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Short Communication

Synthesis and Crystal Structure of a New Tetracoordinated Copper(II) Complex of *N,N'*-Bis(quinolin-2-ylmethyl)-1,5-diazacyclooctane

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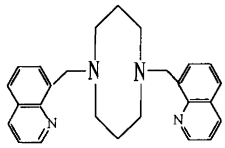
Although remarkable efforts[1] have been made in the study of functionalization of macrocyclic polyamines, the mini-macrocyclic diazaamines have been neglected to some extent. Up to now, only a few examples of a diazamacrocycle bearing functional pendant groups have been reported.[2–4] The stereochemistry of chelated 1,5-diazacyclooctane (daco)[5] suggests that the ligand can be used to design a relatively simple tetradentate ligand which would lead to the formation of planar metal complexes; such complexes might be potential catalysts for some reactions. The class of the daco derivatives can be used as model ligands for square-planar and square-pyramidal complexes. Some examples have indicated that transition-metal complexes with daco-like ligands bearing pendants adopt pentacoordination with square-pyramidal geometry, while tetracoordination complexes are rare.[6]

We report herein a new tetradentate ligand based on the daco mini-macrocycle, *N,N'*-bis(quinolin-2-ylmethyl)-1,5 diazacyclooctane (L) (**1**), and its copper complex, the crystal structure of which has been determined by X-ray diffraction. The geometry of the complex was found to be a square plane distorted towards a tetrahedron. To the best of our knowledge, it is the first example of a crystal structure with tetracoordination for a copper complex with a macrocyclic diazacyclooctane bearing functional pendant groups.

Experimental

Synthesis of ligand and complex. The ligand (L) was synthesized[7] by the reaction of 2-bromomethylquinoline and 1,5-diazacyclooctane in ethanol solution in the presence of KOH, and further purified by column chromatography. Yield: 60%. ^{1}H NMR (D_2O): δ 2.30 (m, 4 H, C–CH_2–C), 3.58 (t, 8 H, C–CH_2–N), 4.94 (s, 4 H, CH_2–Qu), 7.77–8.90 (m, 12 H, Qu). FTIR (KBr, cm^{-1}): 2930, 2750, 1630, 1597, 1560, 1491,1415, 1299, 1209, 951, 830, 770, 710.



The title complex was prepared by mixing 1:1 molar ratio of $Cu(ClO_4)_2$ (0.05 mmol) and L (0.05 mmol) in a methanol–water solution. The pH value was adjusted with aqueous NaOH solution (to pH 8–9). The reaction mixture was filtered, and a blue single crystal suitable for X-ray analysis was obtained. The crystalline material has the formula $Cu(C_{26}H_{28}N_4)(ClO_4)_2 \cdot H_2O$ according to elemental analysis [calcd. for $Cu(C_{26}H_{28}N_4)(ClO_4)_2 \cdot H_2O$ (found) %: C, 46.13 (46.04); H, 4.47 (4.08); N, 8.28 (8.66)]. IR (KBr, cm^{-1}): 3400, 2968, 1595 (quinoline), 1517, 1467, 1404, 1317, 1991 (ClO_4^-), 837, 810, 780, 624 (ClO_4^-).

Crystallographic studies. Diffraction data were collected at room temperature with an Enraf-Nonius CAD-4 diffractometer, using graphic monochromated Mo Kα radiation (λ = 0.710 73 Å). A total of 6342 independent reflections were recorded ($\theta_{max} \leq 27°$). The reflection data

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were corrected by empirical absorption correction (T_{min} = 0.952 and T_{max} = 0.999). The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were determined by successive Fourier syntheses and were isotropically refined. The refinement, including 3073 reflections with $I \geqslant 3.0\ \sigma(I)$, converged at $R = 0.071$ and $R_w = 0.075$. All calculations were carried out with the CAD4, MolEN and MULTAN programs.

Crystal parameters and refinement results are compiled in Table 1. Atom coordination of non-hydrogen atoms are listed in Table 2. Selected bond distances and bond angles in Table 3.

Results and discussion

X-Ray crystal and molecular structure. The structure of the title complex consists of a discrete monomeric $[Cu(C_{26}H_{28}N_4)]^+$ cation, two uncoordinated perchlorate anions and a H_2O molecule. Figure 1 shows a perspective view of the cationic entity of the complex. The copper(II) ion is in a four-coordinated environment and is involved in four six-membered metalla rings in the complex. Those derived from the daco portion of the ligand are in a chair and boat configuration. The pendant quinoline arms coordinate to the copper atom in an intersecting fashion. The dihedral angle between the two quinoline planes is 82.61°. This results in the formation of a strictly crowded pocket on the 'upper face' of the metal complex. It is different from five-coordinated complexes having a more open environment on the upper face.[3,5] On the other face, the central methylene C–H group from the boat form of the metalladiazacyclohexane ring shields the metal center. Therefore, the results interrupt the possibility of further coordination from 'upper and under

Table 1. Crystallographic data for $[Cu(C_{26}H_{28}N_4)](ClO_4)_2 \cdot H_2O$.

