Novel copper macrocyclic leaflet with *N*-phosphonomethyl-monoaza-18-crown-6

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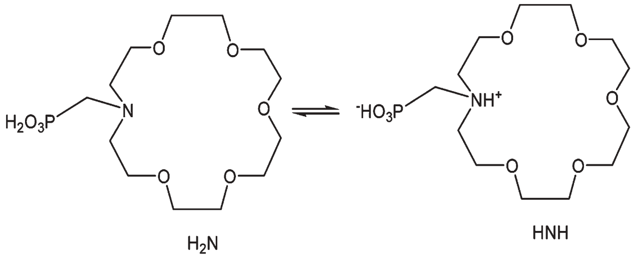
A novel 1D copper macrocyclic leaflet chain has been synthesized hydrothermally and its crystal structure determined.

Metal phosphonates have potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and materials chemistry.[1] Many of the metal phosphonates are layered species in which the metal octahedra are bridged by phosphonic acid tetrahedra to form two-dimensional layers that are separated by hydrophobic regions of the organic moieties. The hydrothermal method has proved to be a promising technique in the preparation of highly stable, infinite metal–ligand frameworks exhibiting many interesting properties.[2] Integration of the macrocyclic ligands into a polymeric matrix leads to a relatively new class of compounds with a wide range of applications. Alberti and our groups have shown that macrocyclic ligands can be embedded into rigid layered frameworks of zirconium phosphates through exocyclic phosphorylation of crown ethers.[3] Our results have shown that the crystal structure of metal(II) phosphonates containing monoazacrown ethers (such as aza-15-crown-5 and aza-18-crown-6) feature a one-dimensional chain, in which the metal ions are bridged by phosphonate groups. The crown ether moiety usually encapsulates a lattice water molecule, and its amine group remains protonated. Those ligands themselves also feature macrocyclic leaflets through pairs of hydrogen bonds between phosphonated groups.

Monoaza-18-crown-6 was phosphonomethylated by reacting it with phosphorous acid and formaldehyde in the presence of concentrated HCl. Isolation and purification of the *N*-(phosphonomethyl)-aza-18-crown-6, **H$_2$N**, was achieved by treatment of the reaction mixture with an anion exchange column followed by the recrystallization with acetone (Scheme 1 shows the zwitter ion properties of this ligand).



Scheme 1

The hydrothermal reaction of Cu(II) with **H$_2$N** in the presence of Na$_2$C$_2$O$_4$ and 4,4′-bipyridine at a 1 : 1 : 1 : 1 molar ratio, at 150 °C led to the formation of deep blue cubic **1**. A small amount of methanol was layered onto the surface of a mixed solution to increase the pressure in the 15 ml Teflon vessel. The IR spectrum of **1** clearly shows the presence of a strong peak at 1650 cm^{-1} characteristic of νC=O. A sharp medium vibration band for NH$^+$ centered at 3011 cm^{-1} is present. Compound **1** showed an intense and broad band in the O–H stretching vibration region at 3372–3020 cm^{-1}, which is consistent with the presence of lattice water molecules interacting by hydrogen bonding. The corresponding bending H–O–H (δHOH) vibration bands of the lattice water in **1** is located at *ca.* 1660 m^{-1}. The symmetrical and unsymmetrical vibration bands of PO$_2$ from PO$_3$H$^-$ groups in **1** are observed at 1150 and 1054 cm^{-1} respectively. The peaks that occur at 980 cm^{-1} were assigned to ν_s(PO$_3$).[4] The bands centered at 2330 and 1050 cm^{-1} are attributed to (PO–H) and (POH) vibrations, respectively, due to unprotonated PO– groups in this compound. Asymmetric vibrational stretching bands of POH (ν(P–OH)) groups are situated at 980 cm^{-1}. **1** also showed typical C–H stretching vibrations and bending vibrations of low intensities of CH$_2$ both inside the ring and/or attached to nitrogen atoms, near 2850 and 1478 cm^{-1}, respectively. The νP=O and νP–C vibration bands of all compounds are centered at 1230 and 760 cm^{-1}, respectively. The TGA of **1** demonstrated that it lost the lattice water molecules at 50 °C and decomposition of organic parts at 220 °C. The total weight loss is 83.83% indicating the final residue would be CuO.

