

Synthesis and Characterization of New Hexaaza Macrotricyclic Copper(II) Complexes with a 5-6-6-6 Chelate Ring Sequence

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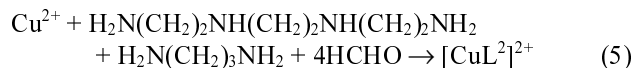
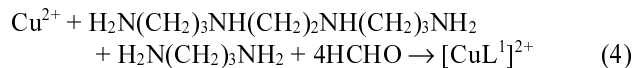
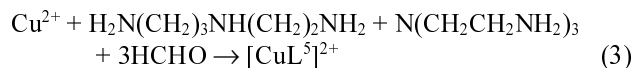
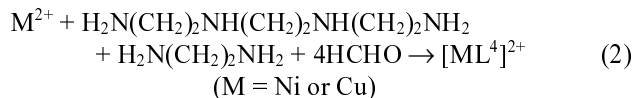
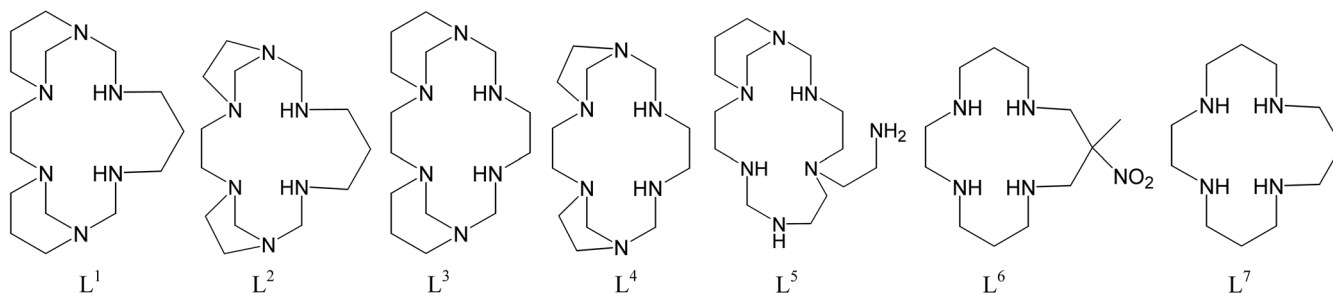
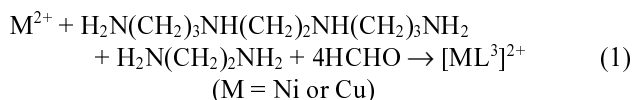
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The design and synthesis of new polyaza macrocyclic complexes have received much attention, since their chemical properties are strongly influenced by the structural characteristics of the ligands.¹⁻³ Metal-directed condensation reactions of coordinated amines with formaldehyde are useful for the preparation of polyaza macrocyclic complexes containing N-CH₂-N linkages.⁴⁻¹³ For instance, the square-planar complexes [ML³]²⁺ and [ML⁴]²⁺ (M = Cu(II) or Ni(II)) with a 5-6-5-6 chelate ring sequence have been prepared by the one-pot reaction of Eq. (1) or (2).⁷ Although numbers of polyaza macrocyclic complexes containing N-CH₂-N linkages have been prepared and investigated, most of them contain 14-membered hexaaza macrocycles and have square-planar coordination polyhedron with a 5-6-5-6 chelate ring sequence. Some 15-membered hexaaza macrocyclic complexes with a 5-6-5-5-4 chelate ring sequence, such as [NiL⁵]²⁺ (Eq. (3)), have been also investigated.⁸⁻¹⁰ As far as we know, however, the preparation of 15-membered hexaaza macrocyclic copper(II) or nickel(II) complexes with a 5-6-6-6 chelate ring sequence is not reported to date.

Herein, we report new copper(II) complexes [CuL¹]²⁺ and [CuL²]²⁺ with a 5-6-6-6 chelate ring sequence. They were prepared by the metal-directed reactions (Eqs. (4) and (5)) of appropriate amines with formaldehyde. Interestingly, [CuL¹]²⁺ is considerably inert against decomposition even in concentrated acid solution, unlike [CuL²]²⁺ and other polyaza macrocyclic copper(II) complexes with a 5-6-6-6 chelate ring sequence. Synthesis and chemical properties of the copper(II) complexes are described.