Chemical formula	$C_{26}H_{30}Cl_2N_4CuO_9$
FW	677.00
Space group	$P2_1/c'$
a/Å	8.155(5)
b/Å	14.948(4)
c/Å	20.443(3)
β/°	90
V/Å	2816.4(9)
Z	4
D (calcd.)/g cm^{-3}	1.60
λ/Å	0.71073
μ/mm^{-1}	1.03
T/K	293
Max. 2θ/°	54
No. of unique reflections	6342
No. of refl. in refinement	3074 [$I > 3\sigma(I)$]
Parameters refined	379
R	0.0710
R_w	0.0752
S	1.10
ρ_{max}/e Å^{-3}	0.80
ρ_{min}/e Å^{-3}	−0.15

Table 2. Atomic coordinates for $[Cu(C_{26}H_{28}N_4)](ClO_4)_2 \cdot H_2O$.

Atom	X	Y	Z
Cu	1.0042(1)	0.22894(6)	0.63533(5)
Cl1	0.4000(3)	0.2450(1)	0.9695(1)
Cl2	1.7138(3)	0.0647(1)	0.7503(1)
O1	0.242(1)	0.2599(9)	0.9639(7)
O2	0.464(2)	0.2181(7)	1.0299(5)
O3	0.443(1)	0.1924(6)	0.9253(5)
O4	0.472(2)	0.3155(7)	0.9624(8)
O5	1.675(1)	0.1337(5)	0.7137(4)
O6	1.608(1)	0.0040(5)	0.7307(5)
O7	1.868(1)	0.0435(6)	0.7370(7)
O8	1.721(2)	0.0753(8)	0.8116(4)
O9	0.618(2)	0.2531(9)	0.8271(7)
N1	0.8894(8)	0.3050(4)	0.5708(3)
N2	0.9906(8)	0.2975(4)	0.7133(3)
N3	1.2266(8)	0.1923(4)	0.6729(3)
N4	0.9331(8)	0.1291(4)	0.5894(3)
C1	0.913(1)	0.2927(5)	0.5088(4)
C2	0.872(1)	0.3468(6)	0.4592(5)
C3	0.803(1)	0.4155(6)	0.4727(5)
C4	0.772(1)	0.4318(5)	0.5366(4)
C5	0.815(1)	0.3747(5)	0.5861(4)
C6	0.784(1)	0.3886(5)	0.6518(4)
C7	0.707(1)	0.4577(6)	0.6654(5)
C8	0.662(1)	0.5135(6)	0.6168(6)
C9	0.694(1)	0.5023(6)	0.5550(5)
C10	0.823(1)	0.3308(5)	0.7062(4)
C11	0.775(1)	0.1260(5)	0.5688(4)
C12	0.688(1)	0.0563(5)	0.5527(4)
C13	0.770(1)	−0.0119(5)	0.5602(4)
C14	0.939(1)	−0.0133(5)	0.5809(4)
C15	1.022(1)	0.0602(5)	0.5954(4)
C16	1.192(1)	0.0611(5)	0.6152(4)
C17	1.274(1)	−0.0094(6)	0.6227(5)
C18	1.192(1)	−0.0816(6)	0.6090(5)
C19	1.030(1)	−0.0830(5)	0.5889(5)
C20	1.286(1)	0.1359(5)	0.6248(5)
C21	1.339(1)	0.2634(6)	0.6791(5)
C22	1.253(1)	0.3419(6)	0.6736(6)
C23	1.121(1)	0.3592(5)	0.7168(5)
C24	1.012(1)	0.2480(5)	0.7735(5)
C25	1.165(1)	0.2048(7)	0.7879(5)
C26	1.222(1)	0.1517(6)	0.7374(4)

Table 3. Selected bond distances (in Å) and bond angles (in °) for $[Cu(C_{26}H_{28}N_4)](ClO_4)_2 \cdot H_2O$.

