Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 3691–3693 **3691**
DOI: 10.1021/ic100254t

Decanuclear Copper Framework Supported by a Tripodal Adenine Ligand

Ashutosh Kumar Mishra and Sandeep Verma*

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016 (UP), India

Received February 8, 2010

This Communication describes the synthesis, crystal structure, and magnetic properties of a unique decanuclear copper complex of a tripodal adenine ligand built around a phenyl ring core. This complex comprises two μ_4-oxo tetranuclear copper(II) units of the type $Cu_4OCl_6L_4$, bridged together by two pentacoordinated copper centers. Variable-temperature magnetic susceptibility data reveal the possibility of interaction between copper sites.

Consideration of symmetry aspects in the design of new molecules and ligands affords the creation of intricate structural motifs, which could possibly be tailored for diverse applications. In this context, the symmetry features engendered in the rotational axes have been extensively used for the design of molecules because their occurrence is compatible with chirality. More specifically, C_3-symmetric tripodal frameworks have been used for asymmetric catalysis, coordination chemistry, molecular recognition, and nanoscale architectures, to name a few.[1]

Polynuclear transition-metal clusters offer fascinating structural organization, thereby serving as a valuable source of inspiration in achieving novel coordination motifs and architectures.[2] In addition to the generation of complex hierarchical frameworks, potentially useful chemical and physical properties could be manifested from such polynuclear complexes. A judicious selection of ligand systems and metal ions may lead to the formation of extended self-assembled coordination ensembles or discrete complexes.[3] In this vein, high-nuclearity copper complexes have been intensively studied for their structural diversity,[4] as metalloenzyme models for catalysis of various oxidation reactions[5] and magnetic properties, and for the creation of interesting architectural topologies.[6]

Our laboratory has earlier reported the coordination behavior of modified adenine analogues with coinage metal ions, especially copper and silver, and their propensity to form ordered ensembles on surfaces and exhibit luminescence properties.[7] We recently reported silver and copper complexes of an adenine-based, C_2-symmetric molecule where fold-back geometry, leading to a discrete unit, was observed for copper complexes, while the silver complex preferred an extended structure in the lattice.[7e] We now report the synthesis of a tripodal C_3-symmetric adenine analogue, *N*,*N*′,*N*″-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tris(9-propyl-9*H*-purin-6-amine) (**L**) and describe the crystal structure of its copper complex to generate adenine-based structures of increased complexity (Scheme 1).

Crystals suitable for X-ray diffraction were grown by mixing a methanolic solution of the ligand with a methanolic solution of copper chloride, which was left undisturbed for crystallization via slow evaporation. Careful inspection of the crystal data confirmed monoclinic space group *C*2/*c* (No. 15) (Table S1 in the Supporting Information).

---

*To whom correspondence should be addressed. E-mail: sverma@iitk.ac.in.

(1) (a) Moberg, C. *Angew. Chem., Int.Ed.* **1998**, *110*, 260–281. (b) Moberg, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 228–268. (c) Gibson, S. E.; Castaldi, M. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 4718–4720. (d) Gibson, S. E.; Castaldi, M. P. *Chem. Commun.* **2006**, 3045–3062. (e) Ohi, H.; Tachi, Y.; Itoh, S. *Inorg. Chem.* **2006**, *45*, 10825–10835. (f) Blackman, A. G. *Eur. J. Inorg. Chem.* **2008**, 2633–2647. (g) Liu, H.-K.; Huang, X.; Lu, T.; Wang, X.; Sun, W. Y.; Kang, B. S. *Dalton Trans.* **2008**, 3178–3188. (h) Su, S. U.; Cai, Y. P.; Chen, C. L.; Smith, M. D.; Kaim, W.; Loye, H. C. Z. *J. Am. Chem. Soc.* **2003**, *125*, 8595–8613. (i) Chen, C. H.; Zhang, J. Y.; Su, C. Y. *Eur. J. Inorg. Chem.* **2007**, 2997–3010.

(2) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141–143. (b) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804–1816. (c) Friedman, J. R.; Sarachik, M. P.; Tejada, J.; Ziolo, R. *Phys. Rev. Lett.* **1996**, *76*, 3830–3833. (d) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145–147. (e) Winpenny, R. E. P. *Dalton Trans.* **2002**, 1–10.

(3) (a) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647–1668. (b) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483–3537. (c) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371–380. (d) Moon, D.; Kang, S.; Park, J.; Lee, K.; John, R. P.; Won, H.; Seong, G. H.; Kim, Y. S.; Kim, G. H.; Rhee, H.; Lah, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 3530–3531.

