

## Crystal Structure of Dinuclear Cu(II) Complex of 1,4-Di(1,4,7-triazonan-1-yl)butan-2-ol

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A new dinucleating ligand, 1,4-di(1,4,7-triazonan-1-yl)butan-2-ol (L-OH), was synthesized, and a dinuclear Cu(II) complex was prepared and characterized by X-ray crystallography. The compound crystallized in a monoclinic system, and was characterized thus:  $P2_1$ ,  $a = 9.808(9)$ ,  $b = 14.308(13)$ ,  $c = 10.951(10)$  Å,  $\beta = 103.075(15)^\circ$ ,  $Z = 2$ ,  $V = 1497(2)$  Å<sup>3</sup>. The crystal structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  to final values of  $R1 = 0.0823$  and  $wR2 = 0.2051$ .

(Received September 12, 2008; Accepted December 26, 2008; Published on web February 10, 2009)

A number of polyodal ligands derived from 1,*n*-diaminoalcohols and acyclic amines, such as pyridyl, phenolic, or imidazolyl moieties, have been used in modeling studies related to the active sites of metalloenzymes including dioxygen binding.<sup>1</sup> Such examples of macrocyclic polyamine derivatives are relatively rare. Recently, an endogenously bridged Cu(II) complex incorporating a deprotonated form of the dinucleating ligand, 1,3-di(1,4,7-triazonan-1-yl)propan-2-ol (T<sub>2</sub>PrOH), has been reported.<sup>2</sup> The two Cu centers were in slightly different distorted square pyramidal Cu(II) geometries and 3.582(1) Å apart.

In order to investigate the effect of changes in the ligand structure, we prepared a new dinucleating ligand, 1,4-di(1,4,7-triazonan-1-yl)butan-2-ol (L-OH). The bridging unit in L-OH is 2-hydroxybutane, while it was 2-hydroxypropane in T<sub>2</sub>PrOH. The asymmetrical ligand, L-OH was synthesized according to modified literature procedures.<sup>3,4</sup> The Cu<sub>2</sub>(L-O)(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub> complex was prepared by the reaction of L-OH (0.3 mmol, 100 mg), Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.64 mmol, 237 mg) and triethylamine (0.3 mmol, 42.4 μl) in absolute ethanol (10 ml). The solution turned to dark blue with precipitation, and was stirred for overnight. The reaction mixture was evaporated to dryness and washed with cold ethanol. The solid was dissolved in methanol (60°C), and was slowly evaporated to give blue plate crystals for X-ray structure analysis. The crystal and structure-refinement data are summarized in Table 1. H atoms, except for water hydrogen atoms, were placed at the calculated positions, with

C-H distances of 0.97 Å and N-H distances of 0.91 Å, and treated as riding atoms, with  $U_{iso}(H) = 1.2 U_{eq}(C)$ . The selected bond distances and angles are listed in Table 2. A chemical diagram is shown in Fig. 1, and the structure is shown in Fig. 2.

The title compound was obtained as a rod crystal with the monoclinic space group  $P2_1$ . A symmetric unit contains a Cu<sub>2</sub>(L-O<sup>-</sup>) cation, two water molecules, and three ClO<sub>4</sub><sup>-</sup> anion.

Table 1 Crystal data and experimental data

|  |
|--|
| Chemical formula: C <sub>16</sub> H <sub>39</sub> Cl <sub>3</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>15</sub> |
| Formula weight: 788.96   |
| $T = 293$ K  |
| Crystal system: monoclinic   |
| Space group: $P2_1$  |
| $a = 9.808(9)$ Å   |
| $b = 14.308(13)$ Å   |
| $c = 10.951(10)$ Å   |
| $\beta = 103.075(15)^\circ$  |
| $V = 1497(2)$ Å <sup>3</sup>   |
| $Z = 2$  |
| Calculated density: 1.750 g/cm <sup>3</sup>  |
| Radiation: 0.71073 Å (Mo $K_\alpha$ )  |
| $\lambda(\text{Mo } K_\alpha) = 1.765$ mm <sup>-1</sup>  |
| $F(0\ 0\ 0) = 812$   |
| Crystal size = 0.10 × 0.08 × 0.02 mm   |
| No. of reflections collected = 8199  |
| No. of reflections used = 4753   |
| $\theta$ range for data collection: 2.13 to 26.00°   |
| Data/Restraint/Parameters = 4753/8/391   |
| Goodness-of-fit on $F^2 = 0.974$   |
| $R$ indices [ $I > 2\sigma(I)$ ]: $R1 = 0.0820$ , $wR2 = 0.2046$   |
| $R$ indices [all data]: $R1 = 0.1004$ , $wR2 = 0.2219$   |
| $(\Delta\sigma)_{\max} < 0.001$  |
| $(\Delta\rho)_{\max} = 1.347$ e.Å <sup>-3</sup>  |
| $(\Delta\rho)_{\min} = -1.663$ e.Å <sup>-3</sup>   |
| Measurement: Bruker SMART AXIS   |
| Program system: Bruker SAINT PLUS  |
| Structure determination: SHELXTL   |
| Refinement: full-matrix least-squares on $F^2$   |
| CCDC deposition number: 695103   |

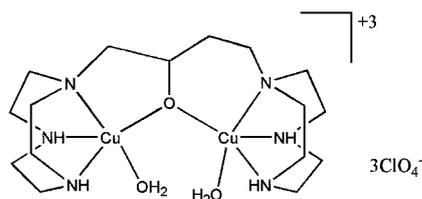


Fig. 1 Structural chemical diagram.

