Å; thus, the temperature factor is 18 Å^2. These values can be compared with 0.59 Å and 9.2 Å^2 of the X-ray refinement[6]. The average rms fluctuations of the bases, riboses, and phosphates are 0.78, 0.83, and 0.97 Å, respectively; thus, their temperature factors are 16, 18, 25 Å , respectively. This shows that the phosphates are more mobile than the bases. The corresponding values from the x-ray refinement are 0.53, 0.58 and 0.76 Å, respectively, and thus, 7.3, 8.9, 15.2 Å^2, respectively. For the rms fluctuations or temperature facors, our simulation results are somewhat larger than those from the X-ray refinement. But, there exists a good consistency between the simulation and the X-ray.

Acknowledgements. This research was supported by Korea Science and Engineering Foundation (KOSEF) and Korean Ministry of Science and Technology (MOST). We would like to thank Dr. E. Westhof for providing us with the X-ray data of Z-DNA.

References

1. F. M. Pohl and T. M. Jovin, *Mol. Biol.*, **67**, 375 (1972).
2. A. H.-J. Wang, G. J. Quigley, F. J. Kolpak, J. L. Crawford, J. H. van Boom, G. van der Marel, and A. Rich, *Nature* **282**, 680 (1979).
3. H. Drew, H. T. Takano, S. Tanaka, K. Itakura, and R. E. Dickerson, *Nature* (London), **286**, 567 (1980).
4. A. Rich, A. Nordheim, and A. H.-J. Wang, *Ann. Rev. Biochem.*, **53**, 791 (1984), and references therein.
5. R. V. Gessner, C. A. Frederick, G. J. Quigley, A. Rich, and A. H.-J. Wang, *J. Biol. Chem.*, **264**, 7921 (1989).
6. B. Chevrier, A. C. Dock, B. Hartmann, M. Leng, D. Moras, M. T. Thuong, and E. Westhof, *J. Mol. Biol.*, **188**, 707 (1986).
7. Schorschinsky and M. J. Behe, *Biol. Chem.*, **261**, 8093 (1986).
8. R. E. Dickerson, H. R. Drew, B. M. Conner, R. M. Wing, A. V. Fratini and M. Kopka, *Science*, **216**, 475 (1982).
9. E .Westhof, "*Waters and Ions in Biomolecular Systems*", Birkhauser Verlag Basel, p. 11 (1990).
10. M. L. Kopka, A. V. Fratini, H. R. Drew, and R. E. Dickerson, *J. Mol. Biol.*, **163**, 129 (1983).
11. S. Neidle, H. M. Berman, and H. S. Shieh, *Nature* (London), **288**, 129 (1981).
12. P. S. Ho, G. J. Quigley R. F. Tilton, and A. Rich, *J. Phys. Chem.*, **92**, 939 (1988).
13. S. Devarajan, N. Pattabiraman, and R. H. Shafer, *Biopolymers*, **27**, 187 (1988).
14. K. S. Kim and E. Clementi, *J. Am. Chem. Soc.*, **107**, 227 (1985).
15. K. S. Kim and E. Clementi, *J. Am. Chem. Soc.*, **107**, 5504 (1985).
16. K. S. Kim, H. L. Nguyen, P. K. Swaminathan, and E. Clementi, *J. Phys. Chem.*, **89**, 2870 (1985).
17. K. S. Kim, *J. Comput. Chem.*, **6**, 256 (1985).
18. K. S. Kim, D. P. Vercateren, M. Welti, S. Chin, and E. Clementi, *Biophys. J.*, **47**, 327 (1985).
19. K. S. Kim and E. Clementi, *J. Comput. Chem.*, **8**, 57 (1987).
20. E. Westhof, Th. Prange, B. Chevrier, and D. Moras, *Biochimie*, **67**, 811 (1985).
21. S. J. Weiner, P. A. Kollman, D. A. Case, U. C. Singh, C. Ghio, G. Alagona, S. Profeta, and P. Weiner, *J. Am. Chem. Soc.*, **106**, 765 (1984).
22. K. S. Kim, D. P. Vercauteren, M. Welti, S. L. Fornili, and E. Clementi, *Croat. Chem. Acta*, **59**, 369 (1986).
23. P. K. Swaminathan, D. P. Vercauteren, K. S. Kim, and E. Clementi, *J. Biolog. Phys.* **30**, 49 (1986).
24. K. S. Kim, *Chem. Phys. Lett.*, **156**, 261 (1989).
25. H. Drew, S. Samson, and R. E. Dickerson, *Proc. Natl. Acad. Sci U.S.A.*, **79**, 4040 (1982) .

