One-Pot Reaction Involving Three Different Amines and Formaldehyde Leading to the Formation of New Hexaaza Macrobicyclic Copper(II) Complexes

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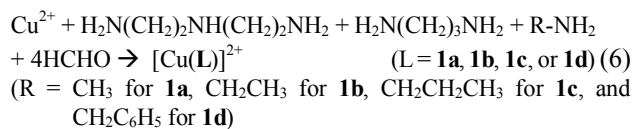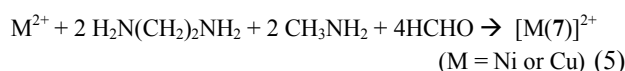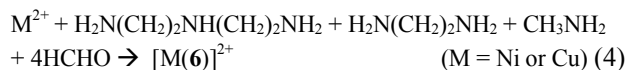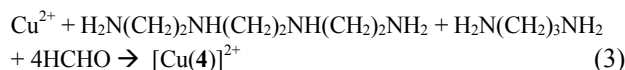*Received April 2, 2009, Accepted May 21, 2009*

Multi-component reactions, which generally mean one-pot processes involving several easily accessible reagents to produce a single product, have become an important area in modern synthetic chemistry.[1-10] Especially, multi-component reactions involving metal ion, amines, and formaldehyde have been utilized for the preparation of polyaza macrocyclic and macropolycyclic complexes containing N-CH$_2$-N linkages.[2-10] For instance, the 14-membered hexaaza macrotricyclic complexes $[M(\mathbf{2})]^{2+}$ (M = Cu(II) or Ni(II)) containing two 1,3-diazacyclopentane rings have been prepared by the reaction (Eq. (1)) of formaldehyde with one kind of triamine (diethylenetriamine) in the presence of the metal ion.[5] Recently, the 15-membered hexaaza macrotricyclic complexes $[Cu(\mathbf{3})]^{2+}$ and $[Cu(\mathbf{4})]^{2+}$ have been also prepared by the reaction (Eq. (2) or (3)) of formaldehyde with two different amines.[6,7] It has been revealed that such one-pot metal-template condensation reactions are useful routes toward various types of polyaza macrocyclic complexes that could not be synthesized by other methods.[2-10] In most cases, however, formaldehyde reacts with only one or two kinds of amine species.

There has been minimal research on the one-pot metal-template condensations involving three different amines or more.[9] To the best of our knowledge, $[M(\mathbf{6})]^{2+}$ (Cu(II) or Ni(II)) is a rare example that prepared from the reaction of three different amines with formaldehyde.[9] Although $[M(\mathbf{6})]^{2+}$ bearing one *N*-Me group is prepared by the reaction (Eq. (4)) of formaldehyde with diethylenetriamine, ethylenediamine, and methylamine in the presence of the metal ion, it is formed at best in low yield (~ 10%) because of competing reactions, such as Eqs. (1) and (5).[9] Furthermore, the preparation of other hexaaza macrobicyclic complexes containing bulkier pendant arm, such as *N*-CH$_2$CH$_3$ or *N*-CH$_2$CH$_2$CH$_3$ group, could not be achieved; $[M(\mathbf{2})]^{2+}$ was prepared as the major product when ethylamine or *n*-propylamine was reacted instead of methylamine.[9]

It has been reported that 15-membered hexaaza macrocyclic copper(II) complexes with a 5-6-6-6 chelate ring sequence, such as $[Cu(\mathbf{3})]^{2+}$, $[Cu(\mathbf{4})]^{2+}$, and $[Cu(\mathbf{5})]^{2+}$, are readily decomposed in low pH, unlike the 14-membered macrocyclic complexes $[Cu(\mathbf{2})]^{2+}$ and $[Cu(\mathbf{6})]^{2+}$.[6,7] Interestingly, their decomposition reaction rates are strongly influenced by the ligand structure. For instance, the reaction rate ratios for $[Cu(\mathbf{5})]^{2+}$: $[Cu(\mathbf{3})]^{2+}$: $[Cu(\mathbf{4})]^{2+}$ in 0.3 M HClO$_4$ solution are approximately 1:10^2:10^4.[6,7] However, the reasons for such kinetic behaviors have not been thoroughly investigated, since examples of 15-membered hexaaza macrocyclic

complexes with a 5-6-6-6 chelate ring sequence are limited in number. Therefore, we have been interested in the preparation of various types of 15-membered hexaaza macrocyclic complexes with a 5-6-6-6 chelate ring sequence.

