bonds and quaternary ammonium salts as chiral building blocks that could be useful for enantioseparation.

1 was prepared in refluxing acetone and *N*,*N*-dimethylformamide from the corresponding cinchona and 4-vinylbenzyl chloride. The reaction of **1** with Cu^{I}Cl under ethanothermal conditions in EtOH affords **2**·EtOH at 70 °C. Broad and strong peaks at 3448 and 3359 cm^{-1} in the IR spectrum of **2**·EtOH suggest that there is one solvent molecule in the formula unit. Thermogravimetric analysis (TGA) of the polycrystalline complex **2**·EtOH clearly shows that one strikingly clean weight loss step occurred between ca. 38 and 131 °C (3.30%), corresponding to the removal of one ethanol molecule per formula unit (3.21% calculated). Most important is the fact that no weight loss was observed between 131 and 230 °C, probably suggesting the formation of stable, solvent-free **2** (a polycrystalline sample of **2** can be obtained through a freshly ground sample of **2**·EtOH being subjected to vacuum at ca. 90 °C for 1 day). The EPR spectrum of **2**·EtOH is silent**,** confirming that the oxidation state of Cu ions in the solid complex is +1.

The crystal structure of **1** reveals that a preferred conformation may occur, based on the formation of one plane (plane of the paper with a dihedral angle of 50.9° between the quinoline ring and 4-vinylbenzyl ring; Figure 1a) composed of a quinoline ring, the C9−O bond, and the *N*-(4-vinylbenzyl)cinchoninium group, while the quinuclidine ring lies in front of the plane. The C9-hydroxyl provides a directional handle for ionic attraction via hydrogen bonding to chloride (Figure 1b) with a bond distance of 2.996 Å (see the Supporting Information).

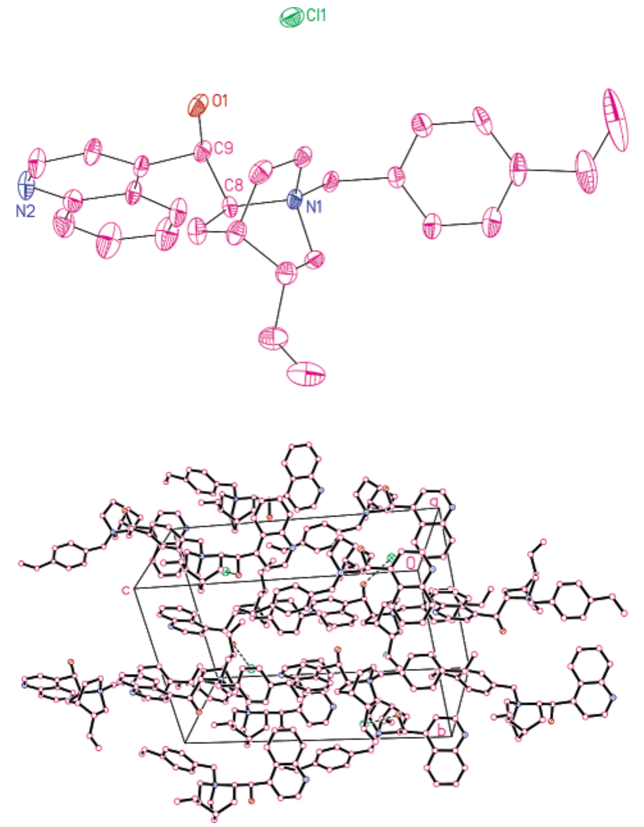


Figure 1. (a, top) ORTEP view of an asymmetric unit in **1** showing 30% probability displacement ellipsoids. The H atoms are omitted for clarity. (b, bottom) Packing view of **1** along the *a* axis showing that an H-bond persists.