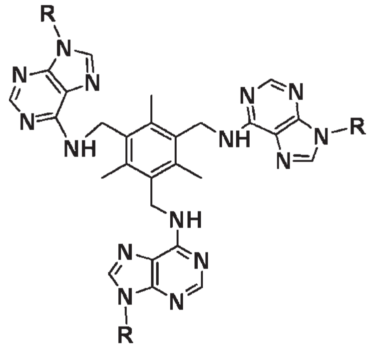
(4) Bai, Y.-L.; Tangoulis, V.; Huang, R.-B.; Zheng, L.-S.; Tao, J. *Chem.—Eur. J.* **2009**, *15*, 2377–2383.

(5) Kirillov, A. M.; Kopylovich, M. N.; Kirillova, M. V.; Haukka, M.; Fátima M.; Guedes da Silva, C.; Pombeiro, A. J. L. *Angew. Chem., Int.Ed.* **2005**, *44*, 4345−4349 and references cited therein.

(6) (a) Yam, V. W.-W.; Lo, K. K.-W. *Chem. Soc. Rev.* **1999**, *28*, 323–334. (b) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625–3647. (c) Sugiura, T.; Yoshikawa, H.; Awaga, K. *Inorg. Chem.* **2006**, *45*, 7584–7586. (d) Li, G.; Xing, Y.; Song, S.; Xu, N.; Liu, X.; Su, Z. *J. Solid State Chem.* **2008**, *181*, 2406–2411.

(7) (a) Purohit, C. S.; Verma, S. *J. Am. Chem. Soc.* **2006**, *128*, 400–401. (b) Purohit, C. S.; Mishra, A. K.; Verma, S. *Inorg. Chem.* **2007**, *46*, 8493–8495. (c) Purohit, C. S.; Verma, S. *J. Am. Chem. Soc.* **2007**, *129*, 3488–3489. (d) Mishra, A. K.; Purohit, C. S.; Kumar, J.; Verma, S. *Inorg. Chim. Acta* **2009**, *362*, 855–860. (e) Mishra, A. K.; Purohit, C. S.; Verma, S. *Cryst. Eng. Comm.* **2008**, *10*, 1296–1298. (f) Kumar, J.; Verma, S. *Inorg. Chem.* **2009**, *48*, 6350–6352. (g) Verma, S.; Mishra, A. K.; Kumar, J. *Acc. Chem. Res.* **2010**, *43*, 79–91. (h) Srivatsan, S. G.; Verma, S. *Chem. Commun.* **2000**, 515–516. (i) Madhavaiah, C.; Verma, S. *Chem. Commun.* **2003**, 800–801. (j) Pandey, M. D.; Mishra, A. K.; Chandrasekhar, V.; Verma, S. *Inorg. Chem.* **2010**, *49*, 2020–2022.

Scheme 1. Schematic Representation of a Tripodal Adenine Analogue (R is an *n*-Propyl Group)



Our investigations revealed the formation of a decanuclear copper complex (**1**) with tripodal adenine analogue **L**, where two tetranuclear copper motifs of the type $Cu_4OX_6L_4$ are connected to each other via two copper ions. Notably, the tetranuclear copper units are connected to each other through two pentacoordinated copper(II) bridges, thereby resulting in a discrete decanuclear copper complex. To the best of our knowledge, this is an unprecedented example of an adenine-based polynuclear copper complex.

Copper coordination in **L** is achieved with the help of three flexible adenine pendants, originating from a phenyl ring core, through the N7 nitrogen atoms of the adenine moieties. While four adenine pendants in two ligands hold four copper ions (Cu1−Cu4) in the tetranuclear unit, the third adenine coordinates to the fifth copper ion (Cu5) (Figure 1).

The overall rendering of complex **1** reveals an interesting discrete decanuclear motif composed of 10 copper ions, 2 μ_4-oxido ions, 4 ligands, 12 μ-chlorido ions, 4 chlorido ions, and 2 methanol molecules, which are part of the crystal lattice (Figure 2). The origin of the oxido ligand could be attributed to the residual water.

The hallmark of the cagelike discrete structure of **1** is the presence of two centrosymmetric $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6$(N7-Ade)$_4$ core units, where four copper ions are coordinated to a central μ_4-oxido ion, in a slightly distorted tetrahedral geometry (Figure 3a). The Cu−O and Cu−Cu bond distances are ~1.921 and 3.093−3.230 Å, respectively, whereas the Cu−O−Cu bond angles are in the range of 107.11−113.95°, which are in the acceptable range for reported tetranuclear complexes having $Cu_4(\mu_4\text{-}O)$ units.[8] Each copper atom in the $Cu_4(\mu_4\text{-}O)(\mu\text{-}Cl)_6$(N7-Ade)$_4$ core unit is bridged together through six μ-chlorido ions. The arrangement of these μ-chlorido ions around a central μ_4-oxido ion results in a distorted octahedron (Figure S4 in the Supporting Information).

