

Hydrothermal Synthesis, Crystal Structure and EPR Property of Tetranuclear Copper(II) Cluster $[\text{Cu}_4\text{OCl}_6(\text{C}_{14}\text{H}_{12}\text{N}_2)_4]$

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The tetranuclear copper(II) cluster compound $[\text{Cu}_4\text{OCl}_6(\text{C}_{14}\text{H}_{12}\text{N}_2)_4]$ has been synthesized by hydrothermal reaction and studied by X-ray diffraction. The four copper(II) atoms locate four vertices of a tetrahedral skeletal structure and an oxygen atom as interstitial atom occupies the center position of the same tetrahedron, and each edge of the Cu-Cu tetrahedron is bridged by one μ_2 -Cl anion. The copper atom possesses slightly distorted trigonal bipyramidal geometry with three μ_2 -Cl atoms in equatorial position and the interstitial O atom and one N atom from 3-benzyl-benzimidazole ligand occupying axial position. The Cu-Cu distances are in the range of 3.0986–3.1162 Å. The EPR spectrum suggested that the copper(II) ground state $d_{x^2-y^2}$ and the coordination geometry was trigonal bipyramidal.

Key Words : Hydrothermal synthesis, Crystal structure, Tetranuclear copper(II) cluster, EPR property

Introduction

Benzimidazole is an interesting heterocyclic ring because it is present in various naturally occurring drugs, such as omeprazole, astemizole and emedastine difumarate.¹ The efficacy of substituted benzimidazoles in the treatment of parasitic infections is well known.^{2,3} Interest in exploring benzimidazole derivatives and their metal complexes has continually increased, since the recognition that many of these materials may serve as models which mimic both the structure and reactivity of metal ion sites in complex biological systems^{4,5} and possess a broad spectrum of biological activity.^{6,7} For these reasons, our group began to synthesize various benzimidazole derivatives and their metal complexes and studied their chemical properties.⁸ However, when we attempted to synthesize an ordinary complex of cupric with benzimidazole derivative by a hydrothermal reaction, the anticipatory complex was not obtained, accidentally, we got a tetranuclear copper(II) cluster $[\text{Cu}_4\text{OCl}_6(\text{C}_{14}\text{H}_{12}\text{N}_2)_4]$. At the same time, we got the single crystal suitable for X-ray diffraction. Also, we repeated this experiment and got this novel copper cluster in high yield. The first example of clusters of the type $[\text{Cu}_4\text{OX}_6\text{L}_4]$ was described by Bertrand and Kelly in 1966, and the $[\text{Cu}_4\text{OCl}_6(\text{Ph}_3\text{PO})_4]$ was prepared by refluxing dichlorobis-(triphenylphosphine oxide) copper(II) in methyl isobutyl ketone.⁹ Since then similar clusters have been reported in the literature.¹⁰⁻¹² The most $[\text{Cu}_4\text{OCl}_6\text{L}_4]$ complexes were prepared by the addition of ligand L in organic solvent to a solution of copper(II) chloride in the same solvent, and refluxing for some time.^{10,13} Several of these have been studied from a magnetostructural point of view, since a

notable feature of the magnetic susceptibility data for some of these copper(II) tetramers has been the occurrence of a maximum in the temperature dependence of the magnetic moment.^{13,14} So the further investigations about this tetranuclear copper(II) cluster are in progress in our laboratory. Here, in this paper, we report the synthesis and the crystal structure of $[\text{Cu}_4\text{OCl}_6(\text{C}_{14}\text{H}_{12}\text{N}_2)_4]$, also the EPR spectrum have been investigated.

Experimental Section

All chemical reagents were obtained from a commercial source and used without further purification.

Synthesis. Benzimidazole (0.12 g, 1.0 mmol) was reacted with benzyl chloride (0.13 g, 1.0 mmol) in 15 mL pyridine. After refluxing for 2 h, an aqueous solution (10 mL) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.25 g, 1 mmol) was added. The slurry was generated, then sealed in a 30 mL stainless-steel reactor with Teflon liner at 120 °C for 36 h resulting in the formation of the blue precipitate. The blue crystals were obtained from ethanol by upon slow evaporation at room temperature for three days. They were all collected, dried and submitted for elemental analysis. Yield: 75%. Calc. for $\text{C}_{56}\text{H}_{48}\text{Cl}_6\text{Cu}_4\text{N}_8\text{O}$: C, 51.11; H, 3.68; N, 8.52. Found: C, 50.78; H, 3.39; N, 8.61%.