It is interesting to note that the chiral phase transfer catalyst **1** acts as a bidentate linker (N atom of qunoline ring and olefin moiety of quinuclidine ring) to connect two different Cu(I) centers, while the olefin moiety of the 4-vinylbenzyl ring failed to take part in the coordination to Cu(I) (Figure 2a) in compound **2**·EtOH. The five Cu(I) centers connect together by four μ_2-Cl and two μ_3-Cl linkers to result in the formation of two clusters composed of two triangles (Cu1−Cu2−Cu3 and Cu3−Cu1A−Cu2A), while two triangles share a corner of Cu3, as shown in Figure 2b. Cu1 and Cu1A and Cu2 and Cu2A are all three-coordinated and coordinate to the N atom of the quinoline ring and olefin moiety of the quinuclidine ring to result in the formation of a 2D square-grid network (Figure 2c,d). The remaining Cu3 only coordinates to four Cl atoms with a tetrahedral geometry. It is noteworthy that two adjacent layers are not in a staggered arrangement but adopt an AA type arrangement (Figure 3). From Figure 3 it is clear that one ethanol molecule is intercalated between two layers of **2** as the framework.

A preliminary attempt at enantioselective separation of racamic 2-butanol under solvothermal conditions shows that the layered **2** network can selectively intercalate (*R*)-2-butanol with an approximately estimated ee of 25% (see the Supporting Information), as shown in the proposed Scheme 2. Thus, to the best of our knowledge, **2** is the first example of a homochiral network coordination polymer with olefin−copper that can selectively intercalate (*R*)-2-butanol.

In conclusion, with solvothermal synthesis techniques and the facile tenability of chiral phase transfer catalyst (PTC), the present work may lead to the development of functional Cu−olefin zeolite analogues that can be used for enantioseparation.