Single crystal X-ray analysis† has revealed that copper atoms are bridged by two μ-oxalate oxygen atoms, two nitrogen atoms of 4,4′-bipyridine and one oxygen atom from **H$_2$N**. The central copper atoms are in the typical square pyramidal enviroment with enlongated Jahn–Teller distortion in the axial position [Cu–O(6) 2.162(3) Å]. The bond distances of all planar Cu–O or Cu–N are in the range of 1.984–1.995 Å. The most of striking features of **1** are: firstly, two types of bridges have been constructed by using small molecular oxalate and bipyridine which complete a hexgonal connection between six equivalent copper atoms. The macrocyclic rings are packed inside the 15.3 × 11.0 Å open channel running through the *a* axis with an 8.2 Å stacking distance (Fig. 1). This structure has a longer interplanar stacking distance between the crown ethers due to the 4,4′-bipyridine spacer pushing the crown ether rings further apart from 3.6 Å to 8.2 Å which provides a new model for the design of macrocyclic tubular channels for transporting ionic species and discotic liquid crystals.[5] The phosphonate groups of **H$_2$N** are deprotonated with protons transferred to aza-nitrogen atoms associated with the ring. The

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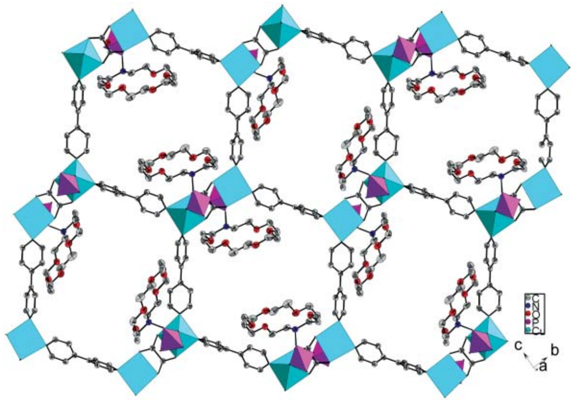

Fig. 1 Hexagonal channel viewed down the *a* axis (the purple tetrahedra represent CPO_3 and the cyan pyramids represent CuN_2O_3).

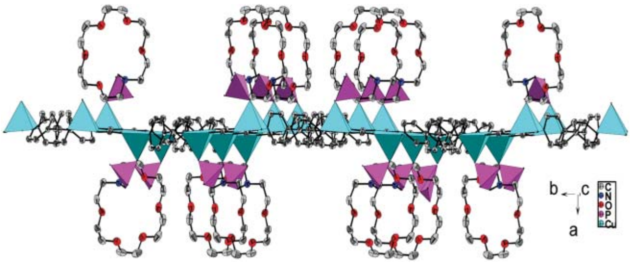

Fig. 2 Macrocyclic leaflet structure formed along the *ab* plane (the purple tetrahedra represent CPO_3 and the cyan pyramids represent CuN_2O_3).

protonated nitrogen atoms form strong hydrogen bonds with the disordered water molecule (N(1)–H(3C)···O(2wA) 2.664(7) Å, 171(4)° N(1)–H(3C)···O(2wB) 2.718(7) Å, 147(4)°). Fig. 2. shows the polymeric chain along the *b* axis. This is similar to the so-called macrocyclic leaflet structure in which the crown ethers are positioned as leaves on a twig. The stem of the leaflet is formed by metal ions bridged by phosphonated groups or hydrogen bonds as in free ligands.[3c–e] In fact, this polymeric chain is positively charged and one perchlorate anion resides in the channel to balance the charge. Only one example in our former studies shows the crown ether moieties are coordinated with the metal ions which featured 1D hydrogen array or 3D network.[3f]