Experimental Section

Measurements. Infrared spectra were recorded with a Shimadzu IR-440 spectrophotometer, electronic absorption spectra with an Analytikjena Specord 200 UV/Vis spectrophotometer, and conductance measurements with a Metrohm Herisau Conductometer E518. FAB-mass spectra and elemental analyses were performed at the Korea Basic Science Institute, Daegu, Korea. Cyclic voltammograms were recorded using a BAS-100 B/W auto cyclic volt/ampere meter. The working and counter electrodes were platinum. The reference electrode was saturated calomel electrode (SCE). The measurements were conducted in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solutions at 20 °C.

Safety Note: Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

Preparation of [CuL¹](ClO₄)₂ (L¹ = 1,3,7,9,13,16-Hexaazatricyclo[14.3.1.1^{9,13}]heneicosane). A methanol solution (ca. 40 mL) of Cu(OAc)₂·H₂O (3.0 g, 15 mmol), *N,N'*-bis(3-aminopropyl)ethylenediamine (2.7 mL, 15 mmol), 1,3-diaminopropane (1.3 mL, 15 mmol), and 35% formaldehyde

(7.7 mL, 90 mmol) was stirred for > 24 h at room temperature. After the addition of excess NaClO₄, the resulting mixture was allowed to stand at room temperature to yield a dark-purple solid. The product was collected by filtration, washed with methanol, and dried in air. The complex was recrystallized from warm acetonitrile-water (1 : 1). Yield: ~40%. Anal. Found: C, 32.03; H, 6.10; N, 14.86. Calc. for C₁₅H₃₂N₆CuCl₂O₈: C, 32.23; H, 5.78; N, 15.04%. FAB mass (*m/z*): 359.2 [CuL¹ - H]⁺, 459.1 [CuL¹ + ClO₄]⁺. IR (Nujol mull, cm⁻¹): 3230 (ν(N-H)) and 3210 (ν(N-H)).

Preparation of [CuL¹(CH₃CN)](PF₆)₂. To a warm acetonitrile solution (*ca.* 10 mL) of [CuL¹](ClO₄)₂ (0.5 g) was added an excess amount of NH₄PF₆. The mixture was cooled to room temperature and was filtered to remove a white solid (NH₄ClO₄). Water (*ca.* 20 mL) was added to the filtrate, and the solvent was evaporated at room temperature. A blue-purple precipitate was filtered, washed with water, and dried in air. Yield: ~90%. Anal. Found: C, 29.41; H, 5.33; N, 14.08. Calc. for C₁₇H₃₅N₆CuP₂F₁₂: C, 29.55; H, 5.11; N, 14.19%.

Preparation of [CuL²](ClO₄)₂ (L² = 1,3,7,9,12,15-Hexaazatricyclo[13.2.1.1^{9,12}]nonacosane). This purple complex was prepared by a method similar to that of [CuL¹](ClO₄)₂, except that triethylenetetraamine (2.6 mL, 15 mmol) was reacted instead of *N,N'*-bis(3-aminopropyl)ethylenediamine. The product was dissolved in minimum volume of water, and excess NaClO₄ dissolved in methanol (*ca.* 30 mL) was added to the solution. The pure product was collected by filtration, washed with methanol, and dried in air. Yield: ~40%. Anal. Found: C, 29.32; H, 5.55; N, 15.82. Calc. for C₁₃H₂₈N₆CuCl₂O₈: C, 29.41; H, 5.33; N, 15.83%. FAB mass (*m/z*): 331.1 [CuL² - H]⁺, 431.0 [CuL² + ClO₄]⁺. IR (Nujol mull, cm⁻¹): 3250 (ν(N-H)).

Crystal Structure Analysis. Single crystals of [CuL¹-(CH₃CN)](PF₆)₂ suitable for X-ray diffraction were obtained by evaporating a water-acetonitrile solution of the complex at room temperature. The data were collected using a STOE STADI4 diffractometer equipped with Mo-Kα radiation (λ = 0.71069 Å) in the ω-2θ scan mode at 298(2) K. The data were corrected for Lorentz and polarization effect. The empirical absorption correction based on a series of φ scans was applied. The data including all Friedel pairs for determination of the absolute structure were collected. Structure analysis and refinement calculations were carried out with X-STEP programs package.^{14(a)} The absolute structure was determined from the Flack parameters.^{14(b)} The structures were solved by the direct method. The crystallographic data for [CuL¹(CH₃CN)](PF₆)₂ are summarized in Table 1. All H atoms bonded to C atoms were included in the structure-factor calculation at idealized positions, and were allowed to ride on their parent atoms with relative isotropic displacement parameters [Uiso(H) = 1.2Ueq(C)].

