

# A novel copper (II) metallacycle as a building block for the assembly of an extended supramolecular array containing channels and helical chains

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## Abstract

Complexation of copper (II) perchlorate with *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (CTA) and *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach) in the presence of triethylamine leads to the formation of a dinuclear metallacycle;  $[\text{Cu}_2(\textit{trans}\text{-tach})_2(\textit{CTA})_2] \cdot 14\text{H}_2\text{O}$  (**1**). The crystal structure of **1** shows an extended hydrogen bonded network comprising linear chains of metallacycles running perpendicular to solvent occupied channels.

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The construction of novel coordination complexes that form structures with large cavities represent extremely interesting and versatile building blocks with a great deal of potential for the design of porous, magnetic and electronically diverse materials [1,2]. In particular, the formation of closed, ring-like coordination complexes such as metallocrowns and metallacycles has attracted specific attention as there has been considerable progress towards application of such materials in molecular recognition, enantioselective sensing and photoluminescence [3,4]. Although the literature contains a large variety of dinuclear metallacycles comprised of aromatic carboxylate ligands such as 1,3-benzenedicarboxylic acid [5–8], there are very few examples of this type of complex with aliphatic carboxylate ligands as the inherent non-rigidity of most aliphatic ligands leads to the preferential formation of polymeric structures in

all but a few cases [9]. Recently, we have shown that ligands with their donor groups arranged around a cyclohexane backbone can exhibit sufficient flexibility to form interesting polynuclear clusters and extended networks, while the rigidity of the cyclohexane backbone prevents the formation of amorphous polymers [10,11]. Herein, we present the synthesis and structure of a new dinuclear metallacycle composed of copper (II) cations and the ligands *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (CTA) and *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach);  $[\text{Cu}_2(\textit{trans}\text{-tach})_2(\textit{CTA})_2] \cdot 14\text{H}_2\text{O}$ , **1**. The crystal structure of **1** has solvent filled channels along the crystallographic *a*-axis with an internal diameter of ca. 4 Å.

Addition of copper perchlorate to a methanol/water solution of CTA and *trans*-tach in a 1:1:1 molar ratio, followed by the addition of triethylamine to deprotonate the carboxylic acid, leads to the formation of a deep purple solution from which purple needle crystals of **1** were grown by acetone diffusion in a yield of 59% based on copper [12].  $\text{C}_{30}\text{H}_{64}\text{Cu}_2\text{N}_6\text{O}_{19}$  (939.95) based on the loss of half the solvent water on drying; found (calc.)%: C,

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39.29 (38.33); H, 6.11 (6.86); N 9.01 (8.94); FTIR ( $\text{cm}^{-1}$ ) 3429 (s), 3290 (m), 2925 (m), 1608 (m), 1553 (m), 1391 (m), 1087 (s), 920 (w), 627 (m).

The molecular structure of **1**, as determined by single crystal X-ray diffraction [13], is shown in Fig. 1. The complex comprises two copper (II) cations with square planar coordination geometry, bridged by two CTA ligands binding in a *bis*-monodentate mode with  $\text{Cu}\cdots\text{O}$  distances of 1.970(3) Å. The coordination sphere of the copper (II) is completed by *trans*-tach binding through its two *cis*-amino groups in the *bis*-axial, *mono*-equatorial conformation, as seen in other *trans*-tach copper (II) complexes [10] with  $\text{Cu}\cdots\text{N}$  distances of 1.992(4) Å. The two binding carboxylic acid groups of each CTA ligand are deprotonated while the remaining group is not, leading to a di-anionic ligand. Further, the triethylamine used to deprotonate the ligand during the complexation is not found in the crystal structure. The crystal lattice is stabilised by strong hydrogen bonding interactions between the amines of each *trans*-tach ligand and the carboxylate groups in adjacent units with  $\text{N}\cdots\text{H}\cdots\text{O}$  distances between 2.8 and 3.0 Å. This type of interaction is found between units that are aligned with one another in the crystallographic *c*-axis, giving rise to hydrogen bonded chains of metallacycles, Fig. 2. Although these chains are helical, the crystals are racemic, being composed of a mixture of left handed and right handed