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Table 2 Selected bond distances [ $\text{\AA}$ ] and angles [ $^\circ$ ]

|                   |           |                   |           |
|-------------------|-----------|-------------------|-----------|
| Cu(1)-O(1)        | 1.948(7)  | Cu(1)-N(12)       | 2.014(10) |
| Cu(1)-O(2)        | 2.030(12) | Cu(1)-N(11)       | 2.037(12) |
| Cu(1)-N(13)       | 2.183(10) | Cu(2)-O(1)        | 1.950(7)  |
| Cu(2)-N(23)       | 1.999(8)  | Cu(2)-O(3)        | 2.001(7)  |
| Cu(2)-N(22)       | 2.101(10) | Cu(2)-N(21)       | 2.215(11) |
| O(1)-Cu(1)-N(12)  | 175.9(5)  | O(1)-Cu(1)-O(2)   | 93.1(4)   |
| N(12)-Cu(1)-O(2)  | 90.7(5)   | O(1)-Cu(1)-N(11)  | 92.6(4)   |
| N(12)-Cu(1)-N(11) | 83.4(5)   | O(2)-Cu(1)-N(11)  | 168.4(4)  |
| O(1)-Cu(1)-N(13)  | 95.3(4)   | N(12)-Cu(1)-N(13) | 85.2(4)   |
| O(2)-Cu(1)-N(13)  | 104.5(4)  | N(11)-Cu(1)-N(13) | 85.1(4)   |
| O(1)-Cu(2)-N(23)  | 87.0(3)   | O(1)-Cu(2)-O(3)   | 88.0(3)   |
| N(23)-Cu(2)-O(3)  | 174.9(4)  | O(1)-Cu(2)-N(22)  | 147.3(4)  |
| N(23)-Cu(2)-N(22) | 85.5(4)   | O(3)-Cu(2)-N(22)  | 98.3(3)   |
| O(1)-Cu(2)-N(21)  | 129.1(4)  | N(23)-Cu(2)-N(21) | 83.7(4)   |
| O(3)-Cu(2)-N(21)  | 100.2(4)  | N(22)-Cu(2)-N(21) | 81.5(4)   |

Figure 2 shows a  $[\{\text{Cu}(\text{H}_2\text{O})_2\}(\text{L}-\text{O})]^{3+}$  cation containing coordinated water molecules on each Cu ion. The asymmetric ligand L-O<sup>-</sup> contains two [9]aneN<sub>3</sub> units linked by a 2-hydroxylbutyl group. Three nitrogen atoms of each [9]aneN<sub>3</sub> moiety are coordinated to each Cu ion, and an oxygen atom of the 2-hydroxylbutyl linker bridges two Cu ions. Each water molecule coordinates each Cu ion, and one of the oxygen atoms bridges two Cu ions asymmetrically with a Cu1-O3 distance of 2.88(1) $\text{\AA}$ . The coordination geometry of the Cu1 ion is a distorted octahedron with a tertiary amine (N13) of the L-O<sup>-</sup> and a water oxygen atom (O3) in *trans* to each other, and that of the Cu2 ion is a trigonal pyramid (tbp) with a tertiary amine of the L-O<sup>-</sup> and a water occupying the axial positions. The Cu1-O1(L-O<sup>-</sup>) and Cu2-O1(L-O<sup>-</sup>) bond distances are 1.948(7) and 1.950(7) $\text{\AA}$ , respectively. The Cu1-O2(water) and Cu2-O3(water) bond distances are 2.032(12) and 2.001(7) $\text{\AA}$ ,

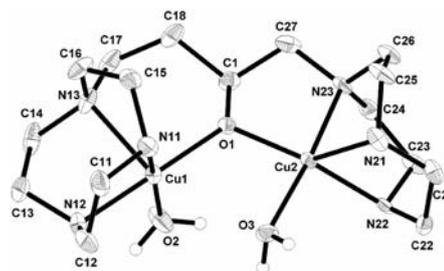


Fig. 2 Structure of  $[\{\text{Cu}(\text{H}_2\text{O})_2\}(\text{L}-\text{O})]^{3+}$  with the labeling scheme at 30% probability. Hydrogen atoms, except for water hydrogen atoms, were omitted, and all counter anions ( $\text{ClO}_4^-$ ) are not shown for clarity.

respectively. The Cu1-O1-Cu2 angle is  $120.0(3)^\circ$ . Two Cu ions are 3.38(3) $\text{\AA}$  apart.

### Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (RO4-2003-000-10097-0).

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