X-ray structure determination. A summary of the key crystallographic information is given in Table 1. The data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). The collected data was reduced by using the program SAINT¹⁵ and empirical absorption correction was done by using the SADABS¹⁶ program. The structure was solved by direct methods using SHELXTL software package.¹⁷ All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. The hydrogen atoms were

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Table 1. Summary of crystallographic results for [Cu₄Cl₆O-(C₁₄H₁₂N₂)₄]

Empirical formula	C ₅₆ H ₄₈ Cl ₆ Cu ₄ N ₈ O
Formula weight	1315.88
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 14.310(3) Å <i>b</i> = 12.944(3) Å <i>β</i> = 91.43(3) ° <i>c</i> = 30.178(6) Å
Volume	5588.1(19) Å ³
Z, Calculated density	4, 1.564 Mg/m ³
Absorption coefficient	1.836 mm ⁻¹
<i>F</i> (000)	2664
<i>θ</i> range for data collection	1.35 to 23.99 °
Limiting indices	0 ≤ <i>h</i> ≤ 16, 0 ≤ <i>k</i> ≤ 14, -34 ≤ <i>l</i> ≤ 43
Reflections collected / unique	9146 / 8752 [<i>R</i> _{int} = 0.0819]
Completeness to <i>θ</i> = 23.99 °	99.6%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	8752 / 0 / 696
Goodness-of-fit on <i>F</i> ²	1.004
Final <i>R</i> indices [<i>I</i> > 2 sigma(<i>I</i>)]	<i>R</i> 1 = 0.0447, <i>wR</i> 2 = 0.0836
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1554, <i>wR</i> 2 = 0.1068
Largest diff. peak and hole	0.540 and -0.414 e.Å ⁻³

located by difference synthesis and refined geometrically. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-210724). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, email: deposit@ccdc.cam.ac.uk.

Results and Discussion

Description of the structure. Selected bond distances and angles are listed in Table 2. Figure 1 shows the molecular structure of the title compound. Figure 2 shows the core of the cluster containing nitrogen atoms coming from the 3-benzyl-benzimidazole ligands.

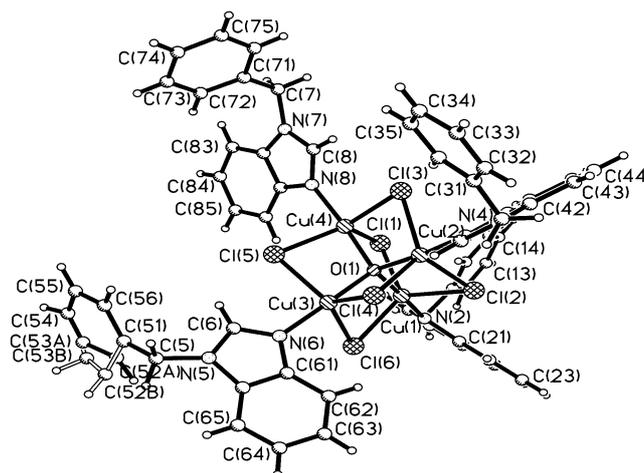
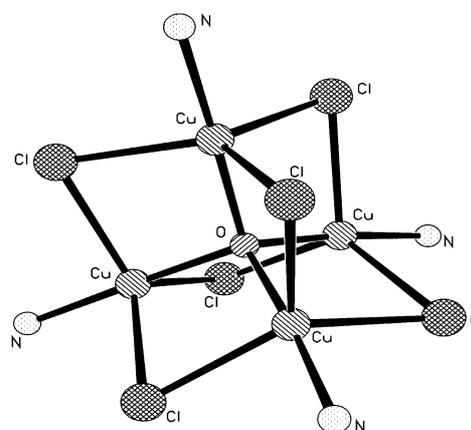
The basic moiety of the molecule structure contains a core of cluster and four 3-benzyl-benzimidazole ligands. The core of cluster consists of four Cu, one O and six μ_2 -Cl atoms. The interesting aspects of the structure are the adamantanoid geometries of the cluster core ($\sim T_d$ point symmetry) in which the copper atoms occupy the bridge-head positions and six μ_2 -Cl atoms occupy the bridging sites. Four Cu(II) ions locate four capsheaves of a nearly ideal tetrahedral skeletal structure with all the Cu-Cu-Cu angles ranging from 59.03 to 61.76°. All the Cu-Cu bond lengths (3.0986-3.1162 Å) are comparable with those found in the similar cluster compound [Cu₄OCl₆(Im)₄·0.83CH₃OH [Im = imidazole] (3.061(1)-3.1677(1) Å)¹⁴

The most distinctive structure feature of the cluster core is that an oxygen atom as interstitial atom occupies the center position of above tetrahedron and it is ideally tetrahedrally

Table 2. Selected bond lengths [Å] and angles [°] for [Cu₄Cl₆O-(C₁₄H₁₂N₂)₄]

