Crystal and Molecular Structure of a Cu(II) Complex with Macrocyclic Ligand of 10,12-dibromo-6-ethylcyanide-3,6,14,18-tetraazapentaicosa-1(25), 8(24),10,12,13,19,21,23-octaene-24,25-diol

Hamid GOLCHOUBIAN[†] and Davod Sadeghi FATEH

Department of Chemistry, University of Mazandaran, Babolsar 47416-95447, Iran

The crystal structure of the title compound was determined by single-crystal X-ray diffraction. The compound crystallizes in a monoclinic system and was characterized thus: $P2_1/n$, $a = 8.6189(2)\text{\AA}$, $b = 17.9591(7)\text{\AA}$, $c = 18.4009(6)\text{\AA}$, $\beta = 102.2560(19)^\circ$, $Z = 4$, $V = 2783.32(16)\text{\AA}^3$. In the mono nuclear macrocyclic complex the copper(II) ion resides at the N(imine)₂O₂ coordination site, whereas the other compartment, N(amine)₂O₂, is occupied by a proton. The geometry around copper(II) is square-planar.

(Received November 30, 2010; Accepted May 14, 2011; Published on web July 10, 2011)

Phenol-based macrocyclic ligands having two dissimilar metal-binding sites sharing two phenolic oxygen atoms received a rapidly growing area of research, because of their importance in biomimetic studies of binuclear metalloproteins, their interesting catalytic properties, their ability to stabilize unusual oxidation states and mixed-valence compounds.¹⁻⁵ So far, many unsymmetrical phenol-based dinucleating ligands with respect to the shape and flexibility of the coordination compartment and the nature of donor atoms have been developed. Among them, special attention has been focused on unsymmetrical compartmental ligands containing two pendant arms and their metal complexes.¹ However, there is no report concerning a dicompartmental ligand with one pendent arm. A mononuclear copper(II) complex of this type ligand is presented in Fig. 1. The macrocyclic phenol-based ligand includes two different compartments, a four-coordinating N₂O₂ site including two imine nitrogen atoms and two phenolic oxygen atoms along with potentially a penta-coordinating N₃O₂ site made by nitrogen atoms of two aminic, a nitrile groups and two phenolic

oxygen atoms. The mononuclear complexes prepared by such a ligand can be used for preparing of heterodinuclear complexes. Additionally, the N-H moiety can be condensed with various types of halo-compounds to produce compartmental ligands with two different pedant arms.

The copper complex was prepared by allowing the macrocyclic ligand to react with an equimolar amount of

Fig. 1 Chemical structure of the title compound.

[†] To whom correspondence should be addressed.
E-mail: h.golchobian@umz.ac.ir

Table 1 Crystal and experimental data

Chemical formula: C ₂₄ H ₂₆ Br ₂ CuF ₆ N ₅ O ₂ P	
Formula weight = 784.83	
T = 150(1)K	
Crystal system: monoclinic	
Space group: $P2_1/n$	
$a = 8.6189(2)\text{\AA}$	$c = 18.4009(6)\text{\AA}$
$b = 17.9591(7)\text{\AA}$	$\beta = 102.2560(19)^\circ$
$V = 2783.32(16)\text{\AA}^3$	
$Z = 4$	
$D_x = 1.873\text{ g/cm}^3$	
Radiation: Mo K_α radiation ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo } K_\alpha) = 3.787\text{ mm}^{-1}$	
$F(0\ 0\ 0) = 1556$	
Crystal size = $0.16 \times 0.08 \times 0.06\text{ mm}^3$	
No. of Reflections collected = 18221	
No. of Independent reflections = 4969 [$R(\text{int}) = 0.0717$]	
Theta range for data collection: 2.67 to 25.18°	
Data/restraints/parameters = 4969/14/384	
Goodness-of-fit on $F^2 = 1.021$	
Final R indices [for 3442 reflections with $I > 2\sigma(I)$]: $R1 = 0.0448$, $wR2 = 0.0990$	
R indices (all data): $R1 = 0.0772$, $wR2 = 0.1129$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.44\text{ e.\AA}^{-3}$	
$(\Delta\rho)_{\text{min}} = -0.44\text{ e.\AA}^{-3}$	
Measurement: Nonius KappaCCD	
Program system: Denzo-SMN	
Structure determination: SHELXTL V6.1 (Sheldrick, 2008)	
Refinement: full-matrix least-square on F^2	
CCDC deposition number: 755141	

Table 2 Selected bond lengths (Å) and angles (°)

Cu(1)-O(1)	1.919 (3)	Cu(1)-N(1)	1.997 (4)
Cu(1)-O(2)	1.914 (3)	Cu(1)-N(2)	1.971(4)
N(1)-C(7)	1.284(6)	N(2)-C(11)	1.294(6)
N(5)-C(24)	1.20(3)	N(5A)-C(24A)	1.04(9)
O(2)-Cu(1)-O(1)	79.92(13)	O(2)-Cu(1)-N(2)	91.37(14)
O(1)-Cu(1)-N(2)	171.14(14)	O(2)-Cu(1)-N(1)	170.46(14)
O(1)-Cu(1)-N(1)	91.12(14)	N(2)-Cu(1)-N(1)	97.67(16)
N(5)-C(24)-C(23)	174(2)	N(5A)-C(24A)-C(23A)	163(7)

Fig. 2 ORTEP plot of the title compound. Thermal ellipsoids drawn at 50% probability level.

copper(II) acetate and twice the mole ratio of triethylamine in ethanol. The copper(II) complex was precipitated almost immediately after adding a saturated solution of NH_4PF_6 in ethanol. A crystal suitable for an X-ray structural determination was grown from acetonitrile.