Template Synthesis and Characterization of Binuclear Nickel(II) and Copper(II) Complexes of Double-ring Macrocyclic Ligands

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

Department of Chemistry, Taegu University, Kyungsan 713-714. *Received January 1, 1991*

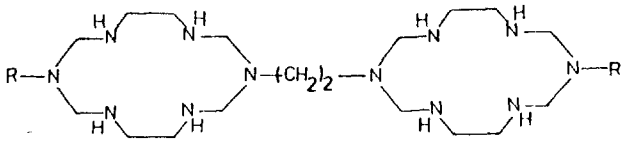
New binuclear Ni(II) and Cu(II) complexes with various alkyl derivatives of 1,2-bis(1,3,6,8,10,13-hexaaza-1-cyclotetradecyl) ethane, in which two fully saturated 14-membered hexaaza macrocyclic subunits are linked together by an ethylene chain, have been synthesized by the one step template condensations of formaldehyde with ethylenediamine and appropriate primary alkyl amines in the presence of the metal ions. Each macrocyclic subunit of the double-ring macrocyclic complexes contains one alkyl pendant arm and has a square planar geometry with a 5-6-5-6 chelate ring sequence. The visible spectra and oxidation properties indicate that the metal-metal interactions of the binuclear complexes are not significant. Synthesis, characterization, and the properties of the complexes are presented.

Introduction

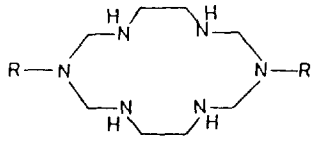
There has been considerable interest in the synthesis of binuclear macrocyclic complexes, since the complexes often represent a helpful tool in the study of metal metal interactions and multi-metal centered catalysts.[1-17] In order to obtain

binuclear macrocyclic complexes, several synthetic strategies have been employed: (i) synthesis of macrocycles containing functional groups,[4-6] (ii) synthesis of large macrocycles able to incoorporate two metal ions,[7-10] (iii) synthesis of double-ring macrocycles in which two macrocyclic subunits are linked together.[11-17] Each binuclear macrocyclic system exhibits its own unique properties. Especially, double-ring macrocycles do not alter significantly the properties of each macrocyclic subunit itself and thus most of the advantages of monomers, such as the kinetic inertness and thermodynamic stability, remain intact.[16] Although some double-ring macrocycles containing triaza or tetraaza macrocyclic subunits have been prepared from preformed monocyclic compounds or from metal template condensations, the synthetic routes for most of them require several steps.[11-17] Moreover, those containing fully saturated hexaaza macrocyclic subunits have not been reported.

Recently, mononuclear complexes of various fully saturated hexaaza macrocyclic ligands were prepared by the metal template condensation reactions of amines and formaldehyde.[18-23] For examples, square planar Ni(II) and Cu(II) complexes of 7-12 were synthesized from the reactions (Eq. 2) of formaldehyde, ethylenediamine, and appropriate primary alkylamines in the presence of the metal ions.[18,19] It has been revealed that formaldehyde is a good reagent to link two amino groups and the synthetic procedures are very simple. In the present work, we have attempted the synthesis of binuclear Ni(II) and Cu(II) complexes of double-ring macrocyclic ligands by the simple one-pot template condensation (Eq. 1) of the amines and formaldehyde. This paper reports the synthesis and properties of new binuclear Ni(II) and Cu



1 : R = CH_3 · 2 : R = CH_2CH_3 · 3 : R = $CH_2CH_2CH_3$
4 : R = $CH_2CH_2CH_2CH_3$ · 5 : R = $CH_2CH(CH_3)_2$ ·
6 : R = $CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$ ·



7 : R = CH_3 · 8 : R = CH_2CH_3 · 9 : R = $CH_2CH_2CH_3$ ·
10 : R = $CH_2CH_2CH_2CH_3$ · 11 : $CH_2CH(CH_3)_2$ ·
12 : R = $CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$ ·

(II) complexes of double-ring macrocyclic ligands, $[M_2(L)](ClO_4)_4$ (L=1, 2, 3, 4, 5, or 6), in which two 14-membered fully saturated hexaaza macrocyclic subunits with an alkyl pendant arm are linked together by an ethylene chain. Comparisons of the properties of the double ring macrocyclic complexes with those of their monomeric analogues are also described.

$$2M^{2+} + 5en + 2R\text{-}NH_2 + 8HCHO \longrightarrow [M_2(L)]^{4+} \quad (1)$$

(M=Ni(II) or Cu(II); L=1, 2, 3, 4, 5, or 6)

$$M^{2+} + 2en + 2R\text{-}NH_2 + 4HCHO \longrightarrow [M(L_M)]^{2+} \quad (2)$$

(M=Ni(II) or Cu(II); L_M=7, 8, 9, 10, 11, or 12)

Experimental

Materials. All chemicals used in synthesis were of reagent grade and were used without purification. Solvents used in spectral and electrochemical measurements were of spectroscopic and electroanalytical reagent grade, respectively.

