

# [1-(Benzimidazol-2-ylmethyl)-1,4,7-triazacyclononane]chlorocopper(II) perchlorate

Qing-Xiang Li, Yi-Zhi Li and  
Qin-Hui Luo\*

Coordination Chemistry Institute, State Key Laboratory, of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: llyyz@nju.edu.cn

## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

$R$  factor = 0.036

wR factor = 0.069

Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title complex,  $[\text{Cu}^{\text{II}}\text{Cl}(\text{C}_{14}\text{H}_{21}\text{N}_5)]\text{ClO}_4$ , the Cu atom is located at the center of a distorted trigonal bipyramid of five coordinating atoms (four N atoms and one Cl atom). Two N atoms are located in axial positions, and the other two N atoms and the Cl atom are in the equatorial plane. The Cu atom is located 0.0670 (2) Å below the equatorial plane.

Received 14 November 2002

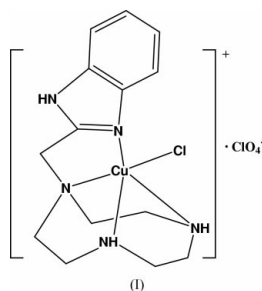
Accepted 2 December 2002

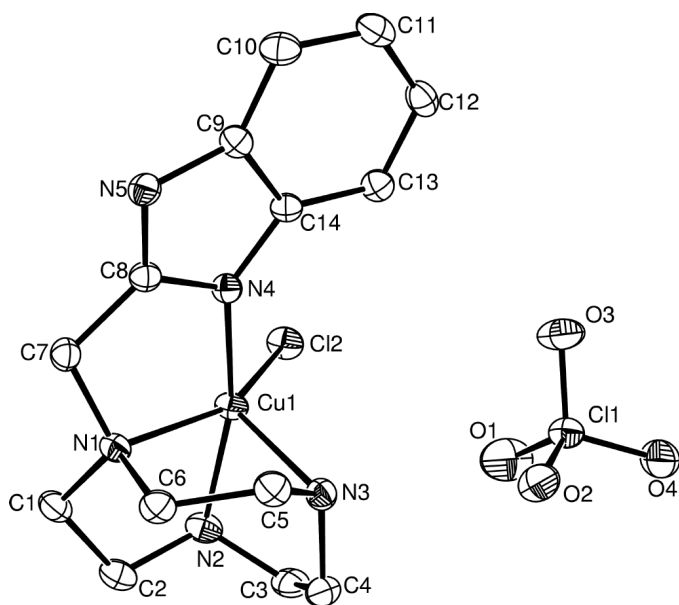
Online 19 December 2002

## Comment

In recent years, N-functionalized 1,4,7-triazacyclononanes (tacn) have attracted attention, since they afford versatile and efficient ligands. Some metal complexes involving such ligands have potential applications: the modeling of enzymes (Wainwright, 1997), radiotherapeutic agents and time-resolved luminescence labels (Charbonnière *et al.*, 2001). Derivatives of tacn with pendant pyridines (Tamura *et al.*, 2000), anilines (Fallis *et al.*, 2000), imidazoles, pyrazoles (Di Vaira *et al.*, 2000), *etc.* have been reported. However, the crystal structures of derivatives of tacn with benzimidazole have not yet been reported.

Here we report the crystal structure of one such complex, *viz.* [1-(benzimidazol-2-ylmethyl)-1,4,7-triazacyclononane]chlorocopper(II) perchlorate, (I), which has potential pharmaceutical application as an SOD (superoxide dismutase) mimic. In this complex, the copper atom is located at the center of a distorted trigonal bipyramid of five coordinating atoms (four N atoms and one chlorine atom). N2 and N4 are located in the axial positions, and N1, N3, Cl2 are in the equatorial plane. The N2–Cu1–N4 angle is 164.01 (9)°; the three axial-equatorial angles N2–Cu1–N1, N2–Cu1–N3, and N2–Cu1–Cl2 are 83.55 (8), 83.43 (9) and 94.26 (7)°, respectively. In the equatorial plane, the angles N1–Cu1–Cl2, Cl2–Cu1–N3 and N3–Cu1–N1 are 153.09 (6), 123.14 (6) and 83.37 (8)°, respectively. The copper atom is located 0.0670 (2) Å below the least-squares plane defined by N1, N3 and Cl2.





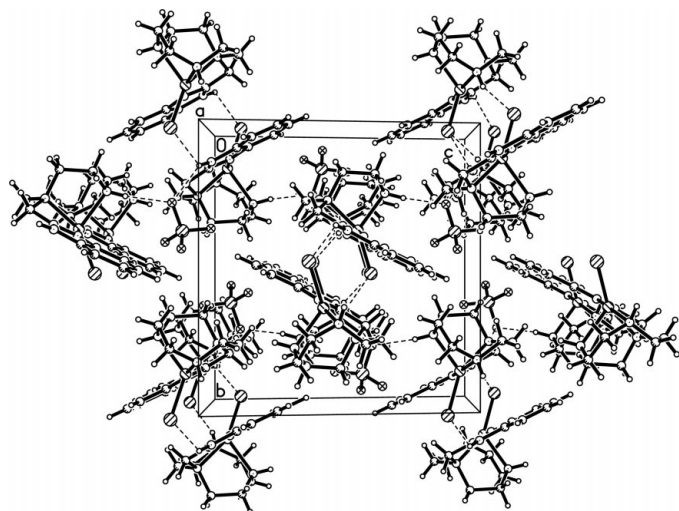
**Figure 1**  
View of the title complex, showing the labeling of the non-H atoms and 30% probability ellipsoids. H atoms have been omitted.

