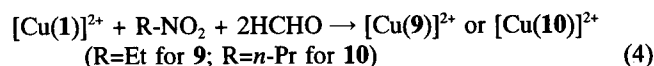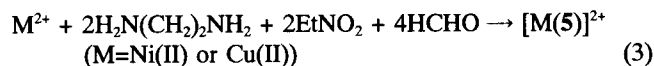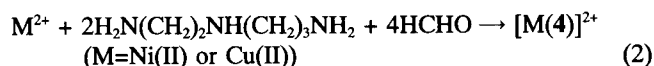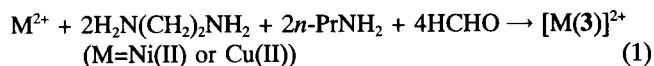# Notes

Synthesis and Characterization of Copper(II) Complexes of Pentaaza Macrocyclic Ligands Containing One C-Nitro Pendant Arm

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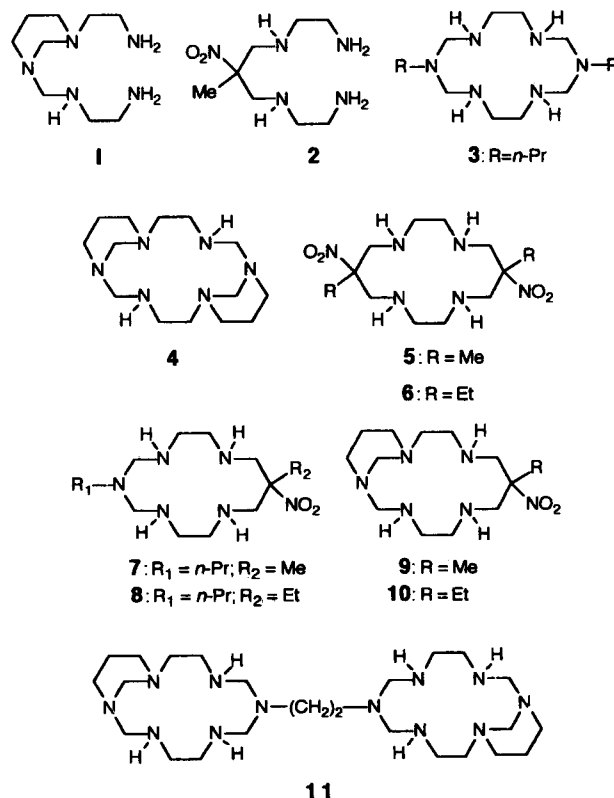*Received April 2, 1997*

There has been considerable interest in the synthesis of new types of polyaza macrocyclic compounds and in the development of effective and selective synthetic methods.[1-3] Metal template condensations involving coordinated amines and formaldehyde have been established as one of the most simple, selective, and inexpensive routes toward saturated polyaza macrocyclic complexes.[4-21] For example, copper(II) and nickel(II) complexes of polyaza macrocycles such as **3**, **4**, and **5** have been synthesized by one-pot reactions as shown in Eqs (1)-(3).[7-11] More recently, this type of reaction was extended to the synthesis of nickel(II) complexes of the pentaaza macrocyclic ligands **7** and **8**.[12,13] The ligand field strength and redox potentials of $[Ni(3)]^{2+}$ are similar to those of $[Ni(cyclam)]^{2+}$ (cyclam=1,4,8,11-tetraazacyclotetradecane).[4,7] However, some chemical properties of the nickel (II) complexes of **7** and **8** are distinctly different from those of the complexes of **3** and **5**.[12,13] Therefore, we have been interested in further investigation of the effects of the pendant group on the properties of copper(II) complexes of various types of polyaza macrocyclic ligands.