Physical Measurements. Conductance measurements were made by using a Metrohm Herisau Conductometer E 518. Infrared spectra were obtained on a Shimadzu IR-440 spectrophotometer from 5050 to 290 cm^{-1}. Visible spectra were measured with a Perkin-Elmer Lambda 5 spectrophotometer. ^1H and ^{13}C-NMR spectra were recorded on Bruker WP 80 FT NMR and Bruker WP 300 FT NMR spectrometers. Elemental Analyses were performed at the Kolon R & D Center. Cyclic voltammograms were recorded using a Yanaco Voltammetric Analyzer P-1000 equiped with a FG-121 B function generator and a Watanabe X-Y recorder. The electrochemical studies were conducted in oxygen free acetonitrile solutions containing 0.1 M $(n\text{-}Bu)_4NClO_4$ or $(n\text{-}Bu)_4NPF_6$ as supporting electrolyte. The working and the counter electrode were platinum disk and wire, respectively. The reference electrode was a saturated calomel electrode (SCE).

Synthesis

$[Ni_2(1)](ClO_4)_4$. $NiCl_2 \cdot 6H_2O$ (6 g) was dissolved in 50 ml of methanol. To this solution were slowly added 99% ethylenediamine (5.0 ml), 40% methylamine (2.1 ml), and paraformaldehyde (4 g). The resulting bluish-green solution was heated at reflux for 30 h unitl a dark orange solution resulted and then cooled to room temperature. Excess perchloric acid was added dropwise to the solution with stirring and then the mixture was kept in a refrigerator. The yellow precipitate formed was filtered off, washed with methanol, and recrystallized from hot water. Yield: ~10%. Anal. Calcd for $C_{20}H_{50}N_{12}Ni_2Cl_4O_{16}$: C, 24.7; H, 5.13; N, 17.3%. Found: C, 25.0; H, 5.11; N, 17.0%.

$[Ni_2(2)](ClO_4)_4$. This compound was prepared by the above procedure using 70% ethylamine (2.1 ml) in place of methylamine. The yellow solid formed was recrystallized from hot water. Yield: ~10%. Anal. Calcd for $C_{22}H_{54}N_{12}$ $Ni_2Cl_4O_{16}$: C, 26.4; H, 5.39; N, 16.8%. Found: C, 26.6; H, 5.43; N, 16.4%.

$[Ni_2(3)](ClO_4)_4 \cdot H_2O$. This compound was prepared by a method similar to that for $[Ni_2(1)](ClO_4)_4$ except that 99% n-propylamine (2.1 ml) was used instead of methylamine. The yellow precipitates obtained were recrystallized from hot water-acetonitrile (4:1) mixture, Yield: ~10%. Anal. Calcd for $C_{24}H_{58}N_{12}$ $Ni_2Cl_4O_{17}$: C, 27.5; H, 5.73; N, 16.0%. Found: C, 27.1; H, 5.21; N, 16.1%.

$[Ni_2(4)](ClO_4)_4$. This complex was prepared by a meth-

od similar to that for $[Ni_2(1)](ClO_4)_4$ except that 99% *n*-butylamine (2.5 m*l*) was used instead of methylamine. Recrystallization of the product was performed by using an water-acetonitrile (3:1) mixture, Yield: ~10%. Anal. Calcd for $C_{26}H_{62}N_{12}Ni_2Cl_4O_{16}$: C, 29.5; H, 5.86; N, 15.8%. Found: C, 29.8; H, 5.57; N, 15.2%.

$[Ni_2(5)](ClO_4)_4$. This compound was prepared by a method similar to that for $[Ni_2(4)](ClO_4)_4$ except that 98% *iso*-butylamine (2.5 m*l*) was used instead of *n*-butylamine. Yield: ~8%. Anal. Calcd for $C_{26}H_{62}N_{12}Ni_2Cl_4O_{16}$: C, 29.5; H, 5.86; N, 15.8%. Found: C, 29.6; H, 5.50; N, 15.1%.

$[Ni_2(6)](ClO_4)_2$. This complex was prepared by a method similar to that for $[Ni_2(1)](ClO_4)_4$ except that 98% 2-ethylhexylamine (4.0 m*l*) was used instead of methylamine. Recrystallization of the yellow product was performed by using an water-acetonitrile (1:1) mixture, Yield: ~8%. Anal. Calcd for $C_{34}H_{78}N_{12}Ni_2Cl_4O_{16}$: C, 34.8; H, 6.66; N, 14.4%. Found: C, 33.9; H, 6.44; N, 14.5%.

$[Ni_2(L)](PF_6)_4$ (L=1, 2, 3, 4, 5, or 6). To a warm acetonitrile (10 m*l*) suspension of $[Ni_2(L)](ClO_4)_4$ (0.3 g) was added excess NH_4PF_6. Then the complex went into the solution and NH_4ClO_4 was precipitated. The solid was removed by filtration and water (20 m*l*) was added to the filtrate. The solution was kept in a refrigerator until yellow precipitates formed. The product was filtered, washed with a cold water-methanol (3:1) mixture, and air-dried.