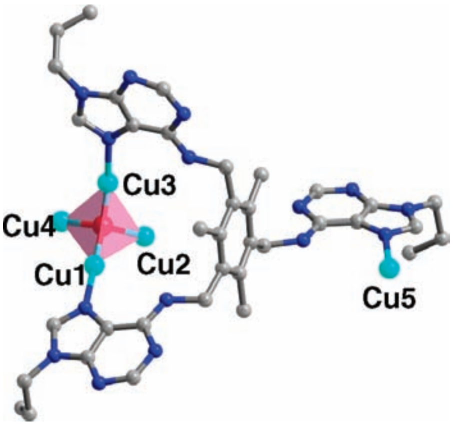


Figure 1. Representation of a tripodal adenine analogue coordinated with copper ions (numbered). Parts of the complex and hydrogen atoms are omitted for clarity.

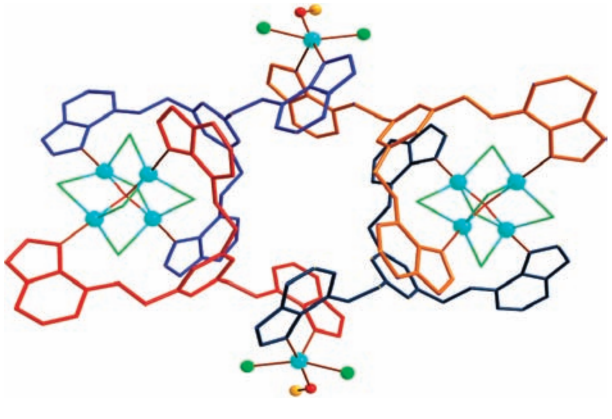


Figure 2. Structure of decanuclear copper complex **1**. The participation of four ligands is highlighted by different colors. Certain functionalities on the ligand, solvent molecules, and hydrogen atoms are omitted for clarity.

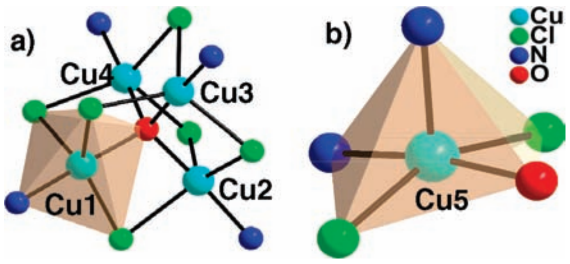


Figure 3. (a) Tetranuclear copper cluster (Cu1−Cu4) in **1**, where each copper ion adopts distorted trigonal-bipyramidal geometry. (b) Coordination environment of Cu5 showing distorted square-pyramidal geometry.

Notably, the decanuclear motif presents two crystallographically unique pentacoordinated copper ions. All four copper ions involved in the tetranuclear copper core adopt a distorted trigonal-bipyramidal geometry, as indicated by the corresponding τ values being in the range of 0.59−0.84, where equatorial coordination sites are occupied by bridged chloride ions and the apical positions correspond to the central oxygen and N7 nitrogen of the coordinated adenine moiety (Figure 3a). The other crystallographically distinct Cu5 ion acquired a slightly distorted square-pyramidal geometry ($\tau = 0.25$), with two chloride ions, a methanol, and N7 nitrogen of the adenine residue present in a plane, with adenine N7 nitrogen from another ligand occupying the apical position (Figure 3b).

Hydrogen-bonding interaction of adenine N1 nitrogen with methanol coordinated with Cu5 of the adjacent decanuclear unit in **1** results in a 1D ribbon-like architecture (Figure 4). A weak interaction between N6 hydrogen of the adenine moieties, involved in the tetranuclear core, and chloride ions could further stabilize the decanuclear architecture (Figure S3 in the Supporting Information).

---

[8] (a) Bera, M.; Wong, W. T.; Aromi, G.; Ribas, J.; Ray, D. *Inorg. Chem.* **2004**, *43*, 4787–4789. (b) Mukherjee, S.; Weyhermuller, T.; Bothe, E.; Wieghardt, K.; Chaudhuri, P. *Eur. J. Inorg. Chem.* **2003**, 863. (c) Li, G.; Xing, Y.; Song, S.; Xu, N.; Liu, X.; Su, Z. *J. Solid State Chem.* **2008**, *181*, 2406–2411.