Results and Discussion

Synthesis. Most polyaza macrocyclic copper(II) complexes containing N-CH₂-N linkages, such as [CuL³]²⁺ and [CuL⁴]²⁺

with a 5-6-5-6 chelate ring sequence, have been prepared by refluxing methanol solutions of appropriate coordinated amines with formaldehyde.⁷⁻¹² However, our initial attempts to prepare the copper(II) complexes of L¹ and L² from the reaction of Eq. (4) or (5) in boiling or hot (*ca.* 50 °C) methanol solution were unsuccessful; the complexes could not be prepared even in boiling acetonitrile or water. As described in Experimental section, [CuL¹](ClO₄)₂ and [CuL²](ClO₄)₂ were prepared by reacting the reactants at room temperature. All our attempts to prepare nickel(II) complexes of L¹ and L² in various solvents, such as methanol, acetonitrile, and water, were unsuccessful. The present result is different from the fact that the nickel(II) complexes of L³ and L⁴ can be prepared in high yield by the reactions of Eqs. (1) and (2).⁷ In general, 15-membered tetraaza macrocyclic nickel(II) and copper(II) complexes with a 5-6-6-6 chelate ring sequence are much less stable than 14-membered macrocyclic complexes with a 5-6-5-6 chelate ring sequence.^{8,9,15} The easy formation of the copper(II) complexes of L¹ and L² can be attributed to the relatively strong Lewis acidity (Cu(II) > Ni(II)) of the metal ion.

Crystal Structure of [CuL¹(CH₃CN)](PF₆)₂. The crystal is racemic twin, and the obtained Flack parameter is 0.48(3). The ORTEP drawing of [CuL¹(CH₃CN)]²⁺ cation is shown in Figure 1. The complex has distorted square-pyramidal coordination geometry with an axially oriented acetonitrile molecule. Four nitrogen atoms of L¹ are coordinated to the metal ion with a 5-6-6-6 chelate ring sequence. The macrocyclic ligand adopts the *trans*-III type conformation. Two 1,3-diazacyclohexane subunits have chair conformations and are anti with respect to the macrocyclic plane.

Table 1. Crystal data and structure refinement for [CuL¹(CH₃CN)](PF₆)₂

Empirical formula (<i>M</i>)	C ₁₇ H ₃₅ CuF ₁₂ N ₇ P ₂ (691.00)
Crystal size (mm)	0.44 × 0.37 × 0.25
Temperature (K)	298(2)
Crystal system/ space group	Orthorhombic / P 21 21 21
<i>a</i> / <i>b</i> / <i>c</i> (Å)	12.142(2) / 13.844(3) / 16.616(3)
<i>V</i> (Å ³)	2793.0(9)
<i>Z</i> / <i>D</i> _{calc} (g cm ⁻³)	4 / 1.643
<i>μ</i> (cm ⁻¹)	0.999
<i>F</i> ₀₀₀	1412
θ range (°)	1.91-27.43
Limiting indices	-15 ≤ <i>h</i> ≤ 15, -17 ≤ <i>k</i> ≤ 17, -21 ≤ <i>l</i> ≤ 21
Reflections collected / unique	7100 / 6342 [<i>R</i> _{int} = 0.0391]
Completeness to theta = 27.43	99.7%
Absorption correction	Numerical
Max. and min. transmission	0.9191 and 0.8489
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6342 / 0 / 354
Goodness-of-fit on <i>F</i> ²	1.093
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0808, <i>wR</i> ₂ = 0.1321
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1634, <i>wR</i> ₂ = 0.1733
Absolute structure parameter	0.48(3)
Largest diff. peak and hole (Å ⁻³)	0.302 and -0.292