A crystal having dimensions of $0.16 \times 0.08 \times 0.06 \text{ mm}^3$ was chosen for X-ray diffraction studies. Measurements were made on a Nonius KappaCCD diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073 \text{ Å}$) at 150 K. The structure was solved by direct methods using SHELXS-2008, and refined by full-matrix least-squares techniques anisotropically for all non-H atoms.⁶ The positions of the H atoms were placed at geometrically idealized positions, and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Restraints were applied to the geometry and displacement parameters of the disorder components using the SADI and EADP commands in SHELXL-97.⁶ Table 1 summarizes the crystal and experimental data. The selected interatomic distances and angles are given in Table 2. An ORTEP plot of the molecular structure along with the atomic numbering scheme is depicted in Fig. 2.

The crystallographic result clearly demonstrates that the Cu(II) resides in the $\text{N}(\text{imine})_2\text{O}_2$ coordination site. The geometry around the copper ion is essentially planar, and similar to that of N,N' -1,3-trimethylenedisalicylideneaminatonickel(II).⁷ The Cu(1)-O(1), Cu(1)-O(2), Cu(1)-N(1) and Cu(1)-N(2) bond distances are 1.919(3), 1.914(3), 1.997(4) and 1.971(4) Å, respectively. The O(2)-Cu(1)-O(1), O(1)-Cu(1)-N(1), O(2)-Cu(1)-N(2) and N(2)-Cu(1)-N(1) angles are 79.92(13), 91.12(14), 91.37(14) and 97.67(16)°, respectively, and the sum of the angles is *ca.* 353°. This fact means a slight distortion of the CuN_2O_2 chromophore to tetrahedron. The dihedral angle

Table 3 Hydrogen bonds for the title compound [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4A)...F(2)	0.92	2.29	3.176(6)	162.3
N(4)-H(4A)...F(4)	0.92	2.54	3.228(6)	131.8
N(4)-H(4A)...F(6)	0.92	2.43	3.198(6)	141.5
N(4)-H(4B)...O(1)	0.92	2.05	2.720(5)	128.1

Symmetry transformations used to generate equivalent atoms.

Fig. 3 Fragment of crystal packing (projection along *c* axis).

between the least-squares plane, defined by O(1)-Cu(1)-N(1), and the plane defined by O(2)-Cu(1)-N(2) is 3.40°, which is much smaller than the dihedral angle (35.56°) found for N,N' -1,3-trimethylenedisalicylideneaminatonickel(II).⁷ The $\text{CH}_2\text{-CH}_2\text{-CH}_2$ group of 1,3-diaminopropane and the $\text{CH}_2\text{-C}\equiv\text{N}$ moiety of the pedant arm are disordered over two sets of sites with ratios of refined occupancies: 0.780(8):0.220(8) and 0.706(17):0.294(17), respectively. The asymmetric nitrogen, N(3), has an *S* configuration. Two protons are bonded to N(4), and make it a quaternary amine. There is hydrogen-bonding between the N(4)-H and O(1) atoms. The hydrogen-bonding distances and angles are presented in Table 3.

It is found that hydrogen bonding affects the molecular packing. Each molecule links to other molecules via hydrogen bonds of Br(1) and N(4) to form a two-dimensional sheet with zigzag structures along the crystallographic *c* axis, as shown in Fig. 3.

Acknowledgements

We are grateful for financial support from Mazandaran University of the Islamic Republic of Iran.

References

1. P. A. Vigato, S. Tamburini, and L. Bertolo, *Coord. Chem. Rev.*, **2007**, 251, 1311.
2. P. Akilan, M. Thirumavalavan, and M. Kandaswamy, *Polyhedron*, **2003**, 22, 3483.
3. H. Golchoubian, W. L. Waltz, and J. W. Quail, *Can. J. Chem.*, **1999**, 77, 37.
4. H. Okawa, H. Furutachi, and D. E. Fenton, *Coord. Chem. Rev.*, **1998**, 174, 51.
5. D. G. McCollum, G. P. A. Yap, L. Liable-Sands, A. L. Rheingold, and B. Bosnich, *Inorg. Chem.*, **1997**, 36, 2230.
6. G. M. Sheldrick, *Acta Cryst.*, **2008**, A64, 112.
7. K.-J. Inoue, M. Ohaba, and H. Okawa, *Bull. Chem. Soc. Jpn.*, **2002**, 75, 99.