$$M^{2+} + 2H_2N(CH_2)_2NH_2 + 2n\text{-}PrNH_2 + 4HCHO \rightarrow [M(3)]^{2+}$$
$$(M=Ni(II) \text{ or } Cu(II)) \qquad\qquad (1)$$

$$M^{2+} + 2H_2N(CH_2)_2NH(CH_2)_3NH_2 + 4HCHO \rightarrow [M(4)]^{2+}$$
$$(M=Ni(II) \text{ or } Cu(II)) \qquad\qquad (2)$$

$$M^{2+} + 2H_2N(CH_2)_2NH_2 + 2EtNO_2 + 4HCHO \rightarrow [M(5)]^{2+}$$
$$(M=Ni(II) \text{ or } Cu(II)) \qquad\qquad (3)$$

$$[Cu(1)]^{2+} + R\text{-}NO_2 + 2HCHO \rightarrow [Cu(9)]^{2+} \text{ or } [Cu(10)]^{2+}$$
$$(R=Et \text{ for } \mathbf{9}; R=n\text{-}Pr \text{ for } \mathbf{10}) \qquad\qquad (4)$$

In this work, we synthesized new copper(II) complexes of the pentaaza macrobicyclic ligands **9** and **10** containing one 1,3-diazacyclohexane ring and one $NCH_2C(R)(NO_2)$ CH_2N bridging group from the reaction of Eq. (4). Copper (II) complexes of **6**, **7**, and **8** were also prepared for an adequate comparison of the properties of the complexes.

Experimental

Measurements. Infrared spectra were obtained with a Shimadzu IR-440 spectrophotometer, electronic spectra with a Shimadzu UV-160 spectrophotometer, and conductance measurements with a Metrohm Herisau E518 Conductometer. Elemental analyses and FAB mass spectra were performed at the Korea Basic Science Institute, Seoul, Korea.

1   **2**   **3**: R=*n*-Pr

4   **5**: R = Me   **6**: R = Et

7: R_1 = *n*-Pr; R_2 = Me
8: R_1 = *n*-Pr; R_2 = Et
9: R = Me
10: R = Et

11

Cyclic voltammograms were recorded using a Yanaco Voltammetric Analyzer p-1000 equipped with a FG-121B function generator and a Watanabe X-Y recorder.

Safety Note. Perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution. **Synthesis.** The complexes $[Cu(1)](ClO_4)_2$,[15] $[Cu(2)](ClO_4)_2$,[11] and $[Cu(5)](ClO_4)_2$[11] were prepared by the previously reported methods.

$[Cu(6)](ClO_4)_2$. A methanol solution (*ca.* 30 mL) of $Cu(OAc)_2 \cdot H_2O$ (3.0 g, 15 mmol), 99.5% ethylenediamine (2.0 mL, 30 mmol), 95% 1-nitropropane (2.8 mL, 30 mmol), triethylamine (0.2 mL), and paraformaldehyde (1.8 g, 60 mmol) was refluxed for 12 h. An excess of perchloric acid was added dropwise to the resulting solution at room temperature. The red-purple product was filtered off, washed with methanol, and recrystallized from hot water-acetonitrile (1 : 1) mixture. Yield: ~70%. Anal. Calcd for $C_{14}H_{30}N_6CuCl_2$-O_{12}: C, 27.62; H, 4.97; N, 13.80. Found: C, 27.85; H, 5.01; N, 13.72%. FAB mass (m/z): 509 ([M-ClO_4]^+) and 410 ([M-

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$2ClO_4$-H]$^+$). IR: 3260 (v(N-H)), 3190 (v(N-H)), and 1555 cm^{-1} (v(NO$_2$)).

[Cu(7)](ClO$_4$)$_2$. To a methanol-water (1:1) solution of [Cu(2)](ClO$_4$)$_2$ (4.0 g, 8.8 mmol) were added 99% n-pro-pylamine (1.0 mL, 12 mmol), paraformaldehyde (0.8 g, 26 mmol), and triethylamine (*ca.* 0.3 mL). The mixture was re-fluxed for 10 h and then an excess of perchloric acid was added. The red-purple solid was filtered off, washed with methanol, and recrystallized from hot water. Yield: ~80%. Anal. Calcd for $C_{13}H_{30}N_6CuCl_2O_{10}$: C, 27.64; H, 5.35; N, 14.88. Found: C, 27.45; H, 5.50; N, 14.97%. FAB mass (m/z): 464([M-ClO$_4$]$^+$) and 365 ([M-2ClO$_4$-H]$^+$). IR: 3230 (v(N-H)) and 1555 cm^{-1} (v(NO$_2$)).