$[Cu_2(1)](ClO_4)_4 \cdot H_2O$. To a methanol solution (30 m*l*) of $CuCl_2 \cdot 2H_2O$ (4.3 g) were slowly added 99% ethylenediamine (5.0 m*l*), 40% methylamine (2.2 m*l*), and paraformaldehyde (4.0 g). The resulting solution was heated at reflux for 30 h until a dark red-purple solution resulted. The solution was cooled to room temperature, and excess perchloric acid was added drowpwise to the solution with stirring. The mixture was kept in a refrigerator and then the pale red precipitates formed. The precipitates were filtered, washed with methanol, and recrystallized from hot water. Yield: ~10 %. Anal. Calcd for $C_{20}H_{52}N_{12}Cu_2Cl_4O_{17}$: C, 23.9; H, 5.23; N, 16.7%. Found: C, 23.6; H, 5.08; N, 16.6%.

$[Cu_2(2)](ClO_4)_4 \cdot 4H_2O$. This red complex was prepared by the above procedure using 70% ethylamine (2.1 m*l*) in place of methylamine. Yield: ~8%. Anal. Calcd for $C_{22}H_{62}N_{12}Cu_2Cl_4O_{20}$: C, 24.3; H, 5.72; N, 15.5%. Found: C, 24.4; H, 5.43; N, 15.3%.

$[Cu_2(3)](ClO_4)_4 \cdot 3H_2O$. This compound was prepared by a method similar to that for $[Cu_2(1)](ClO_4)_4 \cdot H_2O$ by using 99% *n*-propylamine (2.1 m*l*) instead of methylamine. The red complex was recrystallized from a hot water-acetonitrile (4:1) mixture. Yield: ~8%. Anal. Calcd for $C_{24}H_{72}N_{12}Cu_2Cl_4O_{19}$: C, 26.4; H, 5.71; N, 15.4%. Found: C, 26.5; H, 5.55; N, 14.5%.

$[Cu_2(4)](ClO_4)_4$. This complex was prepared by a method similar to that for $[Cu_2(1)](ClO_4)_4 \cdot H_2O$ except that 99% *n*-butylamine was used instead of methylamine. Recrystallization of the product was performed by using a water-acetonitrile (3:1) mixture. Yield: ~8%. Anal. Calcd for $C_{26}H_{62}N_{12}Cu_2Cl_4O_{16}$: C, 29.2; H, 5.85; N, 15.7%. Found: C, 29.6; H, 6.04; N, 15.8%.

$[Cu_2(5)](ClO_4)_4$. This complex was prepared by the above procedure using 99% *iso*-butylamine (2.5 m*l*) instead of n-butylamine. Yield: ~5%. Anal. Calcd for $C_{26}H_{62}N_{12}Cu_2Cl_4O_{16}$: C, 29.2; H, 5.85; N, 15.7%. Found: C, 29.9; H, 6.1; N, 15.3%.

$[Cu_2(6)](ClO_4)_4 \cdot 2H_2O$. This compound was prepared by a method similar to that for $[Cu_2(1)](ClO_4)_4 \cdot H_2O$ by using 98% 2-ethylhexylamine (4.1 m*l*) instead of methylamine. The red complex was recrystallized from a water-acetonitrile (1:1) mixture. Yield: ~5%. Anal. Calcd for $C_{34}H_{82}N_{12}Cu_2Cl_4O_{18}$: C, 33.5; H, 6.74; N, 13.8%. Found: C, 33.3; H, 6.66; N, 13.4%.

Results and Discussion

Synthesis. The yellow binuclear nickel(II) complexes $[Ni_2(L)](ClO_4)_4$ (L=1, 2, 3, 4, 5, or 6) were readly obtained by the reactions of excess formaldehyde with 2:5:2 molar mixtures of $NiCl_2 \cdot 6H_2O$, ethylenediamine, and appropriate alkylamines in methanol solutions, followed by addition of excess perchloric acid or lithium perchlorate. The red copper (II) complexes $[Cu_2(L)](ClO_4)_4$ were also prepared from the similar method using $CuCl_2 \cdot 2H_2O$ instead of $NiCl_2 \cdot 6H_2O$. It has been reported that the reactions of excess formaldehyde with 1:2:2 molar mixtures of the metal ion, ethylenediamine, and primary alkylamines produce the mononuclear complexes of 7-12.[18,19] Therefore, the reaction in this work are expected to give mixtures of the products $[M_2(L)]^{4+}$ and small amounts of the monouclear complexes as by-products. However, the binuclear complexes were readly isolated by fractional recrystallizations of the crude products. The isolation of the mononuclear complexes which formed in this work was not attempted. The synthetic routes for the binuclear complexes may be similar to those for the mononuclear complexes,[18] but the yields are much lower. The present synthetic procedure is quite interesting because it involves simultaneous formation and linking of two fully saturated hexaaza macrocyclic subunits. Moreover, this method for the preparation of the binuclear complexes of double-ring macrocyclic ligands requires the simple starting materials and experimental precedures.

