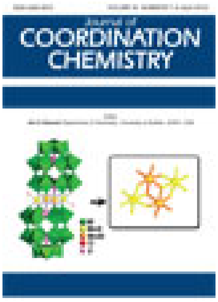

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Template-directed synthesis of macrocyclic copper(II) complexes of diazacyclam, 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane

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Template-directed synthesis of macrocyclic copper(II) complexes of diazacyclam, 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane

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Template reaction of copper(II) nitrate with *N*-(2-aminoethyl)-1,3-diaminopropane and formaldehyde yields a macrocyclic copper(II) complex of 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane (L), [CuL(NO_3)$_2$] (**1**). Replacement of nitrate with perchlorate gives [CuL(ClO_4)$_2$] (**2**). These complexes have been characterized by FT-IR and Raman spectroscopies, electronic absorption, cyclic voltammetry, and X-ray crystallography. The crystal structure of **1** shows that copper has distorted octahedral geometry with two secondary and two tertiary amines of the macrocycle and two oxygen atoms from nitrate coordinating the axial positions. The copper in **2** has the same geometry with axial positions occupied by one oxygen atom of perchlorate. Copper lies on the plane of four coordinated nitrogen atoms and there is no rms deviation from this plane. Cyclic voltammetry of **1** and **2** gives two one-electron waves corresponding to Cu^{II}/Cu^{III} $(-0.75, -0.72)$ and Cu^{II}/Cu^{I} (0.48, 0.24) processes. For understanding of geometry parameters in diazacyclam-based copper(II) complexes, a survey on complexes from CSD structures is presented. In this study the macrocycle hole size was estimated by ionic radii of metal ions located inside of it.

Keywords: Macrocycle; Diazacyclam; Copper complex; Template synthesis; X-ray crystal structure

1. Introduction

Interest in metal template synthesis of multidentate and macromonocyclic ligands in a range of structural motifs has developed. Syntheses of macrocycles were sometimes limited due to side reactions and polymerization, but metal template synthesis offers an alternative high yielding and often selective route to macrocyclic ligands with a range of geometries and potential uses [1, 2]. Macrocyclic complexes of transition metal ions have a number of unique properties offered by the macrocyclic environment, such as extremely high thermodynamic stability, the ability to access unusual oxidation states of

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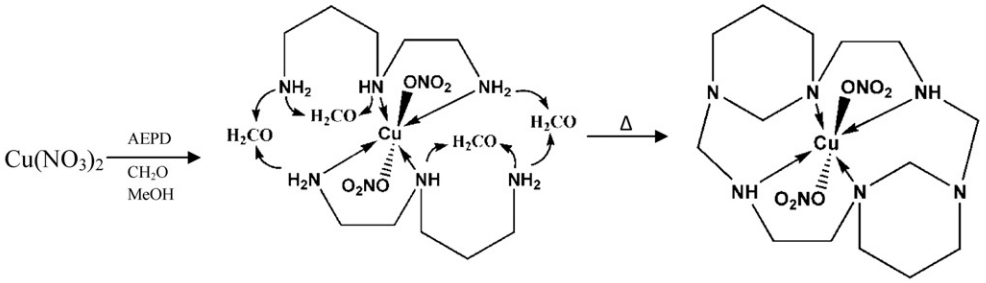


Scheme 1. The proposed synthetic route for **1**.

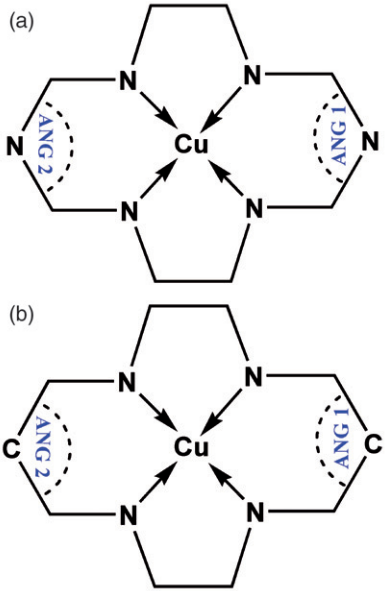
the metal [3], metal ion-selective reagents [4–6], models for metalloenzyme active sites [7, 8], applications in biology and medicine and also as catalysts for conversion of various organic substrates [9–11].

The basic reactions involved in the synthesis of macrocyclic compounds are very simple and of a very few types. In most cases, these reactions involve formation of heteroatom-carbon bonds such as O–C [12], S–C [13, 14], N–C [15, 16], and N=C [17, 18]; C–C bond formation is another type of reaction commonly encountered in preparation of macrocyclic complexes [19, 20]. Other reactions are rare such as B–O bond formation for the same synthesis [21, 22]. Nucleophilic displacement of halide or some other leaving group was used for O–C and S–C bond formation. One-pot metal template condensation reactions involving amines and formaldehyde have been widely employed in formation of N–C bonds and saturated polyaza macrocyclic metallic complexes [23, 24]. The most common reaction encountered in template synthesis of macrocycles is formation of imine bonds (C=N). This imine formation mostly occurs between diamine complexes and dicarbonyl compounds. Reaction between amines, formaldehyde and the carbon acid nitroethane in basic solution was reported for C–C bond formation. Structures and chemical properties of metal complexes with these ligands are influenced by several factors, including metal ion size, anionic groups, and ligand topology, such as cavity size, type and number of donors, and stereochemical rigidity [25, 26].