Cu(1)-O(1)	1.921(4)	Cu(1)-N(2)	1.978(5)
Cu(1)-Cl(6)	2.367(2)	Cu(1)-Cl(1)	2.393(2)
Cu(1)-Cl(2)	2.4959(19)	Cu(2)-O(1)	1.917(4)
Cu(2)-N(4)	1.967(5)	Cu(2)-Cl(4)	2.411(2)
Cu(2)-Cl(3)	2.4164(19)	Cu(2)-Cl(2)	2.4235(18)
Cu(3)-O(1)	1.900(4)	Cu(3)-N(6)	1.966(5)
Cu(3)-Cl(4)	2.3870(19)	Cu(3)-Cl(5)	2.3915(19)
Cu(3)-Cl(6)	2.4121(19)	Cu(4)-O(1)	1.904(4)
Cu(4)-N(8)	1.949(5)	Cu(4)-Cl(3)	2.3802(19)
O(1)-Cu(1)-N(2)	174.49(19)	O(1)-Cu(1)-Cl(6)	85.06(12)
N(2)-Cu(1)-Cl(6)	95.51(15)	O(1)-Cu(1)-Cl(1)	84.92(12)
N(2)-Cu(1)-Cl(1)	90.37(16)	Cl(6)-Cu(1)-Cl(1)	126.55(9)
O(1)-Cu(1)-Cl(2)	82.47(12)	N(2)-Cu(1)-Cl(2)	102.24(16)
Cl(6)-Cu(1)-Cl(2)	113.65(8)	Cl(1)-Cu(1)-Cl(2)	116.76(8)
Cu(4)-Cl(1)-Cu(1)	80.81(6)	Cu(1)-Cl(6)-Cu(3)	81.38(6)
Cu(3)-O(1)-Cu(4)	109.92(18)	Cu(2)-O(1)-Cu(1)	112.04(18)

Symmetry transformations used to generate equivalent atoms.

**Figure 1.** Molecular structure of [Cu₄Cl₆O(C₁₄H₁₂N₂)₄] with the atomic numbering scheme.**Figure 2.** Cluster core of the title compound.

coordinated to four Cu atoms with the average Cu-O-Cu angles 108.88°, which is in agreement with 109.47° of an

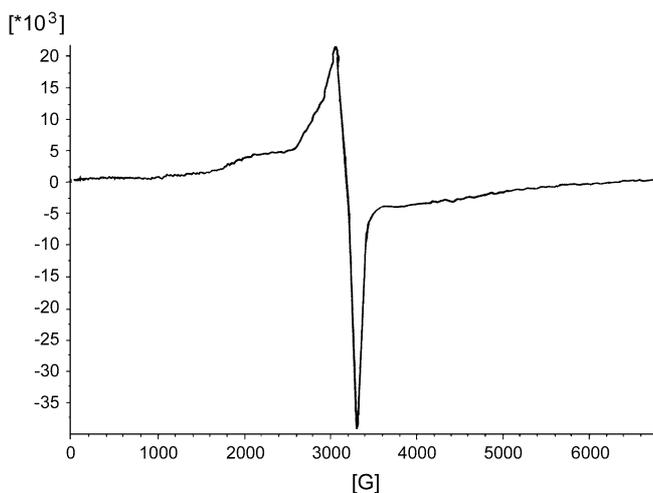


Figure 3. 110 K EPR spectra of the title complex.

ideal tetrahedron. The average Cu-O bond distances are 1.911 Å.

Four copper(II) ions have the similar coordination environment. Each copper atom possesses slightly distorted trigonal bipyramidal geometry with three μ_2 -Cl atoms in equatorial positions and the interstitial O atom and one N atom from 3-benzyl-benzimidazole ligand occupying axial positions. Twelve angles of O-Cu-Cl are all smaller than 90° , average angles are 84.73° . Accordingly, twelve angles of N-Cu-Cl are all larger than 90° , average angles are 95.39° . This phenomenon may be caused by the sterically hindered effect of 3-benzyl-benzimidazole ligands or by the formation of μ_2 -Cl bridges. Six Cu-Cl-Cu bond angles are from $80.48(6)^\circ$ to $81.38(6)^\circ$. Cu-N bond lengths [1.949-1.978 Å] are consistent with those of [1.909(4)-1.960(4) Å] found in complex with trigonal bipyramidal coordination $[\text{Cu}_2(\text{AEPy})_2]\cdot\text{H}_2\text{O}$ (AEPyH₂ = Bis[3-(2-pyridine-carboxamido)ethyl]methylamine).¹⁸ No significant difference of Cu-Cl [average length 2.415 Å] is observed compared with those of in penta-coordinated copper complex $[\text{Cu}_2\text{L}_2\text{Cl}][\text{BF}_4]\cdot\text{H}_2\text{O}$ [2.443(3) and 2.404(3) Å].¹⁹