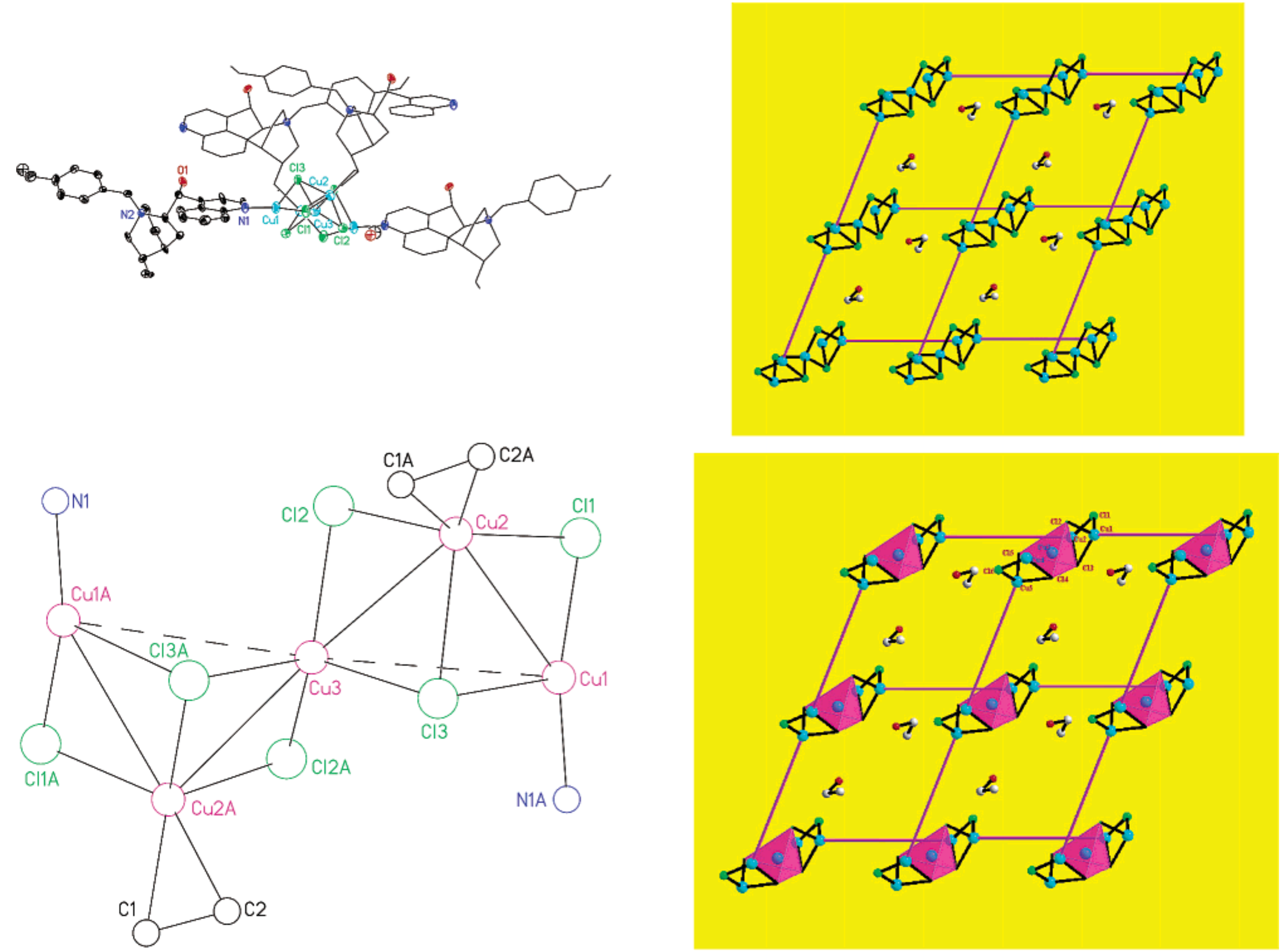


Figure 2. (a, top left) ORTEP view of an asymmetric unit compound **2** showing 30% probability displacement ellipsoids. The H atoms are omitted for clarity. (b, bottom left) Local coordination core representation of **2** showing that there are two Cu−Cu−Cu triangles sharing a Cu corner. (c, top right) Simplified 2D grid network representation of **2** in which each grid node is composed of two Cu−Cu−Cu triangle clusters. The long straight line stands for ligand **1**. (d, bottom right) Simplified 2D grid framework of **2** highlighting the shared Cu having a tetrahedron while other Cu centers are three-coordinated. The long straight line stands for ligand **1**.

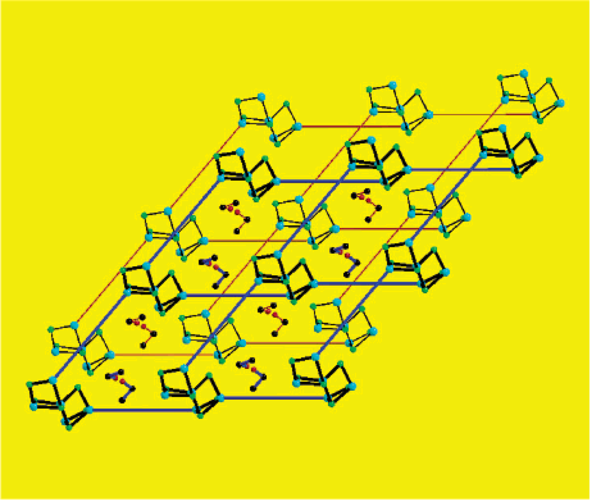
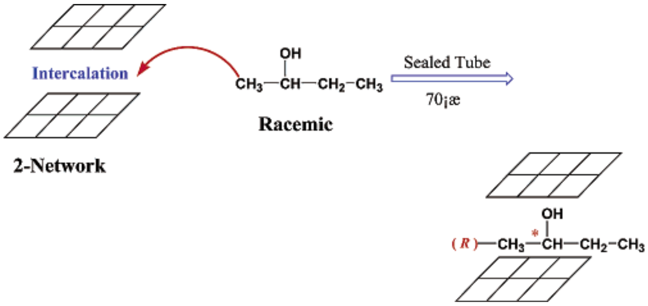


Figure 3. Packing arrangement representation of the two adjacent layers in **2** showing that ethanol molecules are intercalated between two layers. The long straight line stands for ligand **1**.

Scheme 2. Proposed Resolution Process by Intercalation



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Supporting Information Available: Crystallographic data as CIF files (excluding structure factors) and tables of atomic coordinates, thermal parameters, and bond distances and angles for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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