1a: R= CH$_3$ **2**   **3**   **4**
1b: R= CH$_2$CH$_3$
1c: R= CH$_2$CH$_2$CH$_3$
1d: R= CH$_2$C$_6$H$_5$

5   **6**   **7**   **8**

$$M^{2+} + 2\ H_2N(CH_2)_2NH(CH_2)_2NH_2 + 4HCHO \rightarrow [M(\mathbf{2})]^{2+}$$
$$(M = Ni\ or\ Cu)\ (1)$$

$$Cu^{2+} + H_2N(CH_2)_2NH(CH_2)_2NH_2 + H_2N(CH_2)_3NH (CH_2)_3NH_2$$
$$+ 4HCHO \rightarrow [Cu(\mathbf{3})]^{2+} \qquad (2)$$

$$Cu^{2+} + H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2 + H_2N(CH_2)_3NH_2$$
$$+ 4HCHO \rightarrow [Cu(\mathbf{4})]^{2+} \qquad (3)$$

$$M^{2+} + H_2N(CH_2)_2NH(CH_2)_2NH_2 + H_2N(CH_2)_2NH_2 + CH_3NH_2$$
$$+ 4HCHO \rightarrow [M(\mathbf{6})]^{2+} \qquad (M = Ni\ or\ Cu)\ (4)$$

$$M^{2+} + 2\ H_2N(CH_2)_2NH_2 + 2\ CH_3NH_2 + 4HCHO \rightarrow [M(\mathbf{7})]^{2+}$$
$$(M = Ni\ or\ Cu)\ (5)$$

$$Cu^{2+} + H_2N(CH_2)_2NH(CH_2)_2NH_2 + H_2N(CH_2)_3NH_2 + R\text{-}NH_2$$
$$+ 4HCHO \rightarrow [Cu(\mathbf{L})]^{2+} \qquad (L = \mathbf{1a},\ \mathbf{1b},\ \mathbf{1c},\ or\ \mathbf{1d})\ (6)$$
$$(R = CH_3\ for\ \mathbf{1a},\ CH_2CH_3\ for\ \mathbf{1b},\ CH_2CH_2CH_3\ for\ \mathbf{1c},\ and$$
$$CH_2C_6H_5\ for\ \mathbf{1d})$$

In this work, we examined one-pot metal-template condensation (Eq.(6)) of three different amines with formaldehyde under various experimental conditions and successfully prepared new 15-membered hexaaza macrobicyclic complexes $[Cu(L)]^{2+}$ (L = **1a**, **1b**, **1c**, or **1d**) with a 5-6-6-6 chelate ring sequence in high yield. Selective preparation and characterization of the copper(II) complexes are reported.

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 were performed at the Korea Basic Science Institute, Daegu, Korea. Elemental Analyzes were performed at the Research Center for Instrumental Analysis, Daegu University, Korea.

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

Preparation of [Cu(1a)](ClO₄)₂ (1a = 9-methyl-1,3,7,9,11,14-hexaazabicyclo[12.2.1]heptadecane). To a methanol solution (*ca.* 40 mL) of Cu(OAc)₂·H₂O (4.0 g, 20 mmol) were added 99% 1,3-diaminopropane (1.9 mL, 22 mmol), 97% diethylenetriamine (2.0 mL, 18 mmol), and 40% methylamine (2.2 mL, 22 mmol). The solution was stirred in a cold water bath (< 15 °C) for *ca.* 30 min, and 35% formaldehyde (9.4 mL, 120 mmol) was added to the cold solution. The resulting blue solution was stirred at 40-50 °C for 20 h. After the addition of an excess amount of NaClO₄, the mixture was stored at room temperature to produce a purple solid. The crude product often contains a small amount (< 10%) of [Cu(**2**)](ClO₄)₂ as a by-product. The product was collected by filtration and recrystallized from hot water. Yield: 4.5 g (*ca.* 50%). *Anal.* Found: C, 27.75; H, 5.50; N, 16.11. Calc. for $C_{12}H_{28}N_6CuCl_2O_8$: C, 27.78; H, 5.44; N, 16.20%. FAB mass (*m/z*): 418.1 for $[Cu(\mathbf{1a}) + ClO_4]^+$; 319.1 for $[Cu(\mathbf{1a}) - H]^+$. IR (Nujol mull, cm⁻¹): 3253 (ν_{N-H}), 3222 (ν_{N-H}, *br*)).