Properties. All perchlorate salts of binuclear Ni(II) and Cu(II) complexes of 1-6 are soluble in MeCN and DMF, but insoluble in alcohols. In water, the complexes of 1-3 are soluble but those of 4-6 are rarely soluble. The solubility of the binuclear complexes of 1, 2, and 3 in water appeared to be some lower than that of the complexes of 7, 8, and 9, respectively. The binuclear complexes are very stable in solid states and in the solutions. The complexes were decomposed very slowly even in low pH, and the decomposition rates ($k_d \leq 10^{-5}$ sec^{-1}) measured in 0.3 M HNO_3 solutions are comparable to those reported for the complexes of 7-12.[18,19]

The infrared and electronic spectral data of the Ni(II) and Cu(II) complexes are listed in Tables 1 and 2 together with molar conductance data. The infrared spectra of the Ni(II) and Cu(II) complexes show a band near 3200 cm^{-1} assigned to the N-H stretch of the coordinated secondary amino groups. The broad band at about 1100 cm^{-1} due to ClO_4^- showed no remarkable splitting, indicating no coordination of the anion. The conductivity data for $[M_2(L)](ClO_4)_4$ (M =Ni(II) or Cu(II)) show that the complexes are 1:4 elecrtrolytes. The electronic absorption spectra of the binuclear Ni(II) complexes of 1-6 in nitromethane solutions show a d-d transition band at 433-446 nm (ϵ = 134-146 $M^{-1}cm^{-1}$) and those of the Cu(II) complexes in acetonitrile and

Table 1. Infrared and Electronic Spectral Data and Molar Conductance of Binuclear Ni(II) Complexes of Double-ring Macrocyclic Ligand

Complex	IR spectra ν_{N-H}, cm^{-1}	Electronic spectra[a] λ_{max}, nm(ϵ, M^{-1} cm^{-1})	Molar conductance[b] Λ_M, $ohm^{-1}mol^{-1}cm^2$
$[Ni_2(1)](ClO_4)_4$	3218	444 (135) 446 (69)[b] 443 (107)[c]	478
$[Ni_2(2)](ClO_4)_4$	3195	446 (134) 448 (78)[b] 442 (111)[c]	492
$[Ni_2(3)](ClO_4)_4$	3215	445 (134) 450 (81)[b] 443 (117)[c]	475
$[Ni_2(4)](ClO_4)_4$	3210	444 (131) 445 (78)[b]	484
$[Ni_2(5)](ClO_4)_4$	3210	445 (140) 451 (84)[b]	469
$[Ni_2(6)](ClO_4)_4$	3235	446 (137) 455 (85)[b]	483
$[Ni(8)](ClO_4)_2$[d]		449 (64) 461 (35)[b] 445 (47)[c]	
$[Ni(12)](ClO_4)_2$[d]		447 (79) 450 (46)[b]	

[a] In nitromethane solutions at 25℃ unless otherwise specified, [b] In acetonitrile solutions. [c] In aqueous solutions. [d] Ref. 19.

Table 2. Infrared and Electronic Spectral Data and Molar Conductance of Cu(II) Complexes

Complex	IR spectra ν_{N-H}, cm^{-1}	Electronic spectra λ_{max}, nm(ϵ, $M^{-1}cm^{-1}$)	Molar conductance Λ_M, $ohm^{-1}mol^{-1}cm^2$
$[Cu_2(1)](ClO_4)_4$	3240	507 (158)[a] 506 (147)[b]	459[b]
$[Cu_2(2)](ClO_4)_4$	3235	502 (134)[b]	485[b]
$[Cu_2(3)](ClO_4)_4$	3240	501 (165)[b]	470[b]
$[Cu_2(4)](ClO_4)_4$	3235	500 (157)[a]	465[a]
$[Cu_2(5)](ClO_4)_4$	3240	501 (152)[a]	460[a]
$[Cu_2(6)](ClO_4)_4$	3235	504 (186)[a]	495[a]
$[Cu(7)](ClO_4)_2$[c]		498 (76)[a] 500 (80)[b]	
$[Cu(10)](ClO_4)_2$[d]		497 (85)[a] 495 (83)[b]	
$[Cu(12)](ClO_4)_2$[d]		493 (90)[a]	

[a] In acetonitrile solutions at 25℃, [b] In aqueous solutions at 25℃, [c] Ref. 18. [d] Ref. 19.

aqueous solutions show the band near 500 nm (ϵ = 150-180 $M^{-1}cm^{-1}$). The wavelengths for the binuclear complexes are closely similar to those for the mononuclear complexes of 7-12 and are as can be expected for each metal ion in a square planar $M-N_4$ environment.[21,24-27] The molar extinction-coefficients of the binuclear complexes are nearly equal to twice of those for the mononuclear complexes. This strongly indicates that the two chromophores of the binuclear complexes in the present work behave independently.[16] The spectra also show that the ligand field strength of the binuclear complexes are not affected significantly by the introduction of the bridging group and the variation of the alkyl pendant arms at the uncoordinated nitrogen atoms.

