

NMR ($\text{CH}_3\text{CN}/10\%\text{CD}_3\text{CN}$), -11.1 , -15.1 , -21.1 , -34.6 , -37.2 ppm; $^1\text{H-NMR}$ (CD_3CN), 7.74-7.28 (m, phenyl H), 2.35 (s, 9S3 CH_2), 1.14 (s, carboranyl CH).

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A New 14-Membered Tetraaza Macrocycle Having High Selectivity for Cu(II) Complex Formation

Shin-Geol Kang*, Jae Keun Kweon, Soo-Kyung Jung, and Mi-Seon Kim

Department of Chemistry, Taegu University,
Kyungsan 713-714

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Since selective separation and transport of metal ions are important subjects in the field of waste treatment, hydrometallurgy, or biochemistry, many efforts have been made to design ligands which show selectivity for a particular metal ion in the complex formation.^{1,2} It has been widely known that crown ethers exhibit some size-based selectivity toward alkali or alkaline earth metal ions.¹ Although most polyaza macrocyclic ligands form complexes with transition metal ions without showing considerable selectivity for the metal ions, some recent reports show that the selectivity of such ligands can be increased by their structural modification.³⁻¹⁰ For example, the 14-membered tetraaza macrocycle D containing four N-methyl groups shows higher selectivity for complex formation with Cu(II) over Ni(II) ion than the unmethylated macrocycle C.^{8,9} However, the selectivity of most polyaza macrocyclic ligands studied so far is kinetical rather than thermodynamical one and thus not very satisfactory. Therefore, we have been interested in the synthesis of highly selective macrocyclic ligands. We obtained a new per-N-methylated macrocyclic ligand 2,3,6,13,14,17-hexamethyl-2,6,13,

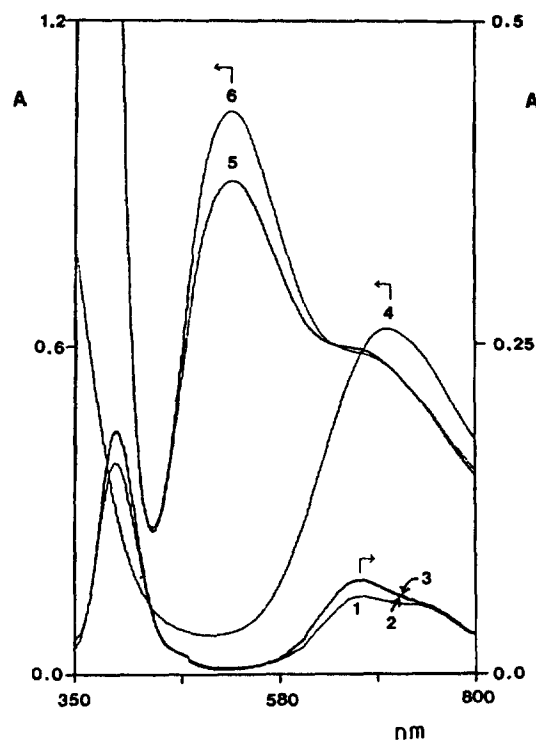
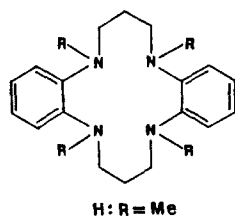
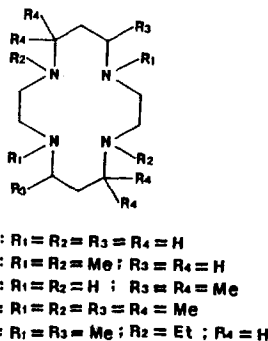
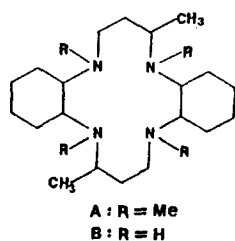


Figure 1. Electronic spectra of methanol solutions of Ni(II) acetate (1), mixture of Ni(II) acetate and A (7.5×10^{-3} M) at room temperature (2), the mixture (2) after heating at 45°C for 6 h (3), Cu(II) acetate (4), mixture of Cu(II) acetate and A (1.5×10^{-3} M) at room temperature (5), and this mixture after heating at 45°C for 6 h (6). $[\text{Ni}^{2+}] = 1.5 \times 10^{-2}$ M. $[\text{Cu}^{2+}] = 3.0 \times 10^{-3}$ M.

17-tetraazatricyclo[16,4,0^{1,18},0^{7,12}]docosane(A) that shows extraordinary high selectivity for complex formation with Cu(II) over Ni(II) ion.