Atoms	Distance	Atoms	Distance
Cu–N1	1.998(6)	Cu–N2	1.985(6)
Cu–N3	1.990(6)	Cu–N4	1.989(6)
N1–C1	1.32(1)	N1–C5	1.38(2)
N2–C10	1.47(1)	N2–C23	1.49(1)
N2–C24	1.48(1)	N3–C20	1.49(1)
N3–C21	1.51(1)	N3–C26	1.49(1)
N4–C11	1.31(2)	N4–C15	1.37(2)
N1–Cu–N2	94.9(3)	N1–Cu–N3	142.6(3)
N1–Cu–N4	98.5(3)	N2–Cu–N3	90.5(3)
N2–Cu–N4	146.7(3)	N3–Cu–N4	146.7(3)
Cu–N1–C1	114.9(6)	Cu–N1–C5	126.0(5)
Cu–N2–C10	106.5(5)	Cu–N2–C23	110.0(5)
Cu–N2–C24	108.9(5)	Cu–N3–C20	107.4(5)
Cu–N3–C21	107.6(5)	Cu–N3–C26	111.5(5)
Cu–N4–C11	114.1(5)	Cu–N4–C15	124.0(6)

faces' of the metal complex. Therefore, the copper(II) ion can be forced to form a four-coordinated complex and adopts the optimum arrangement of a square-planar complex distorted towards a tetrahedron around a copper atom. If the complex adopts regular square planar geometry, the four donor atoms should encounter greater steric hindrance from pendant arms (quinoline groups) of the ligand. The angles in the copper coordination sphere are in the range of 90.5–98.5° being between the angles of square-planar (90°) and tetrahedral (109°). The Cu–N distances of 1.985(6)–1.998(6) Å are in the range of normal Cu–N bonds, but they are slightly short.

At present this is the only example of four-coordination for a copper atom in complexes with ligands having pendant arms to the daco ring.[4]

The molecular stacking of the complex in the unit cell shows that an H_2O molecule links uncoordinated ClO_4^- ions through hydrogen bonding.

Spectral studies. The solution electronic spectra of the complex in a water–methanol mixture display two separate bands [λ_{max} (ε_{max}): 18433 (274 L mol^{-1} cm^{-1}) and 15131 (370) cm^{-1}], suggesting a square-based geometry around copper(II).[8] The average energies of the bands is lower than the range (17000–19000 cm^{-1}) expected for a CuN_4 square environment; this suggests the presence of a tetrahedral twist or a strong axial interaction. The band observed at 32584 cm^{-1} (14340 L mol^{-1} cm^{-1}) for the complex in water–methanol can be assigned to the $N(\pi_{qu}) \rightarrow Cu^{II}$ charge-transfer transition. The band at 42463 and 49383 cm^{-1} (45840 and 53790 L mol^{-1} cm^{-1}) are assigned to $\pi \rightarrow \pi^*$ transitions.

The X-band ESR spectra of the complex in a water–methanol solution at room temperature and 110 K have been obtained. The spectra of the complex are split into four equally spaced absorptions by interactions with the copper nucleus ($I=3/2$). The ESR and bonding parameters of the complex are as follows: $g_{iso}=2.091$, $A_{iso}=0.00776$ cm^{-1}, $g_{\parallel}=2.224$, $g_{\perp}=2.025$, $A_{\parallel}=0.0174$ cm^{-1}, $A_{\perp}=0.0029$ cm^{-1}, $\alpha^2=0.73$. The g values ($g_{\parallel} > g_{\perp} > g_e$) imply that the 3d unpaired electron of the copper(II) ion should occupy the $d_{x^2-y^2}$ orbital. The $g_{\parallel}$-values for CuN_4 chromophores are in the range 2.10–2.22.[8] The slightly higher $g_{\parallel}$-value observed for the present complex suggests the presence of the distortion towards a tetrahedron or axial interaction.[9] The α^2-value shows that the $d_{x^2-y^2}$ character of b_1 is in the range 0.7–0.8. The

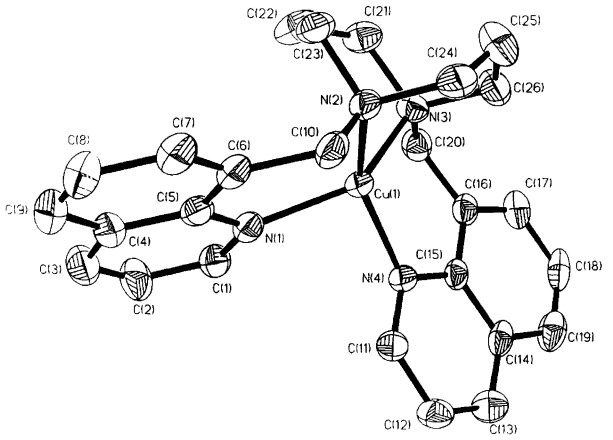

Fig. 1. A perspective view of the cationic entity of complex **1**.

smaller value of α^2 of the complex is indicative of some degree of covalent character for the bond between copper and the ligand.[9] This is in agreement with the result for the crystal structure determined in which the Cu–N bond distances are slightly short.

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