Preparation of [Cu(1b)](ClO₄)₂ (1b = 9-ethyl-1,3,7,9,11,14-hexaazabicyclo[12.2.1]heptadecane). This complex was prepared by a method similar to that for [Cu(**1a**)](ClO₄)₂, except that 70% ethylamine (2.2 mL, 22 mmol) was used instead of methylamine. Yield: 4.7 g (*ca.* 50%). *Anal.* Found: C, 29.24; H, 5.55; N, 15.70. Calc. for $C_{13}H_{30}N_6CuCl_2O_8$: C, 29.30; H, 5.67; N, 15.77%. FAB mass (*m/z*): 432.1 for $[Cu(\mathbf{1b}) + ClO_4]^+$; 333.1 for $[Cu(\mathbf{1b}) - H]^+$. IR (Nujol mull, cm⁻¹): 3256 (ν_{N-H}), 3247 (ν_{N-H}), 3203 (ν_{N-H}).

Preparation of [Cu(1c)](ClO₄)₂ (1c = 9-(*n*-propyl)-1,3,7,9,11,14-hexaazabicyclo[12.2.1]heptadecane). This complex was prepared by a method similar to that for [Cu(**1a**)](ClO₄)₂, except that 99% *n*-propylamine (2.2 mL, 22 mmol) was used instead of methylamine. This compound was recrystallized from hot water-acetonitrile (1:1). Yield: 4.9 g (*ca.* 50%). *Anal.* Found: C, 30.57; H, 5.84; N, 15.24. Calc. for $C_{14}H_{32}N_6CuCl_2O_8$: C, 30.75; H, 5.90; N, 15.37%. FAB mass (*m/z*): 446.1 for $[Cu(\mathbf{1c}) + ClO_4]^+$; 347.2 for $[Cu(\mathbf{1c}) - H]^+$. IR (Nujol mull, cm⁻¹): 3246 (ν_{N-H}), 3210 (ν_{N-H}, *br*).

Preparation of [Cu(1d)](ClO₄)₂ (1d = 9-(phenylmethyl)-1,3,7,9,11,14-hexaazabicyclo[12.2.1]heptadecane). This complex was prepared by a method similar to that for [Cu(**1a**)](ClO₄)₂, except that 99% benzylamine (2.88 mL, 22 mmol) was used instead of methylamine. This compound was recrystallized from hot water-acetonitrile (1:2). Yield: 6.2 g (*ca.* 60%). *Anal.* Found: C, 36.14; H, 5.68; N, 14.30. Calc. for $C_{18}H_{32}N_6CuCl_2O_8$: C, 36.34; H, 5.42; N, 14.13%. FAB mass (*m/z*): 494.1 for $[Cu(\mathbf{1d}) + ClO_4]^+$; 395.2 for $[Cu(\mathbf{1d}) - H]^+$. IR (Nujol mull, cm⁻¹): 3249 (ν_{N-H}), 3231 (ν_{N-H}, *br*), 3050 (ν_{C-H}, phenyl), 1630 ($\nu_{C=C}$, phenyl).

Results and Discussion

Synthesis. Initial attempts to prepare [Cu(**1a**)](ClO₄)₂ from the reaction (Eq. (6)) of formaldehyde with a 1 : 1 : 1 : 1 molar mixture of Cu(OAc)₂·H₂O, diethylenetriamine, 1,3-propanediamine, and methylamine in boiling methanol were not quite successful because of the competing reaction (Eq. (1)) involving diethylenetriamine and formaldehyde; the major product obtained by the addition of NaClO₄ to the reaction solution was [Cu(**2**)](ClO₄)₂. A similar result was also observed in the attempts at room temperature. As described in the Experimental Section, however, [Cu(**1a**)](ClO₄)₂ could be prepared in high yield (~ 50%) by the careful control of the reaction conditions; the temperature of the solution was maintained at ≤ 15 °C during the addition of formaldehyde and then the resulting reaction mixture was stirred at 40 - 50 °C. Although the crude product often contains relatively small amount (< 10%) of [Cu(**2**)](ClO₄)₂ as a by-product, [Cu(**1a**)](ClO₄)₂ can be isolated readily by the fractional recrystallizations of the product. The copper(II) complexes of **1b** - **1d** bearing bulkier *N*-alkyl pendant arm was also prepared as the major products (yield: 50 - 60 %) by reacting appropriate primary alkylamine (ethylamine, *n*-propylamine, or benzyl amine) instead of methylamine.