The electronic spectra of the Ni(II) complexes(Table 1) show that the observed molar extinction coefficients in the coordinating solvents H_2O and MeCN are much lower than in nitromethane, a noncoordinating solvent. This indicates that the binuclear Ni(II) complexes dissolve in the coordinating solvents to give the equilibrium mixtures of yellow square planar $[Ni_2(L)]^{4+}$ and blue pseudo-octahedral $[Ni_2(L)(S)_4]^{4+}$ (S=coordinating solvent) species, in analogy with various macrocyclic Ni(II) complexes.[16,18,19,28-30] The values of molar extinction coefficients near 450 nm indicate that the proportion of the square planar form generally decreases with solvent in the order of H_2O>MeCN, which is quite similar to that observed for the mononuclear Ni(II) complexes of 7-10 and other 14-membered macrocyclic ligands.[18,19,28] The stronger ligation ability of acetonitrile, compared to water, is attributed to its rod-like geometry and relatively weak base character toward interaction with the protons of the coordinated secondary amino groups.[28] The proportion of the square planar from, ϵ MeCN/ ϵ $MeNO_2$,[18] in acetonitrile solutions increases in the order of 1(0.51)<2(0.58)<3(0.59)≦4(0.59)<5(0.60)<6(0.62), indicating that the equilibrium of the square planar-to-octahedral conversion is largely affected by the bulkness of the alkyl pendant arms.

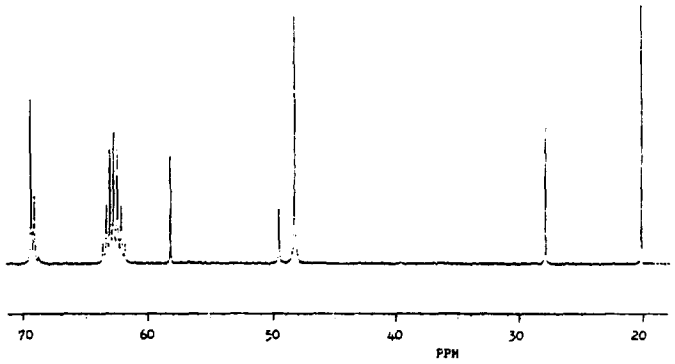


Figure 1. ^{13}C-NMR Spectrum of $[Ni_2(5)](PF_6)_4$ in CD_3NO_2. The extra peaks at 60-65 ppm due to the solvent.

^{13}C-NMR spectrum of $[Ni_2(5)](PF_6)_4$ measured in CD_3NO_2 is shown in Figure 1. The carbon peaks of N-C-C-N chains of the bridge, which linking the two macrocyclic subunits, and the macrocyclic backbone are observed at 49.5 ppm and

Table 3. ^{13}C-NMR Spectral Data of PF_6 Salts of the Nickel (II) Complexes in CD_3NO_2 Solutions

Complex	δ, ppm		
	N-C-C-N	N-C-N	R
$[Ni_2(1)]^{4+}$	46.6 47.7[a]	67.2 68.6	36.5
$[Ni_2(2)]^{4+}$	48.2 49.5[a]	68.2 68.5	13.2 45.1
$[Ni_2(3)]^{4+}$	48.3 49.5[a]	68.8 69.0	11.2 21.7 52.3
$[Ni_2(4)]^{4+}$	46.5 47.7[a]	67.1 67.2	12.3 19.0 29.0 49.5
$[Ni_2(5)]^{4+}$	48.2 49.5[a]	69.0 69.3	20.1 27.9 58.1
$[Ni_2(6)]^{4+}$	48.5 49.9[a]	69.2 69.5	10.7 14.5 24.2 24.4
			29.6 31.2 38.8 54.6
$[Ni(7)]^{2+}$[b]	48.6	70.0	38.3
$[Ni(11)]^{2+}$[c]	48.3	69.4	20.1 28.1 58.8

[a]Peaks of the bridging chain. [b]Ref. 18. [c]Ref. 19.

Table 4. Oxidation Potentials for the Binuclear Ni(II) and Cu(II) Complexes[a]

Complex	$M^2 \longrightarrow M^{3+}$ V *vs* SCE
Ni_2 (1)	+0.97
Ni_2 (2)	+0.99
Ni_2 (3)	+0.98
Ni_2 (4)	+0.98
Ni_2 (5)	+0.99
Ni_2 (6)	+0.97
Ni (7)[b]	+0.93
Ni (12)[c]	+0.95
Cu_2 (1)	+1.38
Cu_2 (2)	+1.32
Cu_2 (3)	+1.33
Cu_2 (4)	+1.36
Cu_2 (5)	+1.35
Cu_2 (6)	+1.35
Cu (7)[b]	+1.32
Cu (12)[c]	+1.33

[a]Measured in 0.1 M $(n\text{-Bu})_4NPF_6$ acetonitrile solutions at 20℃, [b]Ref. 18, [c]Ref. 19.