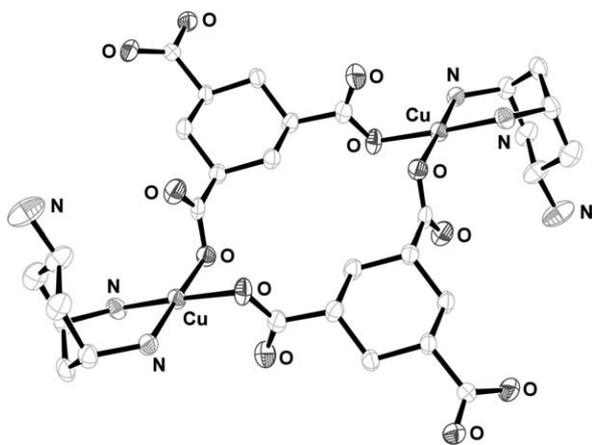


Fig. 1. ORTEP representation of **1** with 50% thermal ellipsoids. All hydrogen atoms and water molecules are omitted for clarity.

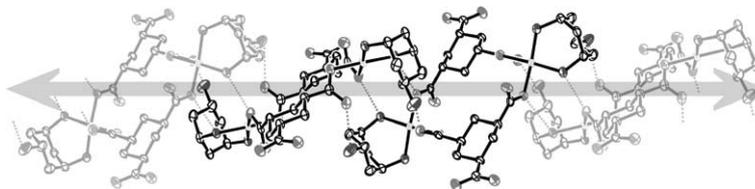


Fig. 2. ORTEP representation of the hydrogen bonded chain of metallacycles. Hydrogen bonds are shown as dashed lines. All hydrogen atoms and water molecules are omitted for clarity. Carbon atoms are displayed as black open spheres with oxygen atoms as grey hatched spheres, nitrogen atoms in dark grey and copper light grey open spheres.

chains. Further hydrogen bonding is found between the pendant carboxylic acid groups of CTA ligands in adjacent chains and between the metallacycles and surrounding water molecules. These serve to cross-link adjacent chains and stabilise the lattice.

The fourteen water molecules per cluster present in the structure occupy channels running parallel to the crystallographic *a*-axis, perpendicular to the hydrogen bonded chains, with an approximate inner diameter of 4 Å, Fig. 3.

In conclusion, we have shown that the complexation of copper (II) with the ligands CTA and *trans*-tach leads to the formation of a dinuclear metallacycle which assembles an extended array of chains, held together

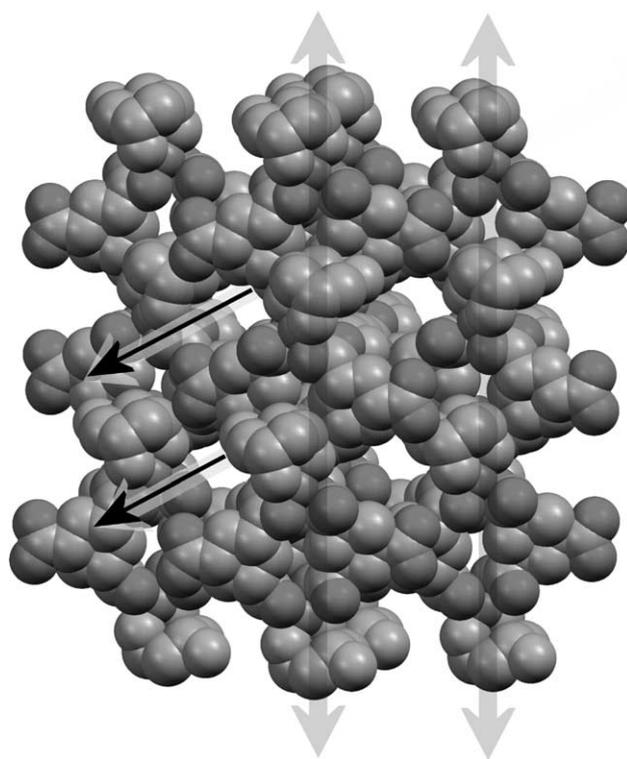


Fig. 3. Space filling representation of the crystalline lattice of **1** showing the relative orientations of the channels and hydrogen bonded chains. The direction of the channels is shown by the arrows on the left while the direction of the hydrogen bonded chains is shown by light grey arrows. All hydrogen atoms and water molecules are omitted for clarity.

by hydrogen bonding interactions and containing 4 Å solvent channels. Further studies will aim to make larger cycles of this class, taking advantage of the inherent rigidity of the ligand cyclohexane rings by subtle alteration of the synthetic control parameters with a view to making functional porous materials for catalytic and sensing applications.