[Cu(8)](ClO$_4$)$_2$. To a methanol solution (*ca.* 30 mL) of Cu(OAc)$_2$·H$_2$O (3.0 g, 15 mmol) were added 97% ethy-lenediamine (2.0 mL, 30 mmol), 95% 1-nitropropane (1.4 mL, 15 mmol), triethylamine (0.1 mL), and paraformal-dehyde (0.9 g, 30 mmol). The mixture was heated at reflux for 15 h. After 99% *n*-propylamine (1.0 mL, 12 mmol) and paraformaldehyde (1.0 g, 34 mmol) had been added, the resulting mixture was further refluxed for 12 h. An excess amount of NaClO$_4$ was added to the solution. The red-pur-ple solids were recrystallized more than twice from hot wat-er. Yield: ~30%. Anal. Calcd for $C_{14}H_{32}N_6CuCl_2O_{10}$: C, 29.05; H, 5.57; N, 14.52. Found: C, 28.85; H, 5.39; N, 14.63%. FAB mass (m/z): 478 ([M-ClO$_4$]$^+$) and 379 ([M-2ClO$_4$-H]$^+$). IR: 3235 (v(N-H)) and 1555 cm^{-1} (v(NO$_2$)).

[Cu(9)](ClO$_4$)$_2$. To a water-methanol (1:3) solution (20 mL) of [Cu(1)](ClO$_4$)$_2$ (2.0 g, 4.3 mmol) were added 95% nitroethane (0.4 mL, 5.2 mmol) and paraformadehyde (0.4 g, 13 mmol). After triethylamine (*ca.* 0.3 mL) had been added, the mixture was refluxed for 15 h. The result-ing purple solution was filtered off to remove any solid, and then an excess of perchloric acid was added to the fil-trate. The red-purple solids were filtered off, washed with methanol, and recrystallized more than twice from hot water. Yield: ~70%. Calcd for $C_{13}H_{28}N_6CuCl_2O_{10}$: C, 27.74; H, 5.01; N, 14.93. Found: C, 27.75; H, 5.02; N, 14.90%. FAB mass (m/z): 462 ([M-ClO$_4$]$^+$) and 363 ([M-2ClO$_4$-H]$^+$). IR: 3265 (v(N-H)), 3225 (v(N-H)), 3200 (v(N-H)), and 1560 cm^{-1} (v(NO$_2$)).

[Cu(10)](ClO$_4$)$_2$. This complex was prepared by a method similar to that for [Cu(9)](ClO$_4$)$_2$ except that 95% 1-nitropropane (0.5 mL, 5.2 mmol) was reacted instead of ni-troethane. Yield: ~80%. Anal. Calcd for $C_{14}H_{30}N_6CuCl_2O_{10}$: C, 29.15; H, 5.24; N, 14.57. Found: 29.06; H, 5.28; N, 14.60%. FAB mass (m/z): 476 ([M-ClO$_4$]$^+$) and 377 ([M-2ClO$_4$-H]$^+$). IR: 3256 (v(N-H)), 3225 (v(N-H)), 3204 (v(N-H)), and 1555 cm^{-1} (v(NO$_2$)).

[Cu(L)Cl]Cl (L=5 or 6). To a hot water-acetonitrile (2:1) (*ca.* 15 mL) solution of [Cu(L)](ClO$_4$)$_2$ (1.0 g) were add-ed excess amount of NaCl. The resulting solution left to stand at room temperature to produce the blue-purple solids. The product was filtered off, washed with methanol, and dri-ed in air (Yield: 70-80%). **[Cu(5)Cl]Cl.** Anal. Calcd for $C_{12}H_{26}N_6CuCl_2O_4$: C, 31.83; H, 5.79; N, 18.56. Found: C, 31.65: H, 5.71; N, 18.63%. IR: 3255 (v(N-H)), 3140 (v(N-H)), and 1555 cm^{-1} (v(NO$_2$)). **[Cu(6)Cl]Cl.** Anal. Calcd for $C_{14}H_{30}N_6CuCl_2O_4$: C, 34.97; H, 6.29; N, 17.47. Found: C, 34.03: H, 6.25; N, 17.40%. IR: 3250 (v(N-H)), 3160 (v(N-H)), and 1555 cm^{-1} (v(NO$_2$)).