48.2 ppm, respectively. The peaks of N-C-N linkages are observed at 69.0 and 69.3 ppm. Three peaks at 20.1, 27.9, and 58.1 ppm are corresponding to the carbons of the pendant *iso*-butyl groups. The spectra of the other binuclear Ni(II) complexes are summarized in Table 3, which are also consistent with the corresponding ligand structures.

The oxidation potentials (Table 4) of the binuclear complexes of 1-6 have been obtained by cyclic voltammograms in acetonitrile solutions containing $(n\text{-Bu})_4NPF_6$ (0.1 M) as supporting electrolyte. The cyclic voltammogram showed no peak seperations and exhibited a two-electron wave corresponding to the $M^{2+} \rightarrow M^{3+}$ oxidation process. This indicates that the binuclear Ni(II) and Cu(II) complexes of the double-ring macrocyclic complexes are able to release two electrons nearly at the same potential.[16] The oxidation potentials for the Ni(II) and Cu(II) complexes are 0.97-0.99 V and 1.32-1.38 V *vs* SCE, respectively. The potentials are slightly higher than those for the complexes of 7-12,[18,19] but the difference is too small to discuss any significant metal-metal interactions of the binuclear complexes.

Results of elemental analyses together with the above chemical and spectral properties suggest that the new complexes, which prepared by the one-step template condensations of the simple amines with formaldehyde, are the binuclear complexes of the double-ring macrocyclic ligands 1-6. Present work shows that the simple metal template condensation of amines anf formaldehyde can be used for the preparation of double-ring macrocyclic complexes of the same class, in which the nature of the pendant arm and/or bridging chain can be varied. This work also shows that the properties of the double-ring macrocyclic complexes are very similar to those of their monomeric analogues. This strongly indicates that the metal-metal interactions of the binuclear complexes, in which the uncoordinated nitrogen atoms of two hexaaza macrocyclic units are linked together by an ethylene chain, are not significant.

References

1. J. P. Collman, C. S. Bencosme, R. R. Durand, R. P. Kreh, and F. C. Anson, *J. Am. Chem. Soc.*, **105**, 2699 (1983) and references therein.
2. L. P. Battaglia, A. Bianchi, A. C. Corradi, E. Gercia-Espana, M. Micheloni, and M. Julve, *Inorg. Chem.*, **27**, 4174 (1988) and references therein.
3. J. -P. Collin, A. Jouaity, and J. -P. Sauvage, *Inorg. Chem.*, **27**, 1986 (1988).
4. I. Murase, M. Mikuriya, H. Sonada, and S. Kida, *J. Chem. Soc. Chem. Commun.*, 692 (1984).
5. I. Murase, M. Mikuriya, S. Sonoda, Y. Hukuda, and S. Kida, *J. Chem. Soc. Dalton Trans.*, 953 (1986).
6. E. Asto, S. Hashimoto, N. Matsumoto, and S. Kida, *J. Chem. Soc. Dalton. Trans.*, 1741 (1990).
7. B. Szepogancz, R. J. Motekaitis, and A. E. Martell, *Inorg. Chem.*, **29**, 1467 (1990).
8. G. A. Lawrance, M. Maeder, T. M. Manning, M. A. O 'Leady, B. W. Skeilton, and A.H. White, *J. Chem. Soc. Dalton Trans.*, 2451 (1990).
9. J. Nelson, B. P. Murphy, M. G. B. Drew, P. C. Yates, and S. M. Nelson, *J. Chem. Soc. Dalton Trans.*, 100 (1988).
10. J. Comarmond, P. Kahn, and I. Morgenstein-Badarau, *J.*