Table 2 shows that the in-plane Cu-N distances (2.074(7)-2.120(6) Å) of $[\text{CuL}^1(\text{CH}_3\text{CN})]^{2+}$ are distinctly shorter than the axial Cu-N(7) (CH_3CN) distance (2.414(9) Å), as usual. The average in-plane Cu-N distance (2.088 Å) of $[\text{CuL}^1(\text{CH}_3\text{CN})]^{2+}$ is *ca.* 0.05 Å longer than that of $[\text{CuL}^3(\text{H}_2\text{O})]^{2+}$ (2.034 Å) with a 5-6-5-6 chelate ring sequence.¹⁶ The Cu-N(4) distance (2.120(6) Å) is distinctly longer than other in-plane Cu-N distances {2.074(6)-2.084(6) Å} and, furthermore, the N(4)-Cu-N(7) angle {93.3(3) $^\circ$ } is larger than the N(1)-Cu-N(7) angle (85.8(3) $^\circ$). This reflects the steric repulsion between the N-C(8)-C(7)-(C6)-N bridge and the axially coordinated acetonitrile molecule. The N(1)-Cu-N(4) and N(3)-Cu-N(6) angles (176.8(3) and 164.2(3) $^\circ$, respectively) are deviated from 180 $^\circ$. The C(16)-N(17)-Cu angle (158.8(9) $^\circ$) is much smaller than 180 $^\circ$. The N(2)-C(11) and N(2)-C(15) bond distances (1.42(1) Å) are distinctly shorter than the N(1)-C and N(6)-C distances (1.48-1.53 Å). Furthermore, the C(11)-N(2)-C(15) and C(14)-N(2)-C(15) angles (114.7(8) and 118.8(8) are larger than the ideal tetrahedral angle. The bond angles and distances involving N(5) atom are quite similar to those involving N(2) atoms. These results can be attributed to an sp^2 -like hybridization of the uncoordinated N(2) and N(5) atoms.⁷

Spectra and Properties. The infrared and FAB mass spectra of $[\text{CuL}^1](\text{ClO}_4)_2$ and $[\text{CuL}^2](\text{ClO}_4)_2$ are listed in the Experimental Section. The electronic absorption spectra (Table 3) of $[\text{CuL}^1](\text{ClO}_4)_2$ and $[\text{CuL}^2](\text{ClO}_4)_2$ measured in various solvents show a *d-d* transition band at 577-585 and 553-555 nm, respectively. The spectra are comparable with those of $[\text{CuL}^6]^{2+}$ and $[\text{CuL}^7]^{2+}$,^{3,17} supporting the proposal that $[\text{CuL}^2](\text{ClO}_4)_2$ as well as $[\text{CuL}^1](\text{ClO}_4)_2$ has a square-planar coordination geometry with a 5-6-6-6 chelate ring sequence. However, the wavelengths for $[\text{CuL}^1](\text{ClO}_4)_2$ and $[\text{CuL}^2](\text{ClO}_4)_2$ measured in water are longer and shorter, respectively, than that for $[\text{CuL}^7]^{2+}$. The relatively weak ligand field strength of $[\text{CuL}^1](\text{ClO}_4)_2$ is corresponding to the reported result that $[\text{ML}^3]^{2+}$ (M = Cu(II) and Ni(II)) containing 1,3-diazacyclohexane subunits exhibits weaker M-N interactions (or longer M-N distances) than $[\text{ML}^4]^{2+}$ containing 1,3-diazacyclopentane subunits.⁷ The longer wavelengths for $[\text{CuL}^1](\text{ClO}_4)_2$ and $[\text{CuL}^2](\text{ClO}_4)_2$, compared to those for $[\text{CuL}^3]^{2+}$ and $[\text{CuL}^4]^{2+}$,⁷ are attributed to the weaker Cu-N interactions caused by the larger cavity size of the macrocycles.

Cyclic voltammograms of $[\text{CuL}^1](\text{ClO}_4)_2$ and $[\text{CuL}^2](\text{ClO}_4)_2$ measured in acetonitrile showed one electron oxidation peak corresponding to Cu(II)/Cu(III) process. As expected from the electronic spectra, the oxidation potentials of $[\text{CuL}^1](\text{ClO}_4)_2$ (+1.67 V *vs.* SCE) and $[\text{CuL}^2](\text{ClO}_4)_2$ (1.37 V *vs.* SCE) are distinctly higher and lower, respectively, than that of $[\text{CuL}^7]^{2+}$ (+1.56 V *vs.* SCE)¹⁷ (Table 3). This trend means that the electron density on the metal ion of $[\text{CuL}^1](\text{ClO}_4)_2$ is considerably lower than that of $[\text{CuL}^2](\text{ClO}_4)_2$ because of the relatively weak Cu-N interactions of the former complex.