[Cu(L)Cl]ClO$_4$ (L=9 or 10). To a hot water-acetonitrile (2:1) (*ca.* 15 mL) solution of [Cu(L)](ClO$_4$)$_2$ (1.0 g) were added excess amount of NaCl and NaClO$_4$. The resulting solution left to stand at room temperature to produce the blue-purple solids. The product was filtered off, washed with methanol, and dried in air (Yield: 80-90%). **[Cu(9)Cl] ClO$_4$.** Anal. Calcd for $C_{13}H_{28}N_6CuCl_2O_6$: C, 31.30; H, 5.66; N, 16.85%. Found: C, 31.10: H, 5.48; N, 16.90%. IR: 3250 (v(N-H)), 3210 (v(N-H)), 3180 (v(N-H)), and 1550 cm^{-1} (v(NO$_2$)). **[Cu(10)Cl]ClO$_4$.** Anal. Calcd for $C_{14}H_{30}N_6CuCl_2$-O$_6$: C, 32.79; H, 5.90; N, 16.39%. Found: C, 32.55: H, 5.83; N, 16.25%. IR: 3240 (v(N-H)), 3210 (v(N-H)), 3180 (v(N-H)), and 1550 cm^{-1} (v(NO$_2$)).

Results and Discussion

Synthesis and Characterization. The copper(II) complex [Cu(6)](ClO$_4$)$_2$ can be readily prepared by a method similar to that reported for [Cu(5)]$^{2+}$.[11] The two-step metal template condensation (see Experimental) of ethy-lenediamine, formaldehyde, *n*-propylamine, and appropriate nitroalkane in the presence of copper(II) ion, followed by addition of NaClO$_4$, yielded the pentaaza macrocyclic com-plex [Cu(7)](ClO$_4$)$_2$ or [Cu(8)](ClO$_4$)$_2$. The reaction (Eq. (4)) of [Cu(1)](ClO$_4$)$_2$ with formaldehyde and nitroethane or *n*-ni-tropropane in the presence of trace triethylamine produced new copper(II) complex [Cu(9)](ClO$_4$)$_2$ or [Cu(10)](ClO$_4$)$_2$ in high yield (70-80%).

The non-macrocyclic complex [Cu(1)]$^{2+}$ reacts with ethy-lenediamine and formaldehyde to produce the dinuclear complex [Cu$_2$(11)]$^{2+}$.[15] However, unexpectedly, all efforts to prepare copper(II) complexes of hexaaza macrocycles (A) from the reaction of [Cu(1)]$^{2+}$ with R-NH$_2$ (R=Me or *n*-Pr) and formaldehyde were unsuccessful. In all attempts the only product isolated as a solid was a salt of [Cu(4)]$^{2+}$. It has been reported that [Cu(4)]$^{2+}$ is produced by the reaction of [Cu(1)]$^{2+}$ with an excess of formaldehyde.[15]

A
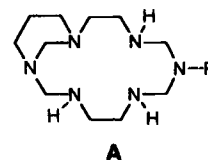
The formula of the new copper(II) complexes [Cu(L)] (ClO$_4$)$_2$ (L=6, 7, 8, 9, or 10) could be confirmed by their fast atom bombardment (FAB) mass spectra, together with elemental analyses and infrared spectra (see Experimental). The molar conductance of the diperchlorate salts [Cu(L)] (ClO$_4$)$_2$ in nitromethane (130-140 Ω - 1 mol^{-1} cm^2) and wat-er (200-220 Ω^{-1} mol^{-1} cm^2) indicates that each complex is a 1:2 electrolyte. Visible spectra of the copper(II) com-plexes (1.0×10^{-3} M) in 0.3 M HClO$_4$ aqueous solutions in-dicated that less than 3% of the complexes are decomposed in 10 h at room temperature; the similar behavior is also ob-served for copper(II) complexes of other 14-membered po-lyaza macrocyclic ligands.[4-9,15]

The electronic absorption spectra (Table 1) of the copper (II) complexes [Cu(L)](ClO$_4$)$_2$ prepared in this work measur-ed in nitromethane show a d-d transition band at 484-508 nm, indicating that the complexes have a square-planar coor-dination geometry.[4,7,9,15,19] The wavelength of the band for **9**