All our efforts to prepare nickel(II) complexes of **1a** - **1d** from the similar one-pot reaction in the presence of nickel(II) ion were unsuccessful. The only macrocyclic complex obtained from each attempt was [Ni(**2**)](ClO₄)₂. The present result is different from the fact that $[Ni(\mathbf{6})]^{2+}$ can be prepared from the reaction of Eq. (4). This may be intimately linked with the trend that polyaza macrocyclic complexes with a 5-6-6-6 chelate ring sequence are much less stable than those with a 5-6-5-6 chelate ring sequence.[6,7,11,12] The formation of the copper(II) complexes of **1a** - **1d** with a 5-6-6-6 chelate ring sequence implicates that the metal ion, which is stronger Lewis acid than Ni²⁺ ion, stabilizes the coordinated secondary amino groups involved in the N-CH₂-N linkages of the complexes.[6,7] It should be pointed out that the yield (50 - 60%) of the copper(II) complexes of **1a** - **1d** is considerably higher than that reported for [Cu(**6**)](ClO₄)₂ (10%), which has been prepared from the reaction of Eq. (4).[9]

Spectra and Properties. Unfortunately, we could not obtain single crystals of [Cu(L)](ClO₄)₂ (L = **1a**, **1b**, **1c**, or **1d**) suitable for X-ray crystallography. However, the formation of the complexes could be confirmed by their FAB mass and infrared spectra as well as the elemental analyses (*see* Experimental

Notes

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Table 1. Electronic Absorption Spectra of the complexes[a]

Complex	λ_{max}, nm (ε, $M^{-1}cm^{-1}$)[a]			
[Cu(**1a**)](ClO$_4$)$_2$	532(148)	543(142)[b]	544(165)[c]	540[d]
[Cu(**1b**)](ClO$_4$)$_2$	533(155)	545(143)[b]	543(170)[c]	530[d]
[Cu(**1c**)](ClO$_4$)$_2$	530(151)	544(147)[b]	546(146)[c]	540[d]
[Cu(**1d**)](ClO$_4$)$_2$	530(147)	544(147)[b]	545(156)[c]	535[d]
[Cu(**3**)](ClO$_4$)$_2$[e]	566(235)	574(196)[b]	596(210)[c]	
[Cu(**4**)](ClO$_4$)$_2$[f]	553(175)	555(173)[b]	555(150)[c]	
[Cu(**6**)](ClO$_4$)$_2$[g]	490(102)	506(109)[b]	502(113)[c]	

[a]Measured in nitromethane at 20 °C unless otherwise specified. [b]In acetonitrile. [c]In water. [d]In Nujol mull. [e]Ref. 6. [f]Ref. 7. [g]Ref. 9.

Section). In the FAB mass spectra of the complexes, two groups of peaks corresponding to the fragments [Cu(L) + ClO$_4$]$^+$ and [Cu(L) − H]$^+$ are observed. The infrared spectra of the complexes show ν_{N-H} of the coordinated secondary amino groups at *ca.* 3200 cm^{-1}. The molar conductance values of the complexes measured in water (210 - 230 $\Omega^{-1}mol^{-1}cm^2$) and acetonitrile (240 - 260 $\Omega^{-1}mol^{-1}cm^2$) show that they are 1:2 electrolytes. In the electronic absorption spectrum (Table 3) of [Cu(**1a**)](ClO$_4$)$_2$ measured in nitromethane, a *d-d* transition band is observed at 532 nm (ε = 148 $M^{-1}cm^{-1}$). The spectra of [Cu(**1b**)](ClO$_4$)$_2$, [Cu(**1c**)](ClO$_4$)$_2$, and [Cu(**1d**)](ClO$_4$)$_2$ are quite similar to that of [Cu(**1a**)](ClO$_4$)$_2$, showing that their ligand field strengths or Cu-N interactions are not affected significantly by the nature of the *N*-alkyl groups. The spectra of the copper(II) complexes of **1a** - **1d** are comparable with those of other square-planar copper(II) complexes with a 5-6-6-6 chelate ring sequence, such as [Cu(**3**)](ClO$_4$)$_2$ and [Cu(**4**)](ClO$_4$)$_2$.[6,7] However, the wavelengths for the complexes of **1a** - **1d** are 20 - 36 nm shorter than those for [Cu(**3**)] (ClO$_4$)$_2$ and [Cu(**4**)](ClO$_4$)$_2$ containing two coordinated tertiary amino groups, indicating that the former complexes exhibit stronger ligand field strength than the latter ones. This trend corresponds to the general observation that the stepwise alkylation on the coordinated secondary amino groups of a polyaza macrocyclic copper(II) complex weakens the Cu-N interactions. The wavelengths for the copper(II) complexes of **1a** -**1d** are *ca.* 40 nm longer than that for [Cu(**6**)](ClO$_4$)$_2$. This is attributed to the relatively large