The complexes $[\text{CuL}^1](\text{ClO}_4)_2$ and $[\text{CuL}^2](\text{ClO}_4)_2$ are extremely stable in the solid state. However, they are decomposed in low pH. The decomposition rate of the

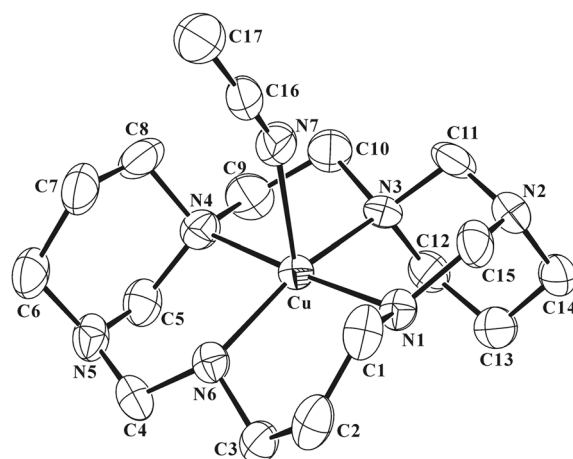


Figure 1. ORTEP drawing of $[\text{CuL}^1(\text{CH}_3\text{CN})]^{2+}$ in $[\text{CuL}^1(\text{CH}_3\text{CN})](\text{PF}_6)_2$. Thermal ellipsoids are drawn to include 30% probability. The H atoms are omitted for clarity.

Table 2. Selected Bond Distances [Å] and Angles [$^\circ$] for $[\text{CuL}^1(\text{CH}_3\text{CN})](\text{PF}_6)_2$

Cu-N(1)	2.084(6)	Cu-N(3)	2.074(7)
Cu-N(4)	2.120(6)	Cu-N(6)	2.074(6)
Cu-N(7)	2.414(9)	N(1)-C(15)	1.51(5)
N(2)-C(11)	1.42(1)	N(2)-C(15)	1.42(1)
N(3)-C(10)	1.49(1)	N(3)-C(11)	1.52(1)
N(4)-C(8)	1.51(1)	N(5)-C(4)	1.41(1)
N(5)-C(5)	1.42(1)	N(6)-C(3)	1.48(1)
N(6)-C(4)	1.53(1)	N(7)-C(16)	1.12(1)
N(1)-Cu-N(4)	176.8(3)	N(3)-Cu-N(6)	164.2(3)
N(1)-Cu-N(6)	89.8(3)	N(1)-Cu-N(3)	92.3(3)
N(1)-Cu-N(7)	85.8(3)	N(3)-Cu-N(4)	84.8(3)
N(3)-Cu-N(7)	95.6(3)	N(6)-Cu-N(4)	93.4(3)
N(4)-Cu-N(7)	93.3(3)	N(6)-Cu-N(7)	100.2(3)
C(11)-N(2)-C(15)	114.7(8)	C(15)-N(2)-C(14)	118.8(8)
C(4)-N(5)-C(5)	114.6(7)	C(4)-N(5)-C(6)	119.3(8)
C(16)-N(7)-Cu	158.8(9)	N(5)-C(4)-N(6)	117.5(7)
N(5)-C(5)-N(4)	112.2(9)	N(7)-C(16)-C(17)	178.1(12)