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Table 1. Electronic Spectra and Molar Conductance Data of the Copper(II) Complexes at 20 °C

Complex	λ_{max}, nm (ε, M^{-1} cm^{-1})			Nujol mull
	MeNO$_2$	H$_2$O	MeCN	
[Cu(1)](ClO$_4$)$_2$[a]	523(79)			
[Cu(4)](ClO$_4$)$_2$[b]	505(122)	529(142)		
[Cu(5)](ClO$_4$)$_2$	495(69)	512(70)	512(69)	495
[Cu(6)](ClO$_4$)$_2$	494(72)	515(73)	504(71)	495
[Cu(7)](ClO$_4$)$_2$	488(89)		502(84)	
[Cu(8)](ClO$_4$)$_2$	484(97)		496(92)	
[Cu(9)](ClO$_4$)$_2$	508(108)	519(107)	522(104)	505
[Cu(10)](ClO$_4$)$_2$	507(108)	525(110)	522(106)	505
[Cu$_2$(11)](ClO$_4$)$_4$[a]	486(182)	512(213)	505(220)	
[Cu(5)Cl]ClO$_4$		514(69)		555
[Cu(6)Cl]ClO$_4$		513(74)		555
[Cu(9)Cl]ClO$_4$	581(222)	522(110)	580(180)	575
[Cu(10)Cl]ClO$_4$	580(215)	525(113)	579(180)	575

[a] Ref. 15. [b] Ref.9.

or **10** is *ca.* 20 nm longer than that for **7** or **8**. This parallels with the reported trend that the alkylation on coordinated secondary nitrogens of 14-membered polyaza macrocyclic complexes weakens M-N (M=metal atom) interactions.[8,9,16,18,22–25] Table 1 also shows that the molar absorption coefficient varies with the ligand structure in the order of **5** < **7** < **9** or **6** < **8** < **10**. The larger molar absorption coefficients for the complexes of **7-10**, compared to those of **5** and **6**, may be resulted from the more distorted structures of the complexes caused by the unsymmetrical ligand structure.[22,24,26–28] The wavelengths of the *d-d* bands of the square-planar copper(II) complexes measured in coordinating solvents such as water and acetonitrile are distinctly longer than those in nitromethane. This may be attributed to the axial coordination of the solvent molecule.[15,29]

Cyclic voltammograms of the square-planar copper(II) complexes of **6-10** showed one irreversible oxidation peak corresponding to a Cu(II)/Cu(III) process (Table 2). The higher oxidation potentials of the complexes of **9** and **10**, compared to those of **7** and **8**, agree with the generally observed trend that alkylation on coordinated nitrogens of polyaza macrocyclic complexes lengthens the M-N bond distances and makes the oxidation more difficult.[22,26,28,30,31] The

Table 2. Oxidation Potentials (Volt *vs.* SCE) for the Copper(II) Complexes[a]

Complex	[Cu(L)]$^{2+}$ → [Cu(L)]$^{3+}$
[Cu(5)](ClO$_4$)$_2$	+1.58
[Cu(6)](ClO$_4$)$_2$	+1.56
[Cu(7)](ClO$_4$)$_2$	+1.48
[Cu(8)](ClO$_4$)$_2$	+1.48
[Cu(9)](ClO$_4$)$_2$	+1.56
[Cu(10)](ClO$_4$)$_2$	+1.55
[Cu(11)](ClO$_4$)$_4$[b]	+1.34

[a] Measured in 0.1 M (*n*-Bu)$_4$NClO$_4$ acetonitrile solutions at 20 °C. [b] Ref.15 .

potentials for **6** and **8** (or **10**) are quite similar to those for **5** and **7** (or **9**), respectively, indicating that the electron density on the metal is not affected by the C-alkyl groups. However, the potentials for **7** and **8** are distinctly lower than those for **5** and **6**. Furthermore, the potentials for **9** and **10** are higher than that for **11** but are similar to those for **5** and **6**.