We are interested in design and synthesis of complexes of N- and NS-donors with five-membered chelate rings [27–31]. In this article, preparation of the copper(II) complex of 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane (L) by template reaction is described (scheme 1). Previously, the nickel(II) complex with the same process has been reported [32]. Replacement of nitrate in [CuL(NO_3)$_2$] (**1**) with perchlorate gave [CuL(ClO_4)$_2$] (**2**). Spectroscopic characteristics, cyclic voltammetry, and crystal structures of these complexes were determined. Furthermore, a brief survey of geometry parameters on diazacyclam- and cyclam-based copper(II) complexes between Cambridge Structural Database (CSD) [33] structures was carried out (scheme 2).

1.1. *Survey of diazacyclam-based copper(II) complexes in CSD*

For understanding geometric factors that are effective in diazacyclam-based copper(II) complexes and comparing these complexes with cyclam-based copper(II) complexes, a survey was run on these complexes between their corresponding CSD structures.



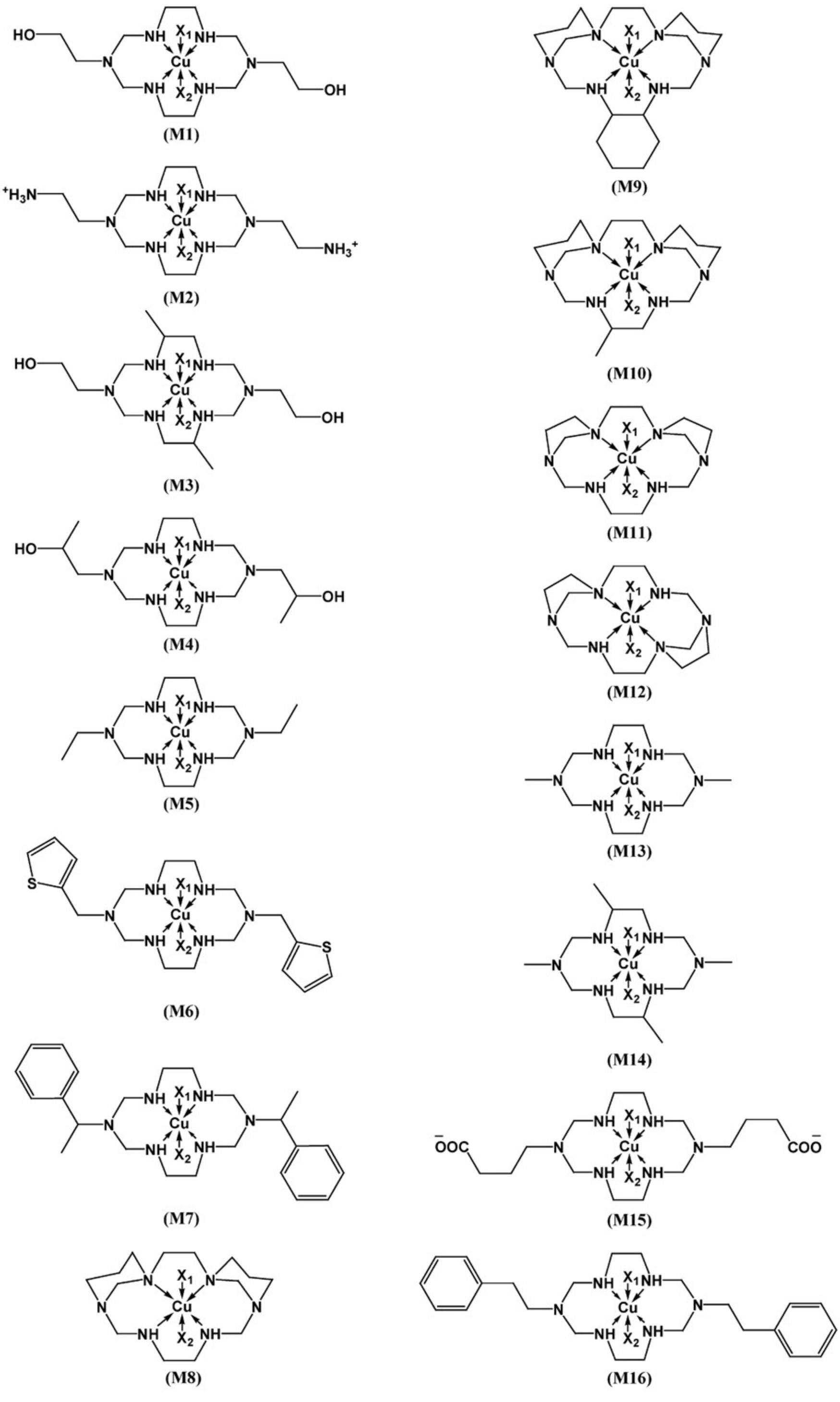
Scheme 2. (a) Diazacyclam coordinated to copper(II) and (b) cyclam coordinated to copper(II).

All complexes of diazacyclam-based with copper(II) ion, except poly metal and polymer structures that have been deposited in CSD, were studied (scheme 3). Each amino group in the form RR′R″N after coordination to metal becomes a chiral center and all coordinated nitrogen atoms in five-membered chelate rings of diazacyclam-based complexes are chiral centers. In crystal structures of **1** and **2**, the two nitrogen atoms in five- and six-membered chelate rings have same and different enantiomeric forms, respectively, but there are two exceptions including M8 ($X_1 = ClO_4^-$) [34] and M12 ($X_1 = Cl^-$) [33].