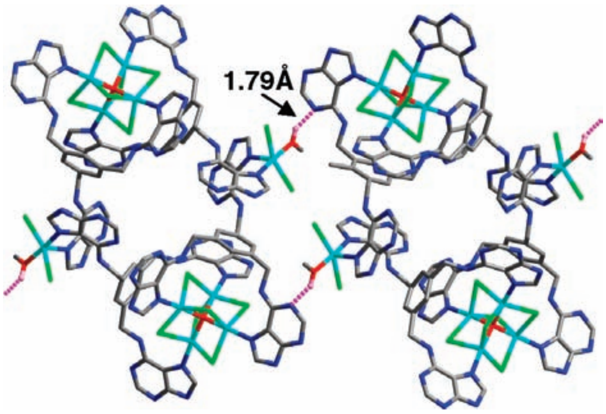


Figure 4. Part of the crystal lattice showing the connectivity of two decanuclear discrete units through hydrogen-bonding interaction. Parts of the complex and hydrogen atoms are omitted for clarity.

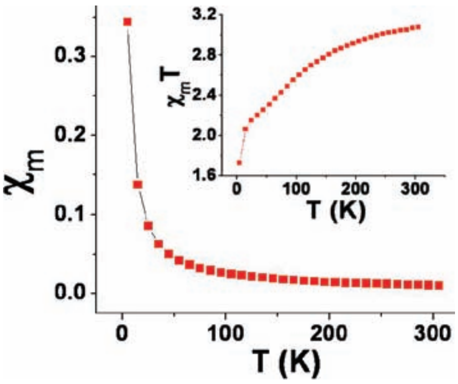


Figure 5. Graph showing the temperature dependence of χ_m for **1**. Inset: plot of $\chi_m T$ versus T.

A preliminary investigation of the magnetic properties of **1** is represented in Figure 5 as χ_m and $\chi_m T$ (inset) versus T plots (where χ_m = molar magnetic susceptibility). Our studies revealed paramagnetic behavior of **1** in the whole range of temperature studied. However, a gradual decrease of the $\chi_m T$ value from 3.07 to 2.06 cm^3 mol^{-1} K, upon decreasing temperature from 300 to 15 K, followed by a sharp decline to 1.71 cm^3 mol^{-1} K at 5 K, was noted. However, the possible existence of multiple interaction pathways between the copper centers makes it difficult to further delineate the magnetic properties.

Thermogravimetric analysis of **1** showed an initial weight loss of 6% (270 °C) corresponding to the loss of methanol molecules, followed by a weight loss of 39% at 403 °C, which could be attributed to the loss of ligand molecules (Figure S1 in the Supporting Information).

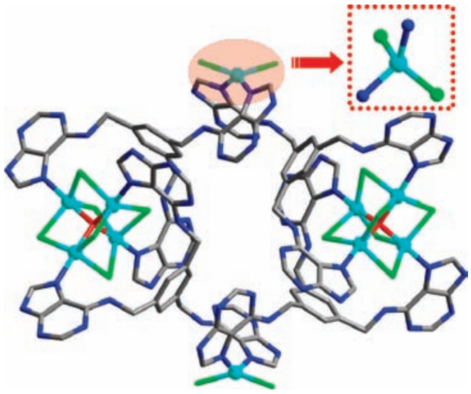


Figure 6. Coordination environment of Cu5 in **2**, showing distorted tetrahedral geometry at Cu5.

Furthermore, this decanuclear architecture was fairly robust in the presence of other nitrogen-coordinating ligands such as pyridine and 2,2′-bipyridine. When **1** was soaked in an aqueous pyridine solution, dark-brownish prismatic crystals were obtained. Crystallographic studies revealed that a methanol molecule at Cu5 was removed, causing a subtle change in the coordination geometry around Cu5, from pentavalent distorted square-pyramidal geometry to tetravalent distorted tetrahedral geometry, without affecting the overall decanuclear core motif (Figure 6). The methanol molecules in the crystal lattice were replaced with water molecules.

In conclusion, we have investigated the solid-state structure of the copper complex with a tripodal adenine analogue built around an aromatic core, and a decanuclear assembly of Cu^{II} ions was observed. The formation of a discrete decanuclear motif and the presence of two crystallographically unique copper ions are fascinating features reported for adenine coordination.

Acknowledgment. DST, India, is gratefully acknowledged for financial support under the Special Bioinorganic Chemistry Initiative (to S.V.). A.K.M. acknowledges CSIR, India, for a senior research fellowship. The laboratory of Prof. R.C. Budhani, Department of Physics, IIT Kanpur, is acknowledged for the acquisition of magnetism data.

Supporting Information Available: Characterization and crystal data and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. The supplementary crystallographic data for this paper with deposition numbers of CCDC 761137 and 764214 have also been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].