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### Appendix A. Supplementary data

Crystal data and structure refinement, atomic coordinates, bond lengths and angles, IR, and TG results of the complex are available from the authors on request. CCDC Reference No. 268195. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2005.05.005](https://doi.org/10.1016/j.inoche.2005.05.005).

### References

- [1] T. Glaser, *Angew. Chem., Int. Ed.* 42 (2003) 5667.
- [2] G.J. Halder, C.J. Kepert, B. Moubaraki, K.S. Murray, J.D. Cashion, *Science* 298 (2002) 1762.
- [3] S. Leininger, B. Olenyuk, P.J. Stang, *Chem. Rev.* 100 (2000) 853.
- [4] F. Würthner, C.-C. You, C.R. Saha-Möller, *Chem. Soc. Rev.* 33 (2004) 133.
- [5] N.J. Burke, A.D. Burrows, A.S. Donovan, R.W. Harrington, M.F. Mahon, C.E. Price, *J. Chem. Soc., Dalton Trans.* 20 (2003) 3840.
- [6] L.-Y. Zhang, G.-F. Liu, S.-L. Zheng, B.-H. Ye, X.-M. Zhang, X.-M. Chen, *Eur. J. Inorg. Chem.* 16 (2003) 2965.
- [7] A.D. Burrows, D.M.P. Mingos, S.E. Lawrence, A.J.P. White, D.J. Williams, *J. Chem. Soc., Dalton Trans.* 8 (1997) 1295.
- [8] H.-P. Xiao, Q. Shi, M.-D. Ye, *Acta Crystallogr. E* 60 (2004) m1498.
- [9] A. Pajunen, S. Pajunen, *Acta Crystallogr. B* 35 (1979) 460.
- [10] G. Seeber, P. Kögerler, B.M. Kariuki, L. Cronin, *Chem. Commun.* 14 (2004) 1580.
- [11] G. Seeber, D.L. Long, B.M. Kariuki, L. Cronin, *J. Chem. Soc., Dalton Trans.* 23 (2003) 4498.
- [12] Addition of solid copper (II) perchlorate nonahydrate (115 mg, 0.311 mmol) to a mixture of *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (66 mg, 0.311 mmol) and *cis,trans*-1,3,5-triaminocyclohexane (40 mg, 0.311 mmol) in 3 ml of a 1:1 mixture of methanol and water resulted in the formation of a blue precipitate. Slow addition of triethylamine (1.5 ml) caused this precipitate to dissolve leaving a purple solution which was then filtered. Slow diffusion of acetone into this filtrate over four days resulted in the formation of purple needle crystals of diffraction quality. Yield 84 mg (0.09 mmol, 59%) C<sub>30</sub>H<sub>64</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>19</sub> (939.95); found (calc.)%: C 39.29 (38.33), H 6.11 (6.86), N 9.01 (8.94); FTIR (cm<sup>-1</sup>) 3429 (s), 3290 (m), 2925 (m), 1608 (m), 1553 (m), 1391 (m), 1087 (s), 920 (w), 627 (m).
- [13] Crystal data for C<sub>30</sub>H<sub>78</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>26</sub>: monoclinic, *C2/c*, unit cell parameters *a* = 12.6655(8) Å, *b* = 19.8892(9) Å, *c* = 19.5057(12) Å,  $\beta$  = 104.640(2)°. *V* = 4754.1(5) Å<sup>3</sup>, *Z* = 4,  $\mu$ (Mo-K $\alpha$ ) = 0.986 mm<sup>-1</sup>, 15,490 reflections measured, 4663 unique which were used in all calculations. Final *R*1 = 0.078 and *wR*2 = 0.213 (all data). Data were measured at 150(2) K on a Nonius Kappa-CCD diffractometer equipped with a molybdenum rotating anode source ( $\lambda$  = 0.7107 Å). Structure solution with SHELXS97 and refinement with SHELXL97 via WinGX [14]. Hydrogen atom positions calculated and subsequently riding.
- [14] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.