In another survey, the ANG (mean of two side C–N–C angles in diazacyclam-based copper complexes (ANG1 and ANG2) presented in scheme 2a) and DIST (axial bond length average) were considered. The data listed in table 1 reveal if there are no deviations from rms plane of the four coordinated nitrogen atoms, the DIST and ANG have an inverse relationship. The same results were obtained for **1** and **2** (table 2).

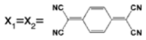
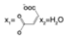
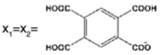
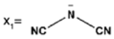
Moreover, the geometry replacement effect of carbon with two non-coordinated nitrogen atoms in diazacyclam generating 1,4,8,11-tetraazacyclotetradecane (cyclam) were studied (scheme 2b). A survey of the CSD gave 459 structures with cyclam-based copper complexes while the number of total structures for diazacyclam-based copper complexes was 67. The results are listed in table 3. The ANG and Cu–N mean distances in diazacyclam- and cyclam-based complexes with copper(II) that were determined by VISTA [35] are 115.313°, 2.018 Å and 115.780°, 2.039 Å, respectively. This study demonstrates that replacement of carbon does not have major effect on geometric parameters. The ANG is significantly larger than those of ideal tetrahedral, thus it seems carbon is suitable than nitrogen for bearing of this angle.

In this study, the macrocycle hole sizes of diazacyclam derivatives were estimated by ionic radii of metal atoms located inside of it (table 4). These metals include Cu^{2+}, Ni^{2+}, and Au^{3+} with ionic radii of 0.73, 0.69, and 0.68 Å [36], respectively, with the hole sizes



Scheme 3. All structures of diazacyclam-based complexes with copper(II) that have been deposited in CSD, poly metal and polymer structures were omitted.

Table 1. Results of the CSD structure survey of diazacyclam-based copper(II) complexes, including the ANG (mean of two side C–N–C angles in diazacyclam-based copper complexes (ANG1 and ANG2) presented in scheme 2a) and DIST (axial bond length average).

	ANG (°)	rms Deviation for Cu atom	Axial groups	DIST (Å)	Reference
M1	115.20	0.000	$X_1 = X_2 = -SCN^-$	2.970	[37]
M1	115.80	0.000		2.521	[38]
M1	115.10	0.039		2.491	[39]
M1	116.60	0.000		2.481	[40]
M5	115.15	0.000	$X_1 = X_2 = Cl^-$	2.826	[41]
M5	115.83	0.000	$X_1 = X_2 = ClO_4^-$	2.586	[42]
M13	115.20	0.000	$X_1 = X_2 = ClO_4^-$	2.645	[43]
M13	116.10	0.137		2.311	[44]
M9	116.50	0.177	$X_1 = Cl^-$	2.654	[45]
M9	115.80	0.054	$X_1 = -ONO^-$	2.500	[46]
M9	116.00	0.353	$X_1 = Cl^-$	2.448	[45]
M9	116.25	0.098	$X_1 = N_3^-$	2.321	[47]
M9	115.65	0.146	$X_1 = -NCS^-$	2.256	[48]
M12	112.00	0.000	$X_1 = ClO_4^-$	2.660	[49]
M12	115.00	0.294	$X_1 = Cl^-$	2.496	[50]
M12	114.60	0.286	$X_1 = Cl^-$	2.495	[51]
M12	114.00	0.300	$X_1 = Cl^-$	2.487	[52]
M12	114.00	0.316	$X_1 = Cl^-$	2.483	[50]
1	115.55	0.000	$X_1 = X_2 = NO_3^-$	2.673	This article
2	115.80	0.000	$X_1 = X_2 = ClO_4^-$	2.628	This article

ranging from 0.68–0.73 Å. Based on the hole size, other metal ions can be selected by these macrocycles.

Finally, the N–Cu–N angle averages in five- and six-membered chelate rings were compared. The results confirmed the N–Cu–N angle average of six-membered chelate rings [93.911°] is larger than N–Cu–N angle average [86.039°] of five-membered chelate rings. Similar results were obtained for N–Cu–N angle averages of **1** and **2** (table 2).

2. Experimental

2.1. *Instrumentation and reagents*

Chemicals and solvents were of reagent or analytical grade and used as received. Conventional three-electrode system voltammetry was employed with a PGSTAT101 and glassy carbon working electrode. The scan rate for cyclic voltammetry was 100 mV s^{-1}. Electronic spectra were recorded in H_2O using a Shimadzu model 2550 UV-Vis spectrophotometer (190–900 nm). Carbon, hydrogen, and nitrogen contents