Am. Chem. Soc., **104**, 6330 (1982).
11. M. Ciampolini, M. Micheloni, N. Nardi, F. Vizza, A. Buttafaba, L. Fabbrizzi, and A. Perotti, *J. Chem. Soc. Chem. Commun.*, 998 (1984).
12. K. Wieghardt, I. Talksdorf, and W. Herrmann, *Inorg. Chem.*, **24**, 1230 (1985).
13. I. Murase, K. Hamada, and S. Kida, *Inorg. Chim. Acta.*, **54**, 1174 (1981).
14. A. Buttafava, L. Fabbrizzi, A. Perotti, A. Poggi, and B. Seghi, *Inorg. Chem.*, **23**, 3917 (1984).
15. L. Fabbrizzi, F. Forlini, A. Perotti, and B. Seghi, *Inorg. Chem.*, **23**, 807 (1984).
16. L. Fabbrizzi, L. Montagna, A. Poggi, T. A. Kaden, and L. C. Siegfried, *J. Chem. Soc. Dalton Trans.*, 2631 (1987).
17. L. Fabbrizzi, L. Montagna, A. Poggi, T. A. Kaden, and L. C. Siegfried, *Inorg. Chem.*, **25**, 2671 (1986).
18. M. P. Suh, and S. -G. Kang, *Inorg. Chem.*, **27**, 2544 (1988).
19. S. -K. Jung, S. -G. Kang, and M. P. Suh, *Bull. Korean Chem. Soc.*, **10**, 362 (1989).
20. S. -G. Kang, S. -K. Jung, and J. K. Kweon, *Bull. Korean Chem. Soc.*, **11**, 431 (1990).
21. M. P. Suh, W. Shin, S. -G. Kang, M. S. Lah, and T. -M. Chung, *Inorg. Chem.*, **28**, 1602 (1989).
22. M. P. Suh, J. Choi, S. -G. Kang, and W. Shin, *Inorg. Chem.*, **28**, 1763 (1989).
23. M. P. Suh, S. -G. Kang, and T. -M. Chung, *Bull. Korean Chem. Soc.*, **11**, 206 (1990).
24. J. W. L. Martin, J. H. Timmons, A. E. Martell, and C. J. Wills, *Inorg. Chem.*, **19**, 2328 (1980).
25. N. F. Curtis, *J. Chem. Soc. Dalton Trans.*, 347 (1974).
26. R. W. Hay and D. P. Piplani, *J. Chem. Soc. Dalton Trans.*, 1956 (1977).
27. D. -T. Wu and C. -S. Chung, *Inorg. Chem.*, **25**, 3583 (1986).
28. E. Iwamoto, T. Yokoyama, S. Yamasaky, T. Yabo, T. Kumamaru, and Y. Yamamoto, *J. Chem. Soc. Dalton Trans.*, 1935 (1988) and references therein.
29. J. H. Cotes, D. A. Hadi, S. F. Linklon, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **20**, 707 (1981).
30. R. W. Hay, B. Jeragh, B. Kaitner, and B. L. Ruhl, *J. Chem. Soc. Dalton Trans.*, 1531 (1982).

Conformational Analysis of Cyclooctanone: Evidence from ^{13}C Nuclear Magnetic Resonance

Miewon Jung*

Department of Chemistry, Sungshin Women's University, Seoul 136-742. *Received January 14, 1991*

The "frozen-out" ^{13}C-NMR spectrum of cyclooctanone conformer was detected at -150℃ and is reported for the first time. The stable conformation of cyclooctanone deduced by ^{13}C-NMR measurements was a unsymmetrical boat-chair conformation.

Introduction

Among medium rings the cyclooctanone is challenging substrates for conformational studies since early attempts to elucidate the conformation of cyclooctanone were not so successful.[1] Most of the information has been obtained by X-ray diffraction studies of crystalline compounds, molecular mechanics calculations, NMR measurements, and additionally from determinations of IR spectra, and dipole moments. There are limitations for most methods, such as X-ray methods requiring appropriate crystals for conformational analysis. Spectra of medium ring compounds by IR measurements are too complex for analysis (thus earier attemps by IR spectra led to incorrect interpretations.)[2] The diplole moment measurments are largely limited to compounds which have at least two polar groups. Among these methods for analysis of conformation NMR is powerful tool although even it has limitations.

For the conformational analysis of cyclooctanone, Anet's group did an ^1H-NMR study of cyclooctanone at low temperature to freeze out a stable conformation. But they did not deduce stable conformation because of the complexity of the alkyl region in the ^1H-NMR spectrum.[3] They also reported the ^1H and ^{13}C-NMR spectra of the C_9-C_{16} cycloalkanones with changing temperature form -80℃ to -170℃, but they did not report a variable temperature ^{13}C-NMR study of cyclooctanone.[4] ^{13}C-NMR has been successfully utilized in the study of molecular conformation in solution when one deals with stable conformers or molecules where rapid interconversion occurs at ambient temperature.

^{13}C-NMR spectra are obtained in the present work at various temperature from 20℃ to -150℃ in order to find the chemical shifts at the temperature at which the dynamic process can be "frozen-out" on the NMR time scale and cyclooctanone can be observed as a stable conformation.

Experimental

Synthesis of Cyclooctanone-2,2,8,8,D_4. Cyclooctanone-2,2,8,8-D_4 was prepared from cyclooctanone (6.3 g, 0.05 mol) by heating it with D_2O (3.6 g, 0.18 mol) and NaOD (from 0.1 g Na) and freshly dried THF (5 m*l*) for 4 h.[5] The mixture was saturated with NaCl, the organic phase was seperated and the aqueous phase was combined, dried with