complexes (2.0×10^{-3} M) in 0.3 M HClO_4 solution was monitored spectrophotometrically at 590 ($[\text{CuL}^1](\text{ClO}_4)_2$) or 555 nm ($[\text{CuL}^2](\text{ClO}_4)_2$). The pseudo first-order rate constant (*k*) for $[\text{CuL}^2](\text{ClO}_4)_2$ measured at 20 $^\circ\text{C}$ was found to be $1.4 \times 10^{-2} \text{ sec}^{-1}$ ($t_{1/2} = \text{ca. } 50 \text{ sec}$). The reaction rate of $[\text{CuL}^2](\text{ClO}_4)_2$ is somewhat faster than that of $[\text{CuL}^7]^{2+}$ ($k = 3.3 \times 10^{-3} \text{ sec}^{-1}$, $t_{1/2} = \text{ca. } 210 \text{ sec}$) measured in 0.3 M HNO_3 at 25 $^\circ\text{C}$ and is comparable with those of other related 15-membered macrocyclic nickel(II) or copper(II) complexes with a 5-6-6-6 chelate ring sequence.^{15,17,18} However, interestingly, the decomposition rate of $[\text{CuL}^1](\text{ClO}_4)_2$ ($k = 2.5 \times 10^{-6} \text{ sec}^{-1}$, $t_{1/2} = \text{ca. } 77 \text{ h}$) is extraordinarily slow under similar condition (*see* Fig. 2), in spite of the relatively weak Cu-N interactions of the complex. The present results strongly indicate that the decomposition reaction of $[\text{CuL}^1](\text{ClO}_4)_2$ is not directly influenced by the strength of the Cu-N interactions. The crystal structure of $[\text{CuL}^2](\text{ClO}_4)_2$ was not available, and the effects of the 1,3-diazacycloalkane rings on the kinetic behaviors of the two copper(II) complexes

Table 3. Electronic Spectra and Oxidation Potentials of the complexes^a

Complex	Electronic spectra		Potential (Cu(II)/Cu(III)) ^b
	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)		Volt vs. SCE
[CuL ¹](ClO ₄) ₂	577(150)	578(150) ^c 590(160) ^e	+ 1.67(i) ^d
[CuL ²](ClO ₄) ₂	553(175)	555(173) ^c 555(150) ^e 540 ^f	+ 1.37(i)
[CuL ³] ²⁺ ^g	501(112)	527(122) ^e	
[CuL ⁴] ²⁺ ^g	485(138)	506(155) ^e	
[CuL ⁶] ²⁺ ^h	570 ^e		
[CuL ⁷] ²⁺	568(150) ^{e,i}		+ 1.56 ^j

^aMeasured in nitromethane at 20 °C unless otherwise specified.

^bMeasured in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solution at 20 °C; scan rate = 50 mV/s. ^cIn acetonitrile. ^di = irreversible. ^eIn water. ^fIn Nujol mull. ^gRef. 7. ^hRef. 3. ⁱRef. 18. ^jRef. 17.

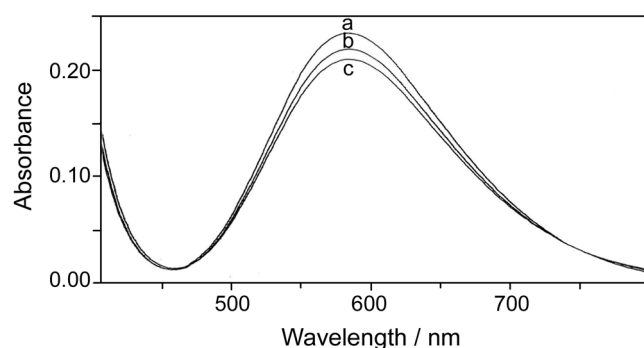


Fig. 2. Visible absorption spectra of [CuL¹](ClO₄)₂ (2.0×10^{-3} M) in 0.3 M HClO₄ water-acetonitrile (1 : 1) solution at 25 °C. Curve a is the first spectrum, and b and c are the spectra measured after 3 and 5 h, respectively.

were not thoroughly investigated at this time. The nitrogen atoms in a 1,3-diazacyclohexane subunit are expected to be less basic than those in a 1,3-diazacyclopentane subunit because of the larger C-N-C bond angle.¹⁹ Therefore, it can be suggested that one of the reasons for the extraordinarily slow decomposition of [CuL¹](ClO₄)₂ in concentrated HClO₄ solution is the relatively weak proton affinity of the nitrogen atoms involved in the 1,3-diazacyclohexane rings.

Supplementary material. Crystallographic data of [CuL¹](CH₃CN)(PF₆)₂ are available from the Cambridge Structural Database, CCDC reference number 280087. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (<http://www.ccdc.cam.ac.uk>, fax: +44-1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk).

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