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Cu(1)–N(1)	2.100(2)	Cu(1)–N(1)	1.994(2)
Cu(1)–N(3)	1.980(2)	Cu(1)–N(3)	2.063(2)
Cu(1)–O(1)	2.673(2)	Cu(1)–O(1)	2.628(2)
N(4)–O(1)	1.256(3)	Cl(1)–O(1)	1.446(17)
N(4)–O(2)	1.243(3)	Cl(1)–O(3)	1.419(2)
N(4)–O(3)	1.261(3)	Cl(1)–O(4)	1.421(2)
		Cl(1)–O(2)	1.407(2)
N(1)–Cu(1)–N(3)	86.79(7)	N(1)^{ii}–Cu(1)–N(3)	86.86(7)
N(3)–Cu(1)–N(1)^{i}	93.21(7)	N(3)–Cu(1)–N(1)	93.14(7)
N(1)^{i}–Cu(1)–N(1)	179.999(1)	N(1)^{ii}–Cu(1)–N(1)	179.999(5)
N(3)–Cu(1)–N(3)^{i}	180.00(7)	N(3)–Cu(1)–N(3)^{ii}	180.0
N(1)–Cu(1)–O(1)	92.86(7)	N(1)–Cu(1)–O(1)	95.72(7)
C(7)–N(2)–C(1)	115.55	C(7)–N(2)–C(2)	115.8(2)
Cu(1)–O(1)–N(4)	124.3(2)	Cu(1)–O(1)–Cl(1)	149.7(1)
O(2)–N(4)–O(1)	120.5(2)	O(3)–Cl(1)–O(2)	109.2(1)
O(2)–N(4)–O(3)	120.4(2)	O(2)–Cl(1)–O(4)	110.5(2)
O(1)–N(4)–O(3)	119.0(2)	O(3)–Cl(1)–O(2)	107.7(1)
O(1)–N(4)–O(3)	119.0(2)	O(3)–Cl(1)–O(2)	110.7(1)

Symmetry code: ^{i} $-x+1, -y+1, -z+1$; ^{ii} $-x, -y, -z+1$.

Table 3. The ANG and Cu–N distances in all diazacyclam- and cyclam-based complexes were analyzed by VISTA.

	Cu–N distance mean (Å)	Cu–N distance range (Å)	ANG (°)	ANG range (°)
Diazacyclam-based complexes with copper(II) ion	2.018	1.904–2.233	115.313	108.315–123.746
Cyclam-based complexes with copper(II) ion	2.039	1.846–2.633	115.780	107.636–141.511
All diazacyclam-based complexes	2.017	1.850–2.233	115.312	104.594–126.054
All cyclam-based complexes	2.058	1.670–2.747	115.557	71.681–157.442

Table 4. Ionic radius of proposed ions that can be placed inside the diazacyclam-based macrocycle rings.

Ion	Coordination number	Ionic radii (Å)	Ion	Coordination number	Ionic radii (Å)
Mg^{2+}	6	0.72	Sn^{4+}	6	0.69
V^{4+}	8	0.72	Hf^{4+}	6	0.71
Cr^{2+}	6	0.73 for LS	Ta^{3+}	6	0.72
Zr^{4+}	6	0.72	Ta^{4+}	6	0.68
Nb^{3+}	6	0.72	Ir^{3+}	6	0.68
Nb^{4+}	6	0.68	U^{6+}	6	0.73
Mo^{3+}	6	0.69	Np^{6+}	6	0.72
Mo^{6+}	7	0.73	Np^{7+}	6	0.71
Ru^{3+}	6	0.68	Pu^{6+}	6	0.71

were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. Infrared (IR) spectra of a KBr pellet were recorded from 4000 to 400 cm^{-1} using a FT-IR 8400-Shimadzu spectrometer. Raman spectra were obtained using a Nicolet Model 910 Fourier-transform spectrometer. Melting points were determined using a Barnsted Electrothermal 9200 electrically heated apparatus.

2.2. *Synthesis*

2.2.1. Synthesis of [CuL(NO_3)$_2$] (1). $Cu(NO_3)_2 \cdot 3H_2O$ (10 mmol, 2.41 g) was dissolved in MeOH (50 cm^3) and added to a mixture of *N*-(2-aminoethyl)-1,3-diaminopropane (AEPD) (20 mmol, 2.34 g) and aqueous formaldehyde (36%, 5 cm^3). The mixture was refluxed for 5 h and the bulk of the solvents removed by a rotary evaporator to get lavender solid which was washed with dichloromethane (10 cm^3) and then recrystallized from H_2O. Violet crystals suitable for X-ray diffraction were collected by filtration. Yield (4.27 g) 91%; m.p. 245°C. Anal. Calcd for $C_{14}H_{30}CuN_8O_6$ (%): C, 35.78; H, 6.43; N, 23.84. Found: C, 35.42; H, 6.43; N, 23.66. IR (KBr, cm^{-1}): 3201 m (ν NH), 2939 m (ν CH_2), 1380 s (ν_4 NO_3), 1272 m (ν_1 NO_3), 1087 w (ν_2 NO_3), 810 w (ν_6 NO_3), 540 w (ν CuN), 432 w (ν CuO). Raman (cm^{-1}): 2964 w (ν CH_2), 1466 s (ν_4 NO_3), 1315 m (ν CN), 1079 s (ν_2 NO_3), 880 m (ν_6 NO_3), 555 and 462 m (ν CuN), 371 m (ν CuO). UV-Vis (H_2O, λ_{max} (nm)/ε): 529/132 (d$\rightarrow$d). Cyclic voltammetry (glassy carbon, 100 mV s^{-1} scan rate): E(Cu^{II}/Cu^{III}) 0.48 V, E(Cu^{II}/Cu^{I}) −0.75 V *versus* Ag/AgCl.