EPR properties. The powder EPR spectra were recorded on a Bruker 2000-SRC spectrometer. The 110 K EPR spectrum of the complex is shown in Figure 3. Spectra of polycrystalline copper(II) complexes, exhibiting two types of g values, g_{\parallel} and g_{\perp} , have been used to distinguish unambiguously between $d_{x^2-y^2}$ and d_{z^2} ground states for which $g_{\parallel} > g_{\perp}$ and $g_{\perp} > g_{\parallel} \approx 2.00$, respectively.²⁰ The copper(II) complex studied here shows a pronounced peak ($g_{\perp} = 2.107$) and another pronounced peak ($g_{\parallel} = 2.210$) typical of a d^9 complex possessing axial symmetry and with the unpaired electron present in the $d_{x^2-y^2}$ orbital.²¹ In axial

symmetry the g values are related by the expression $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between copper centers in the polycrystalline solid. If $G > 4$, the exchange interaction is negligible; $G < 4$ indicates considerable exchange interaction. In this complex, $G = 1.95$ indicates there is a little strong interaction between Cu atom.

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References

- Sakai, T.; Hamada, T.; Awata, N.; Watanabe, J. *Pharmacobio. Dyn.* **1989**, *12*, 530.
- Brown, H. D.; Matzuk, A. R.; Ilves, I. R.; Peterson, L. H.; Harris, S. A.; Saret, L. H.; Egerton, J. R.; Yakstis, J. J.; Campbell, W. C.; Cuckler, A. C. *J. Am. Chem. Soc.* **1961**, *83*, 1764.
- Preston, P. N. *Chem. Rev.* **1974**, *74*, 279.
- Bouwman, E.; Driessen, W. L.; Reedijk, J. *Coord. Chem. Rev.* **1990**, *104*, 143.
- Pujar, M. A.; Bharamgoudar, T. D.; Sathyanarayana, D. N. *Transition Met. Chem.* **1988**, *13*, 423.
- O'Sullivan, D. G.; Wallis, A. K. *J. Med. Chem.* **1972**, *15*, 103.
- Mylonas, S.; Valavanidis, A.; Dimitropoulos, K.; Polissiou, M.; Tsiftoglou, A. S.; Viziranakis, I. S. *J. Inorg. Biochem.* **1988**, *34*, 265.
- (a) Bei, F. L.; Jian, F. F.; Lu, L. D.; Yang, X. J.; Wang, X. *Acta Cryst.* **2000**, *C56*, 718. (b) Jian, F. F.; Bei, F. L.; Yang, X. J.; Lu, L. D.; Wang, X. *Acta Cryst.* **2001**, *C57*, 176. (c) Bei, F. L.; Jian, F. F.; Yang, X. J.; Lu, L. D.; Wang, X. *Acta Cryst.* **2001**, *C57*, 45.
- Bertrand, J. A.; Kelly, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 4746.
- (a) Bertrand, J. A.; Kelly, J. A. *Inorg. Chem.* **1969**, *9*, 1982. (b) Gill, N. S.; Sterns, M. *Inorg. Chem.* **1970**, *9*, 619. (c) Dickinson, R. C.; Helm, F. T.; Baker, A.; Black, T. D.; Watson, D. H. *Inorg. Chem.* **1977**, *16*, 1530.
- Drake, R. F.; Crawford, V. H.; Hatfield, W. *J. Chem. Phys.* **1974**, *60*, 4525.
- Norman, R. E.; Rose, N. J.; Stenkamp, R. E. *Acta Cryst.* **1989**, *C45*, 1707.
- Atria, A. M.; Vega, A.; Contreras, M.; Valenzuela, J.; Spodine, E. *Inorg. Chem.* **1999**, *38*, 5681.
- Jones, D. H.; Sams, J. R.; Thompson, R. C. *J. Chem. Phys.* **1983**, *79*, 3877.
- Sheldrick, G. M. *SAINTE V4 Software Reference Manual*; Siemens Analytical X-ray Systems, Inc.: Madison Wisconsin, USA, 1996.
- Sheldrick, G. M. *SADABS. Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Germany, 1996.
- Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
- Rowland, J. M.; Thornton, M. L.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **2001**, *40*, 1069.
- Fang, C. J.; Duan, C. Y.; Guo, D.; He, C.; Meng, Q. J.; Wang, Z. M.; Yan, C. H. *Chem. Commun.* **2001**, 2540.
- Hathaway, B. J.; Tomlinson, A. A. G. *Coord. Chem. Rev.* **1970**, *5*, 1.
- Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1196.