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Notes and references

† Single crystal of $Cu[C_{12}H_{24}O_5NH(CH_2PO_3H)(C_{10}N_2H_8)(C_2O_4)_{0.5}]\cdot(ClO_4)\cdot 2H_2O$ (**1**) $Mr = 755.5$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.2187(6)$, $b = 24.1485(17)$, $c = 17.1040(12)$ Å, $\beta = 103.590(10)°$, $V = 3299.6(4)$ Å^3 and $Z = 4$, $D_c = 1.528$ g cm^{-3}, $\mu = 0.868$ cm^{-1}. Data collection ($2.55° < \theta < 28.27°$) was performed at 110 K on a Bruker Smart CCD-1000 diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The structure was solved using direct methods and refined with full-matrix least-squares (SHELX-97)[6] with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, giving a final R_1 value of 0.0608 for 459 parameters and 5617 unique reflections with $[I > 2\sigma(I)]$ and wR_2 of 0.1507 for all 30926 reflections for **1**.[6] CCDC 246771. See http://www.rsc.org/suppdata/cc/b4/b412209g/ for crystallographic data in .cif or other electronic format.

1 A. Clearfield, Metal Phosphonate Chemistry, in *Progress in Inorganic Chemistry*, ed. K. D. Karlin, John Wiley & Sons, New York, 1998, vol. 47, pp. 371–510 and references therein.
2 (*a*) A. Rujiwatra, C. J. Kepert, J. B. Claridge, M. J. Rosseinsky, H. Kumagai and M. Kurmoo, *J. Am. Chem. Soc.*, 2001, **123**, 10584; (*b*) W. B. Lin, A. Y. Wang and L. Ma, *J. Am. Chem. Soc.*, 1999, **121**, 11249.
3 (*a*) B. Zhang and A. Clearfield, *J. Am. Chem. Soc.*, 1997, **119**, 2751; (*b*) G. Alberti, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle and J.-M, Lehn, Pergamon, Oxford, 1996, vol. 7, p. 151; (*c*) G. Alberti, L. Boccali, C. Dionigi, R. Vivani, V. I. Kalchenko and L. I. Atamas, *Supramol. Chem.*, 1996, **7**, 129; (*d*) C. V. K. Sharma and A. Clearfield, *J. Am. Chem. Soc.*, 2000, **122**, 1558; (*e*) A. Clearfield, C. V. K. Sharma and B. Zhang, *Chem. Mater.*, 2001, **13**, 3099; (*f*) C. V. K. Sharma, A. J. Hessheimer and A. Clearfield, *Polyhedron*, 2001, **20**, 2095; J. G. Mao, Z. K. Wang and A. Clearfield, *Inorg. Chem.*, 2002, **41**, 3713.
4 (*a*) B. C. Barja, J. Herszage and M. Santos Alfons, *Polyhedron*, 2001, **20**, 1821; (*b*) A. Cabeza, M. A. G. Aranda and S. Bruque, *J. Mater. Chem.*, 1999, **9**, 571; (*c*) M. M. Gomez-Alcantara, A. Cabeza, M. A. G. Aranda, A. Guagliardi, J. G. Mao and A. Clearfield, *Solid. State. Sci.*, 2004, **6**, 479; (*d*) S. K. Sahni, E. V. Bebbekom and J. Reedijk, *Polyhedron*, 1985, **4**, 1643.
5 (*a*) T. M. Fyles and W. F. Straaten-Nijenhuis, Ion Channel Models, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogetle and J.-M. Lehn, Pergamon, Oxford, 1996, vol. 10, p. 53; (*b*) E. Abel, G. E. M. Maguire, O. Murillo, I. Suzuki, S. L. De Wall and G. W. Gokel, *J. Am. Chem. Soc.*, 1999, **121**, 9043.
6 *SMART version 5.0 and SAINT+ Version 6.01 area detector instrument control, data acquisition and area detector data integration software*, Bruker AXS, Inc., Madison, WI, 1999; G. M. Sheldrick, *SHELXTL (SADABS, XS, XL) Crystallographic software Package, Version 6.10*, Bruker, AXS, Inc., Madison, WI, 2000.