2.2.2. Synthesis of [CuL(ClO_4)$_2$] (2). A solution of $NaClO_4 \cdot H_2O$ (2 mmol, 0.28 g), dissolved in H_2O (10 cm^3), was added to solution of **1** (1 mmol, 0.47 g) in H_2O (20 cm^3). The reaction mixture was stirred at 60°C for 2 h. Purple crystals of the product suitable for X-ray diffraction were obtained by slow evaporation of the solution. The crystals were then collected by filtration. Yield (0.48 g) 88%; m.p. 239°C. Anal. Calcd for $C_{14}H_{30}Cl_2CuN_6O_8$ (%): C, 30.86; H, 5.55; N, 15.42. Found: C, 30.53; H, 5.54; N, 15.36. IR (KBr, cm^{-1}): 3263 m (ν NH), 2939 m (ν CH_2), 1280 m (ν CN), 1110 s (ν_1 ClO_4), 1018 m (ν_4 ClO_4), 973 m (ν_2 ClO_4), 810 m (ν_3 ClO_4), 624 m (ν_5 ClO_4), 540 m (ν CuN), 424 m (ν CuO). Raman (cm^{-1}): 2966 w (ν CH_2), 1293 s (ν CN), 1170 m (ν_1 ClO_4), 1080 m (ν_4 ClO_4), 955 m (ν_2 ClO_4), 616, 461 m (ν CuN), 336 m (ν CuO). UV-Vis (H_2O, λ_{max} (nm)/ε): 525/152 (d$\rightarrow$d). Cyclic voltammetry (glassy carbon, 100 mV s^{-1} scan rate): E(Cu^{II}/Cu^{III}) 0.24 V, E(Cu^{II}/Cu^{I}) −0.72 V *versus* Ag/AgCl.

2.3. *Crystal structure determination and refinement*

Intensity data for **1** were collected on a Bruker APEX II CCD area detector diffractometer with graphite-monochromated Mo-Kα radiation (50 kV, 30 mA) using APEX2 [53] data collection software. The crystal was kept at 173 K during data collection. The collection method involved ω-scans of width 0.5° and 512 × 512 bit data frames. Data reduction was carried out using the program SAINT+ [52] and face indexed absorption corrections were made using XPREP [54]. The crystal structure was solved by direct methods using SHELXTL [55]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms.

A suitable crystal of **2** was placed on an Oxford Diffraction Gemini Ultra diffractometer and kept at 150 K during data collection. Using OLEX2 [56], the structure was solved with the SHELXS [57] structure solution program using direct methods and refined with the SHELXL [57] refinement package using least-squares minimization. Crystallographic data and details of the data collection and structure refinement are listed in table 5. Selected bond lengths (Å) and angles (°) for **1** and **2** are listed in table 2.

3. Results and discussion

3.1. *Spectroscopic and electrochemical characterization*

Complex **1** was synthesized in high yield by template condensation of amines and formaldehyde in the presence of Cu(II). The proposed synthetic routes for **1** are shown in scheme 1. Addition of $NaClO_4$ solution to solution of **1** (2 : 1 molar ratio) gave **2**. The complexes are air-stable and soluble in H_2O. These complexes were characterized by IR and Raman spectroscopies, electronic absorption, cyclic voltammetry, and X-ray crystallography.

IR and Raman spectral assignments for **1** and **2** are listed in section 2. Four bands in the IR spectrum of **1** at 1380, 1272, 1087, and 810 cm^{-1} can be assigned to vibrations of coordinated nitrate (respectively the vibrations ν_4, ν_1, ν_2, and ν_6). The difference between the ν_4 and the ν_1 is 118 cm^{-1}, typical for monodentate nitrate (bidentate nitrate displays a much bigger splitting) [58, 59]. Free nitrate has D_{3h} symmetry and three IR active vibrations but symmetry is lowered to C_{2v} and C_s upon coordination [60, 61], with six IR active vibrations. The C–N stretching vibration overlapped in the complexes with a vibration due to nitrate around 1270 cm^{-1}. Weak bands at 540 and 432 cm^{-1} were assigned to Cu–N and Cu–O stretches, respectively. In the IR spectrum of **2**, characteristic frequencies corresponding to interaction of perchlorate appear at 1110 (ν_1), 1018 (ν_4), 973 (ν_2), 810 (ν_3), and 624 (ν_5) cm^{-1}. Symmetry of free perchlorate is T_d lowers to C_{3v} upon interaction of one oxygen atom [60]. Similar to **1**, weak bands at 540 and 424 cm^{-1} were assigned to Cu–N and Cu–O stretches, respectively.

The low vibration frequency of metal–ligand can be obtained by Raman spectroscopy. In the Raman spectrum of **1**, the Cu–N stretch was assigned to bands at 555 and 462 cm^{-1}, consistent with values reported in the literature [61]. Two values for Cu–N stretching vibrations are in agreement with the results of the X-ray diffraction experiment discussed in the following section. One Cu–N stretch of **2** appeared at higher frequency than that of **1** while the other one did not change.

In both **1** and **2**, one and two Cu–N stretches in IR and Raman spectra were observed, respectively. Also one IR and one Raman active stretch were observed for Cu–O. These molecules have a center of symmetry since Cu–N and Cu–O stretching vibrations are Raman active and IR inactive, based on the principle of mutual exclusion. The crystal structures for **1** and **2** show a center of inversion and C_i symmetry. Similar results have been reported previously [61].

UV-Vis spectra of **1** and **2** in aqueous solution exhibit a broad absorption with λ_{max} at 529 and 525 nm, respectively, assigned to d–d transitions.

Cyclic voltammetry data for the copper(II) complexes from +0.8 to −1 V and 0.10 mol L^{-1} TBAP-DMSO solution are listed in section 2. Overlapped cyclic voltammograms of **1** and **2** are shown in "Supplementary material" in the online version of this article at http://dx.doi.org/10.1080/00958972.2012.669834. Cyclic voltammograms of the two complexes show an irreversible oxidation and reduction wave, corresponding to Cu^{II}/Cu^{III} and Cu^{II}/Cu^{I} couples. The oxidation potential of **1** is more positive than that of **2**, indicating thermodynamic stability of **1**.