[1.964 (2) Å], whereas the average distance for the three bonds to the triazacyclononane-N atoms is 2.103 (6) Å. This value compares well with the corresponding value of 2.080 (1) Å in the related imidazole compound (Di Vaira *et al.*, 2000).

The crystal structure of the title complex is stabilized by hydrogen bonds of the type N—H···O(perchlorate) and N—H···Cl, where Cl belongs to a neighboring cation (Table 1).

## Experimental

1,4,7-Triazacyclononane (tacn) was prepared by a modified literature method (Koyama & Yoshino, 1972), while 2-chloromethylbenzimidazole (cbz) was prepared according to the method of Rousek (1991). The title compound was synthesized as follows: to a methanol



**Figure 2**  
A view of the crystal packing along the *a* axis. Hydrogen bonds are shown as dashed lines.

solution of tacn (0.05 mol) and cbz (0.05 mol) was added a methanol solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.05 mmol), with stirring at reflux. The mixture was stirred continuously for 5 h, and then cooled and filtered. Slow evaporation of the solution give a blue crystalline compound. Crystals suitable for X-ray analysis were obtained by diffusion of diethyl ether into an acetonitrile solution over a period of three days.

## Crystal data

[CuCl(C<sub>14</sub>H<sub>21</sub>N<sub>5</sub>)]ClO<sub>4</sub>  
*M<sub>r</sub>* = 457.80  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 10.336 (1) Å  
*b* = 13.428 (1) Å  
*c* = 13.051 (1) Å  
 β = 99.56 (2)°  
*V* = 1786.2 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.702 Mg m<sup>-3</sup>  
 Mo Kα radiation  
 Cell parameters from 3169 reflections  
 θ = 2.2–25.1°  
 μ = 1.55 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, blue  
 0.3 × 0.2 × 0.2 mm

## Data collection

Bruker APEX CCD area-detector diffractometer  
 φ and ω scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
*T<sub>min</sub>* = 0.696, *T<sub>max</sub>* = 0.733  
 9413 measured reflections

3334 independent reflections  
 2636 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.056  
 θ<sub>max</sub> = 25.5°  
*h* = −11 → 12  
*k* = −13 → 16  
*l* = −14 → 15

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR* (*F*<sup>2</sup>) = 0.069  
*S* = 1.09  
 3334 reflections  
 235 parameters

H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.02*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.39 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = −0.38 e Å<sup>-3</sup>

**Table 1**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2C···Cl2 <sup>i</sup>	0.91	2.49	3.361 (2)	160
N3—H3C···O2	0.91	2.25	3.058 (3)	148
N5—H5C···O2 <sup>ii</sup>	0.86	2.29	3.009 (3)	141
N5—H5C···Cl2 <sup>iii</sup>	0.86	2.73	3.331 (2)	128

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iii)  $1 - x, -y, -z$ .

All H atoms were placed geometrically and refined with a riding model. C—H values were set to 0.97 and 0.93 Å for atoms C1—C7 and C10—C13, respectively; N—H = 0.91 Å for N2 and N3, and 0.86 Å for N5. *U*<sub>iso</sub> was constrained to be 1.2*U*<sub>eq</sub> of the carrier atom.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

This project was supported by the National Science Foundation of China and The Nanjing University Talent Development Foundation (research grant No. 0205005122).

## References

- Bruker (2000). SMART, SAINT, SADABS and SHELXTL (version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.  
 Charbonnière, L., Ziessel, R., Guardigli, M., Roda, A., N. Sabbatini, N. & Cesario, M. (2001). *J. Am. Chem. Soc.* **123**, 2436–2439.  
 Di Vaira, M., Mani, F. & Stoppioni, P. (2000). *Inorg. Chim. Acta*, **303**, 61–69.  
 Fallis, I. A., Farley, R. D., Malik, K. M. A., Murphy, D. M. & Smith, H. J. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3632–3639.

Koyama, H. & Yoshino, T. (1972). *Bull. Chem. Soc. Jpn.* **45**, 481–484.  
Rousek, J. P. (1991). *Collect. Czech. Chem. Commun.* **56**, 1358–1360.

Tamura, M., Urano, Y., Kikuchi, K., Higuchi, T., Hirobe, M. & Nagano, T.  
(2000). *J. Organomet. Chem.* **611**, 586–592.  
Wainwright, K. P. (1997). *Coord. Chem. Rev.* **166**, 35–90.