cavity size of **1a** -**1d**. The wavelength of the *d-d* band for each complex measured in acetonitrile or water is observed at longer wavelength than that in nitromethane, indicating the coordination of the solvent molecule(s).

The copper(II) complexes of **1a** -**1d** are decomposed in acidic aqueous solutions. The pseudo first-order rate constants (*k*) for the decomposition reaction of the complexes (2 × 10^{-3} M) measured in 0.3 M HClO$_4$ aqueous solution at 20 °C are listed in Table 2, along with those reported for the complexes of **3**, **4**, and **8**.[6,7,11] Table 2 shows that the decomposition rates of the complexes of **1a** - **1d** are distinctly slower than those of [Cu(**3**)](ClO$_4$)$_2$, [Cu(**4**)](ClO$_4$)$_2$, and [Cu(**8**)](ClO$_4$)$_2$ under similar experimental conditions. This is probably associated with the relatively strong Cu-N interactions of the former complexes. Interestingly, the *k* value decreases in the order of [Cu(**1a**)](ClO$_4$)$_2$ (2.9 × 10^{-5} s^{-1}) > [Cu(**1b**)](ClO$_4$)$_2$ > [Cu(**1c**)] (ClO$_4$)$_2$ > [Cu(**1d**)](ClO$_4$)$_2$ (2.1 × 10^{-6} s^{-1}), showing that the decomposition reaction rate of the complexes is strongly influenced by the nature of the *N*-alkyl pendant arm. As described above, the ligand field strength of the copper(II) complexes of **1a** - **1d** is nearly independent on the nature of the *N*-alkyl group. The factors affecting the decomposition rate of the complexes are not clearly understood at this point. However, the present result supports the suggestion that one of the most important factors affecting the decomposition reaction may be the "B-strain" of the tertiary amino group involving the *N*-alkyl group.[13] According to the "B-strain", the replacement of the *N*-methyl group in [Cu(**1a**)](ClO$_4$)$_2$ with a bulkier *N*-alkyl group enlarges the C-N-C bond angles and eventually weakens the proton affinity of the amino group. It is also expected that the proton affinity of the coordinated amino groups at the six-membered chelate ring involving the *N*-benzyl group in [Cu(**1d**)](ClO$_4$)$_2$ is weaker than that involving *N*-methyl group in [Cu(**1a**)](ClO$_4$)$_2$ because of the larger ring size caused by the severer B-strain.

Table 2. Decomposition Rate Constants (k_{obsd}) of the Complexes in 0.3 M HClO$_4$ Solutions at 20 °C[a]

Complex	k_{obsd}, s^{-1}
[Cu(**1a**)](ClO$_4$)$_2$	2.9 × 10^{-5} (*ca.* 6.6 h)
[Cu(**1b**)](ClO$_4$)$_2$	9.4 × 10^{-6} (*ca.* 20.5 h)
[Cu(**1c**)](ClO$_4$)$_2$	5.4 × 10^{-6} (*ca.* 35.5 h)
[Cu(**1d**)](ClO$_4$)$_2$	2.1 × 10^{-6} (*ca.* 91.6 h)
[Cu(**3**)](ClO$_4$)$_2$[b]	1.2 × 10^{-4} (*ca.* 1.5 h)
[Cu(**4**)](ClO$_4$)$_2$[c]	1.4 × 10^{-2} (*ca.* 50 sec)
[Cu(**6**)](ClO$_4$)$_2$[d]	very slow
[Cu(**8**)]$^{2+}$[e]	3.3 × 10^{-3} (*ca.* 210 sec)

[a][Complex] = 2.0 × 10^{-3} M.; half-life ($t_{1/2}$) is in parentheses. [b]Ref. 6. [c]Ref. 7. [d]Ref. 9. [e]Ref. 11; measured in 0.3 M HNO$_3$.