Table 5. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{14}H_{30}CuN_8O_6$	$C_{14}H_{30}Cl_2CuN_6O_8$
Formula weight (g mol^{-1})	470.00	544.88
Temperature (K)	173	150
Crystal system	Monoclinic	Orthorhombic
Space group	*P2(1)/n*	*Pbca*
Unit cell dimensions (Å, °)		
a	7.6607(3)	11.9524(7)
b	7.7568(3)	10.8087(8)
c	16.1042(6)	16.3943(9)
β	101.510(2)	90.00
Volume (Å^3), *Z*	937.71(6), 2	2118.0(2), 4
Calculated density (Mg m^{-3})	1.665	1.709
Absorption coefficient (mm^{-1})	1.218	1.340
F(000)	494	1132
Crystal size (mm^3)	0.56 × 0.10 × 0.06	0.12 × 0.11 × 0.1
θ range for data collection (°)	2.58–27.99	3.00–29.30
Limiting indices	$-10 \le h \le 10$; $-10 \le k \le 10$; $-21 \le l \le 21$	$-14 \le h \le 15$; $-7 \le k \le 14$; $-22 \le l \le 20$
Reflections collected	11,071	9629
Independent reflections	2266 [*R*(int) = 0.0565]	2526 [*R*(int) = 0.0464]
Data/restraints/parameters	2266/1/136	2526/0/142
Goodness-of-fit on F^2	1.026	1.067
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0358$, $wR_2 = 0.0752$	$R_1 = 0.0366$, $wR_2 = 0.0905$
R indices (all data)	$R_1 = 0.0573$, $wR_2 = 0.0841$	$R_1 = 0.0474$, $wR_2 = 0.0989$
Largest difference peak and hole (e Å^{-3})	0.384 and −0.303	0.777 and −0.462

3.2. *Description of the crystal structures*

The X-ray single-crystal structures were determined for $[CuL(NO_3)_2]$ and $[CuL(ClO_4)_2]$. ORTEP-3 [62] and Diamond (version 3.2) [63] diagrams of the molecular structures and unit cells are shown in figures 1–3. In the structure of **1**, Cu(II) is in an elongated octahedral coordination environment, in which four nitrogen atoms from L are located at equatorial positions with Cu–N bond length of 1.980(2)–2.100(2) Å. The average of the four Cu–N distances is 2.040 Å, comparable to CSD average (2.018 Å) in table 3. The axial sites are occupied by two oxygen atoms of nitrate with average bond length of 2.673(2) Å, much longer than equatorial ones due to Jahn–Teller effects. The Cu–O bond lengths average for similar structures in CSD is 2.611 Å, so the Cu–O bond lengths in this complex are usual. The N(1)–Cu(1)–N(1) and N(3)–Cu(1)–N(3) bond angles are 180°, and thus those four nitrogen atoms including copper form a perfect plane. The macrocyclic ligand is tetradentate forming both five- and six-membered chelate rings which alternate in the equatorial plane. The 1,3-diazacyclohexane subunits are fused to each of the six-membered chelate rings in a chair conformation and an anticonfiguration with respect to the macrocyclic plane. The average Cu(1)–$N(3)_{secondary}$ distance of 1.980 Å is significantly shorter than the average Cu(1)–$N(1)_{tertiary}$ distance of 2.100 Å, indicating comparatively strong coordination. Similar result was observed in crystal structures of **2**. The nitrate, which acts as a monodendate ligand, is slightly asymmetric (bond lengths range 1.243–1.260 Å and angles 119.05–120.50°). The mean planes through the two nitrates are parallel with copper located in the median of these planes. There are intermolecular N–H⋯O hydrogen bonds in **1** (table 6). Generally, oxygen atoms of nitrates are proton acceptors whereas macrocyclic nitrogen atoms and carbons participate in hydrogen-bonding as proton donors. In the unit cell of **1** (figure 2), two N(3)–H(3) ··· O(3) hydrogen bonds form one $R^2_2(8)$ hydrogen bond motif between two molecules of **1** [64]. In the unit cell of **2** (figure 3), N(1)–H(1) ··· O(4) forms two other types of hydrogen-bond motifs. The first is $R^4_4(24)$, between four molecules of **2**, whereas the second is $R^6_6(36)$, found between six molecules of **2**. In crystal packing of **1**, each nitrate connects to 11 adjacent atoms through hydrogen bonds and short contacts. O1 of each nitrate coordinates to copper and has no other interaction while O2 and O3 have six and five interactions, respectively. There is also a weak O ··· O interaction (3.0299(1) Å) between two O3's in adjacent complexes. The N4–O3 bond length that participated in hydrogen bond is longer than those of other nitrate bonds. In the crystal structure of **1**, there is H ··· H interaction with bond length of 2.3064(1) Å. These interactions have been observed with bond length range 2.348–2.388 Å [65].