New macrocycle A was obtained by the following procedure. A mixture of B (2.0 g)⁹, 85% formic acid (7.3 ml), 35% formaldehyde (7.3 ml), and distilled water (2 ml) was heated at reflux for 26 h and then cooled to *ca.* 5°C . A solution of NaOH (30 g) in water (100 ml) was added to make the pH of the solution higher than 12 and the resulting solution was extracted with chloroform. Chloroform of the extract was removed on a rotary evaporator, and a yellow oily liquid was obtained, which slowly solidified at room temperature. The product was recrystallized from 0.1 M NaOH aqueous solution-methanol mixture (Yield; $\sim 80\%$. Mass: $m/e = 392$ (M^+). $^1\text{H-NMR}$ (CDCl_3): 0.97 (d, C-Me), 2.28 (s, N-Me), 2.30 (s, N-Me). $^{13}\text{C-NMR}$: 18.8 (C-Me), 24.8, 26.2, 30.2, 33.4, 35.4 (N-Me), 35.8 (N-Me), 39.1, 49.4, 52.2, 61.3, 64.3). The infrared spectrum of A shows no peak around 3200 cm^{-1} , showing that all of the nitrogens are methylated.

The reaction of A with Cu(II) acetate in methanol followed by addition of sodium perchlorate produces red-purple crystals $[\text{Cu}(\text{A})](\text{ClO}_4)_2$ in high yield ($>90\%$).¹² The synthesis of Ni(II) complex of A by the reaction similar to that for the Cu(II) complex has also been attempted. Even after prolonged heating (>48 h) at reflux of the methanol solution of the mixture of the ligand and acetate, chloride, or nitrate salt of Ni(II) ion, the spectra of the solution was not changed. In all cases, the addition of sodium perchlorate to the re-

sulting solution produced only white solid $A \cdot 2HClO_4$ ¹³ instead of the complex. We were also unsuccessful in isolating any Co(II), Co(III), or Fe(II) complex of A from the reaction of A and the metal ion. The electronic spectra (Figure 1) of the methanol solution containing the ligand and Ni(II) ion are also very similar to that containing the metal ion only. Moreover, no spectral change is observed even by heating (>45°C) the mixture for more than six hours. The similar result was also observed in the spectra of the mixture of A and Co(II) or Fe(II) ion ($[M^{2+}] = 5.0 \times 10^{-3}$ M; $[A] = 2.5 \times 10^{-3}$ M). This result is quite different from the fact that the addition of A to the solution of Cu(II) acetate even at room temperature changes its spectrum. The stability constant of the Cu(II) complex calculated by the method of continuous variation¹⁴ at 25°C is more than 1.0×10^6 . The results indicate that the ligand A is highly selective for complex formation with Cu(II) over Ni(II) and other 3d-metal ions. The high selectivity for Cu(II) against Ni(II) ion in the complex formation has not been observed for other per-N-methylated 14-membered tetraaza macrocycles such as D, G, and H.^{9,15,16} Although it has been reported that D exhibits some selectivity for Cu(II) over Ni(II) ion,⁹ both $[Cu(D)]^{2+}$ and $[Ni(D)]^{2+}$ are readily isolated by the reaction of the metal ions and the ligand in methanol solution.⁸ The Ni(II) complex of D or F is also obtained by the reaction of $[Ni(C)]^{2+}$ or $[Ni(E)]^{2+}$ with MeI and KOH in DMSO solution.¹⁷ However, in all attempts to prepare Ni(II) complex of A from $[Ni(B)]^{2+}$ by the similar reaction, the complex with four N-methyl groups was never isolated.¹⁸ To our knowledge, the new ligand A prepared in this work is a rare 14-membered tetraaza macrocycle that exhibits the clear-cut recognition of Cu(II) against Ni(II) ion in the complex formation.

The reason for the high selectivity for complexation of A toward Cu(II) over Ni(II) ion is not clearly understood. However, it is likely that the selectivity is caused in part by the presence of the cyclohexane rings and C-methyl groups in addition to the N-methyls in the ligand, that sterically hinder the binding of the metal ion, and the acidity of the metal ions ($Cu(II) \gg Ni(II)$).¹⁹ Further studies on selective extraction, separation, and transport of the transition metal ions by using the noble ligand are in progress.

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13. Elemental analysis. Calcd for $C_{24}H_{50}N_4Cl_2O_8$: C, 47.2; H, 8.20; N, 9.19%. Found: C, 46.8; H, 8.27; N, 9.39%.
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Trimethylsilyl Triflate Promoted Conjugate Addition of Organozinc Compounds to α,β -Enones

Sunggak Kim*, Woo Seok Han, and Joo Moon Lee

*Department of Chemistry,
Korean Advanced Institute of Science
and Technology, Taejon 305-701*

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The conjugate addition of organometallic reagents to α,β -unsaturated carbonyl compounds is one of the most useful and reliable method for carbon-carbon bond formation. It has been normally achieved using organocopper reagents.¹ On the other hand, the use of Lewis acids such as titanium tetrachloride,² boron trifluoride etherate,³ and trialkylsilyl triflate⁴ makes it possible to use relatively mild allylsilanes and allylstannans in conjugate addition to α,β -enones. Organozinc compounds have mainly retained their synthetic usefulness in Reformatsky reaction⁵ but several organozinc compounds such as triorganozincates⁶ and zinc homoenolates⁷ have been employed in conjugate addition to α,β -enones. Since organozinc compounds are less reactive than organometal-