Summary

This study shows that the copper(II) complexes of 15-membered hexaaza macrobicycles (**1a** - **1d**) with one *N*-alkyl pendant arm can be prepared in high yield by the one-pot metal-template condensation of three different amines and formaldehyde. The macrobicyclic complexes are much more inert against decomposition in concentrated HClO$_4$ solution than [Cu(**4**)](ClO$_4$)$_2$

and [Cu(**8**)](ClO$_4$)$_2$. This work clearly shows that the decomposition reaction of the copper (II) complexes with a 5-6-6-6 chelate ring sequence is strongly influenced by the steric factors of the *N*-alkyl group, even though the alkyl group is attached to the uncoordinated nitrogen atom.

References

1. (a) Yan, C. G.; Song, X. K.; Wang, Q. F.; Sun, J.; Siemeling, U.; Bruhn, C. *Chem. Commun*. **2008**, 1440 and references cited therein; (b) Ohta, Y.; Oishi, S.; Fujii, N.; Ohno, H. *Chem. Commun*. **2008**, 835.

2. (a) Comba, P.; Kerscher, M.; Lampeka, Y. D.; Lotzbeyer, L.; Pritzkow, H.; Tsymbal, L. *Inorg. Chem*. **2003**, *42*, 3387; (b) Walker, G. W.; Geue, R.; Haller, K. J.; Rae, A. D.; Sargeson, A. M. *J. Chem. Soc., Dalton Trans*. **2003**, 279.

3. (a) Kang, S.-G.; Lee, Y. H.; Jeong, J. H. *Inorg. Chem. Commun*. **2007**, *10*, 1429; (b) Kang, S.-G.; Nam, K.; Kim, S.-D. *Bull. Korean Chem. Soc*. **2004**, *25*, 1973; (c) Kang, S.-G.; Ryu, K.; Jung, S.-K.; Kim, J. *Inorg. Chim. Acta* **1999**, *293*, 140.

4. (a) Harrowfield, J.; Kim, Y.; Lee, Y. H.; Thuéry, P. *Eur. J. Inorg. Chem*. **2003**, 2913; (b) Robertson, M. J.; De Iuliis, G. N.; Meader, M.; Lawrance, G. A. *Inorg. Chim. Acta* **2004**, *357*, 557; (c) Salavati-Niasari, M.; Davar, F. *Inorg. Chem. Commun*. **2006**, *9*, 175; (d) Angus, P. M.; Elliott, A. J.; Sargeson, A. M.; Wills, A. C. *J. Chem. Soc., Dalton Trans*. **2000**, 2933.

5. (a) Suh, M. P.; Shin, W.; Kang, S.-G.; Lah, M. S.; Chung, T.-M. *Inorg. Chem*. **1989**, *28*, 1602; (b) Suh, M. P.; Kang, S.-G.; Chung, T.-M. *Bull. Korean Chem. Soc*. **1990**, *11*, 206.

6. Kang, S.-G.; Lee, Y. H.; Jeong, J. H. *Bull. Korean Chem. Soc*. **2008**, *29*, 1273.

7. Kang, S.-G.; Nam, K.; Kweon, J. K.; Jung, S.-K.; Lee, U. *Bull. Korean Chem. Soc*. **2006**, *27*, 577.

8. (a) Suh, M. P.; Choi, J.; Kang, S.-G.; Shin, W. *Inorg. Chem*. **1989**, *28*, 1763; (b) Kang, S.-G.; Song, J.; Jeong, J. H. *Inorg. Chim. Acta* **2004**, *357*, 605.

9. Kang, S.-G.; Jung, S.-K.; Kweon, J. K. *Bull. Korean Chem. Soc*. **1990**, *11*, 431.

10. Suh, M. P.; Kang, S.-G. *Inorg. Chem*. **1988**, *27*, 2544.

11. Lan, W.-J.; Chung, C.-S. *J. Chem. Soc., Dalton Trans*. **1994**, 191.

12. (a) Micheloni, M.; Paoletti, P.; Poggi, A. *J. Chem. Soc., Dalton Trans*. **1982**, 61. (b) Busch, D. H. *Acc. Chem. Res*. **1978**, *11*, 392.

13. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th Ed.; HarperCollins College Publishers: New York, 1993; pp 341-342.