In **2**, copper is coordinated by two secondary and two tertiary amines of the macrocycle and one oxygen of the perchlorates in a distorted octahedral geometry. The average of the four Cu–N distances is 2.0285 Å, comparable to CSD average (2.018 Å) in table 3. Axial sites are occupied by two oxygen atoms of perchlorate. Similar to **1** the axial bond lengths (average of 2.628(2) Å) are much longer than those of equatorial due to Jahn–Teller effects. The two Cu–O bond lengths in **2** (2.628 Å) are equal and comparable to average of similar structures in CSD (2.619 Å). In **2,** copper lies in the plane of four coordinated nitrogen atoms with no rms deviation from this plane. All bond lengths and angles in two perchlorates are equal and each monodendate perchlorate is slightly asymmetric (bond lengths range 1.407(2)–1.447(2) Å and angles 107.7(1)–110.7(1)°). In crystal packing of **2**, each perchlorate connects to seven adjacent atoms through hydrogen bonds and short contacts. O1 of

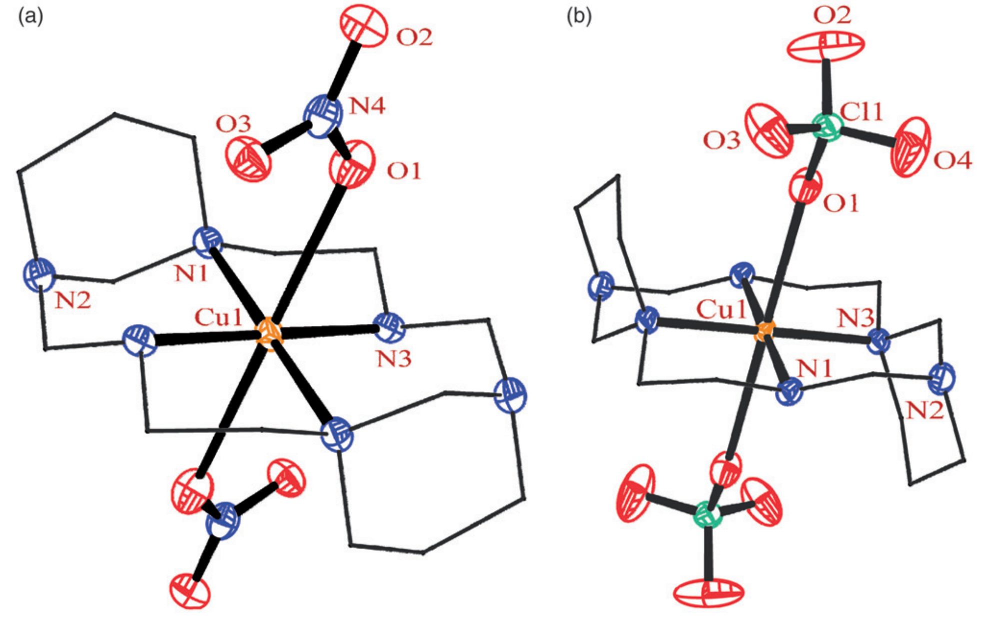


Figure 1. The ORTEP-3 diagrams of the molecular structures of **1** (a) and **2** (b). The ellipsoids are drawn at the 50% probability level. The hydrogen atoms were omitted for clarity.

each perchlorate coordinates to copper and has no other interaction while O2 and O4 have three and four interactions, respectively. O3 does not have interaction with adjacent atoms.

4. Conclusion

The 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane complexes of copper(II) were template synthesized and their spectral (IR, Raman, UV-Vis), electrochemical, and structural properties were investigated. The complexes exhibit distorted octahedral geometry. Copper lies in the plane of four coordinated nitrogen atoms with no rms deviation from this plane. All distances in these complexes are usual. Electrochemistry of these systems indicates irreversible behavior. A brief survey of geometric parameters on similar macrocyclic copper(II) complexes was carried out and the macrocycle hole

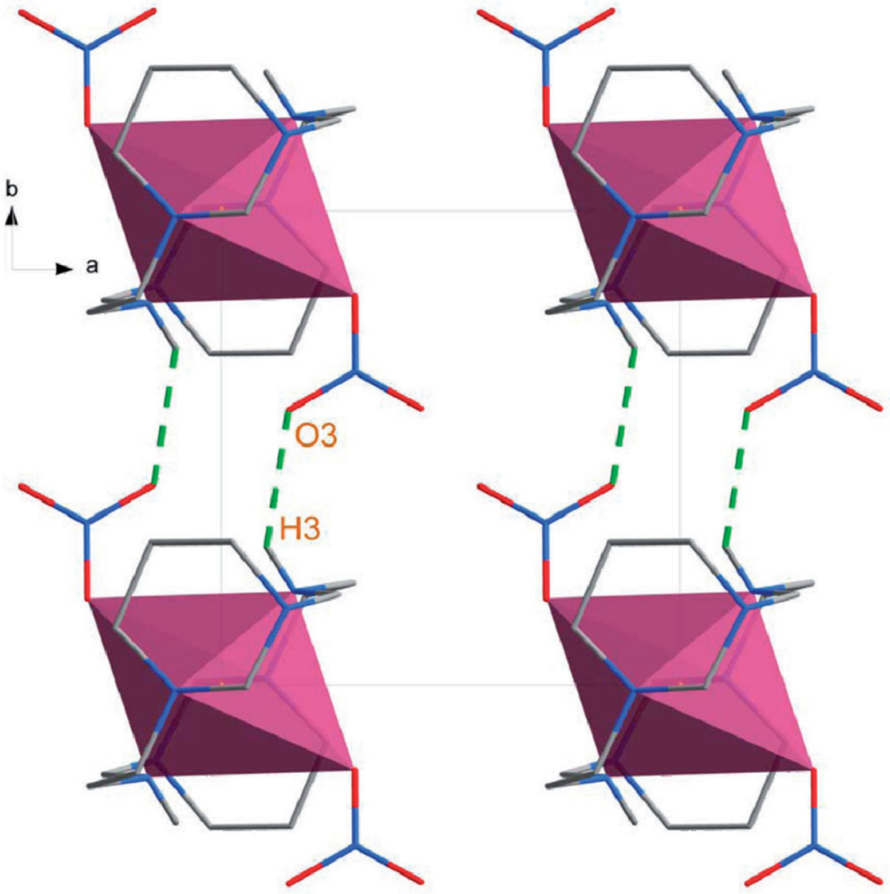


Figure 2. Packing of **1** showing the $R_2^2(8)$ hydrogen bond in *ab*-plane. Only the hydrogen atom (H3) involved in hydrogen-bonding is shown. Each CuN_4O_2 unit is shown as octahedron.