Above results support that the incorporation of the nitroalkane group instead of the alkylamino group of [Cu(7)]$^{2+}$, [Cu(8)]$^{2+}$, and [Cu(11)]$^{2+}$ to give [Cu(5)]^2, [Cu(6)]$^{2+}$, and [Cu(9)]$^{2+}$ (or [Cu(10)]$^{2+}$), respectively, weakens the Cu-N interactions and reduces the electron density on the metal ion.

Five-coordinate Complexes. Addition of NaCl to a water-acetonitrile solution of the square-planar copper(II) complex of **5**, **6**, **9**, or **10** produces the five-coordinate complex [Cu(L)Cl]X (X=Cl or ClO$_4$$^-$; L=**5**, **6**, **9**, or **10**) (see Experimental). However, all attempts to prepare such a five-coordinate complex of **7** or **8** from the similar conditions were unsuccessful. The only complex isolated as a solid was the reactant [Cu(7)](ClO$_4$)$_2$ or [Cu(8)](ClO$_4$)$_2$ even in the concentrated NaCl solutions. The molar conductances of [Cu(9)Cl]ClO$_4$ or [Cu(10)Cl]ClO$_4$ measured in acetonitrile (*ca.* 160 Ω^{-1} mol^{-1} cm^2) and nitromethane (*ca.* 85 Ω^{-1} mol^{-1} cm^2) correspond to 1 : 1 electrolytes; the complexes [Cu(5)Cl]Cl and [Cu(6)Cl]Cl are insoluble in the non-aqueous solvents. Visible absorption spectra (Table 1) of the complexes [Cu(L)Cl]X (L=**5**, **6**, **9**, or **10**) in Nujol mull, acetonitrile and/or nitromethane show one absorption band at 555-575 nm, indicating that each complex has a square-pyramidal coordination geometry.[9,32] In water, however, the conductance (*ca.* 220 Ω^{-1} mol^{-1} cm^2) of each complex corresponds to a 1 : 2 electrolyte. The visible spectrum of the complex in water is also similar to that for the corresponding square-planar complex. It is clear that the chloride ion of the copper(II) complexes is coordinated to the metal ion in the solid state and/or in nitromethane or acetonitrile but is readily removed from the coordination sphere in water.

In conclusion, square-planar copper(II) complexes of **6-10** can be prepared by the simple metal template condensation. The properties of the complexes are affected significantly by the pendant groups.

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Tetrathiafulvalene (TTF) Charge Transfer Compounds of $FeCl_2$ and $Fe_2(SO_4)_3$; $(TTF)_3FeCl_3 \cdot 0.5CH_3OH$ and $(TTF)_{2.5}Fe(SO_4)_2 \cdot CH_3OH$

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Tetrathiafulvalene (TTF) and its analogues have been used as electron donors to form highly electrical conductive charge transfer compounds.[1] Their electrical properties can be varied over a wide range by changing the nature of the acceptor species. The use of metal chelates as acceptor is expected to be a versatile route for the preparation of a wide variety of conductive TTF compounds which exhibit different electrical properties, because various types of metal chelate anions can be employed with different geometries and oxidation states of the central metal ion. Among the metal complexes, Fe(III) complexes have been widely used as electron acceptors since Fe(III) is readily reduced to Fe(II) due to the relatively high reduction potential (Fe(III) → Fe(II); $E_{1/2}=0.771$ V in H_2O), for example, $(TTF)_{2-3}FeX_3$[2]

and $(BEDT-TTF)FeX_4$[3] (BEDT-TTF: bis(ethylenedithio) tetrathiafulvalene, X=Cl and Br) were reported. However the reported compounds showed different charge transfer process during the reaction. In the former compound, the electron has transferred from TTF to the central Fe(III) ion to form reductive Fe(II) state, whereas in $(BEDT-TTF)FeX_4$, charge transfer has occurred to the FeX_4^- moiety as a result of the addition of halide anion to FeX_3 in solution. In this study, even Fe(II) cannot be reduced readily, we tried to prepare $TTF-FeCl_2$ charge transfer compound since iron(II) chloro-anion, $FeCl_3^-$, can be obtained by interaction of $FeCl_2$ with chloride anion. $TTF-Fe_2(SO_4)_3$ compound was also prepared to ascertain the charge transfer behavior. The prepared compounds were characterized by spectroscopic,