Table 6. Dimensions of hydrogen-bonds (Å and °) in **1** and **2**.

	D–H···A	d(D–H)	d(H···A)	∠(DHA)	d(D···A)	Symmetry code on A atom
1						
	N(3)–H(3)···O(3)	0.87	2.30	138.06	2.999(2)	$x, y-1, z$
	C(7)–H(7A)···O(3)	0.991	2.710	114.29	3.246(3)	$x, y-1, z$
	C(6)–H(6A)···O(2)	0.990	2.708	140.22	3.526(3)	$x, y-1, z$
	C(7)–H(7A)···O(2)	0.991	2.494	152.18	3.402(3)	$x, y-1, z$
	C(6)–H(6A)···O(2)	0.990	2.589	113.45	3.199(3)	$2-x, 1-y, 1-z$
	C(2)–H(2A)···O(3)	0.990	2.648	129.57	3.367(3)	$1-x, 1-y, 1-z$
	C(1)–H(1A)···O(2)	0.989	2.596	139.46	3.409(3)	$1.5-x, -0.5+y, 1.5-z$
	C(2)–H(2B)···O(2)	0.991	2.655	138.51	3.460(3)	$1.5-x, -0.5+y, 1.5-z$
2						
	C(5)–H(5A)···O(2)	0.990	2.459	153.29	3.373(4)	$-0.5+x, y, 0.5-z$
	C(1)–H(1A)···O(2)	0.990	2.698	110.78	3.186(3)	$-0.5+x, -0.5-y, 1-z$
	C(6)–H(6B)···N(2)	0.991	2.682	128.58	3.390(3)	$0.5-x, -0.5+y, z$
	N(1)–H(1)···O(4)	0.931	2.192	133.78	2.914(4)	$0.5-x,-0.5+y, z$
	C(1)–H(1B)···O(4)	0.990	2.658	115.03	3.205(3)	$0.5-x, -0.5+y, z$

size of 1,3,5,8,10,12-hexaazacyclotetradecane-based was estimated by ionic radii of metals that located in it. In continuation of our research, we will try to separate the 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane for synthesis of new complexes with metal ions that can be located in macrocycle ring and also to prepare the corresponding coordination polymers by ambidentate ligands.

Supplementary material

CCDC 859410 and 859411 for [CuL(NO_3)$_2$] and [CuL(ClO_4)$_2$], respectively, contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk]. Structure factor table is available from the authors.

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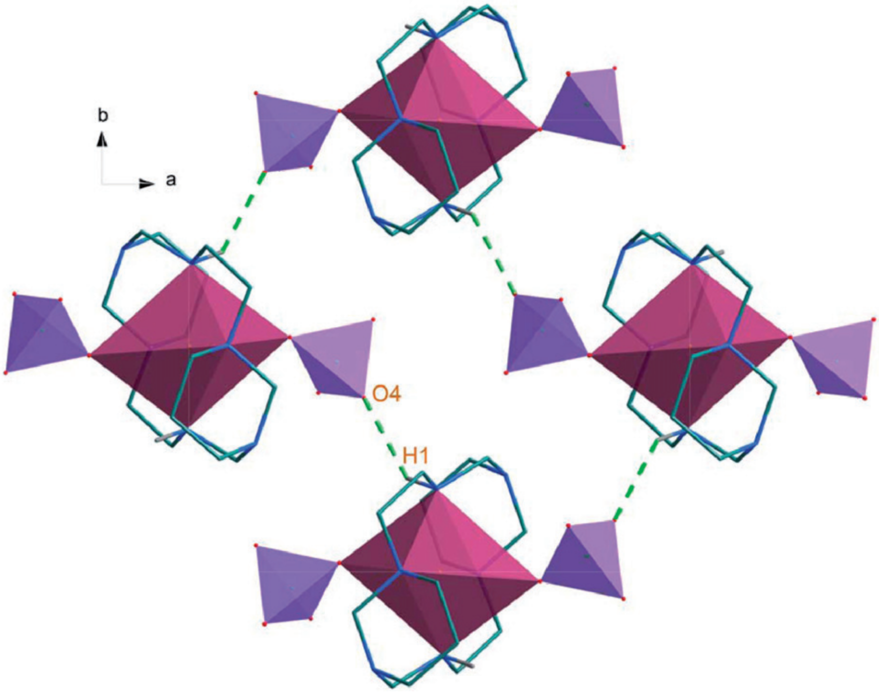

Figure 3. Packing of **2** showing the $R_4^4(24)$ hydrogen bonds in the *ab*-plane. Only the hydrogen atom (H1) involved in hydrogen-bonding is shown. In this figure, CuN_4O_2 and ClO_4 units are shown as octahedron and tetrahedron, respectively.

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