11. M. Chanon and M. L. Tobe, *Angew. Chem. Int. Ed. Engl.*, **21**, 1 (1982).
12. (a) H. Schechter and R. B. Kaplan, *J. Am. Chem. Soc.*, **75**, 3980 (1953); (b) N. Kornblum, H. Singh, and W. J. Kelly, *J. Org. Chem.*, **45**, 5294 (1980).
13. G. A. Russell, M. Jawdosiuk, and M. Makosza, *J. Am. Chem. Soc.*, **101**, 2355 (1979).

Synthesis of Nickel(II) and Copper(II) Complexes with Macrocyclic Ligand: 1,8-Diethyl-5, 12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4, 11-diene(L^3)

Yu Chul Park*, Seong Su Kim, and Jong Chul Byun†

Department of Chemistry, Kyungpook National University, Taegu 702-701
†*Department of Chemistry, Chechu National University, Chechu 690-756*

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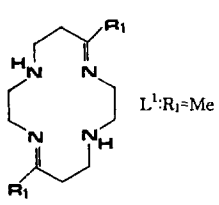
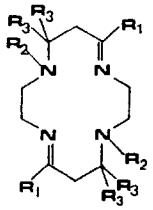
The reaction of the monohydroperchlorate salt of 1,2-diaminoethane with but-3-en-2-one in methanol solution gives the dihydroperchlorate salt of the macrocyclic ligand, 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^1)[1]. This synthesis is an extension of the procedure devised by Curtis[2] for the preparation of the macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. However, most macrocycles[3] obtained by Curtis method have no substitutes at the nitrogen atoms. Miyamura[4] first reported the N-methyl tetra-aza macrocycle (L^2) by the non-template reaction, but no further N-alkyl 14-tetra-aza diene macrocycles have been reported.

In this paper, we report the synthesis of the new macrocycle 1,8-diethyl-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4, 11-diene (L^3) by the non-template reaction of but-3-en-2-one with N-ethyl-1,2-diaminoethane hydroperchlorate salt and its Ni(II) and Cu(II) complexes.





We could not obtain the macrocycle (L^4) from the reaction of 4-methyl-3-penten-2-one with N-ethyl-1,2-diaminoethane. We suspect that it may be attributable to the effect of steric hindrance of the starting materials on the formation of the macrocycle (L^4). A new ligand (L^3) without having such a problem of streic hindrance might be readily obtained by reaction (Eq. 1) of but-3-en-2-one with N-ethyl-1,2-diaminoethane hydroperchlorate[5]. The ligand was, however, turned out to be unstable and decomposed within a few hours of its isolation at room temperature. Its instability was only managed to be prevented us from doing analytical, IR or NMR measurements. Thus, the analysis for the ligand was performed on its Ni(II) and Cu(II) complexes. The latters were prepared and isolated as their perchlorate salts according to Eq. 2 as shown[6];

$$2CH_3CH_2NHCH_2CH_2NH_2HClO_4 + 2CH_2CHCOCH_3 \longrightarrow L^3 \cdot 2HClO_4 \quad (1)$$

$$L^3 \cdot 2HClO_4 + M(II) \longrightarrow [ML^3](ClO_4)_2 \quad [M=Ni(II), Cu(II)] \quad (2)$$

The reaction of the ligand with **Cu(II)** salt gives to the reddish purple complex, **$[CuL^3](ClO_4)_2$**. The infrared spectra (Table 1) shows the presence of the characteristic vibrations for **C=N** bond at $\nu_{C=N}$ (1663 cm^{-1}) and perchlorate bands (1107 and 625 cm^{-1}). But no absorption of **N-H** vibration around 3200 cm^{-1} is shown. The electronic spectra of this complex shows a single d-d band at λ_{max}=532 nm with a molar extinction coefficient of 207. The position of this band and the value compare quite well with those reported by other copper(II) tetra-aza macrocyclic complexes[2]. Also the ligand forms the yellow complex with **Ni**, **$[NiL^3](ClO_4)_2$**. Its infrared spectrum also shows the bands expected for the characteristic vibrations of **C=N** bond at $\nu_{C=N}$ (1650 cm^{-1}) and perchlorate bands (1092 and 624 cm^{-1}) (Table 1). This complex **$[NiL^3](ClO_4)_2$** shows a strong band in aqueous solution at λ_{max}=455 nm (ε=134 $dm^3mol^{-1}cm^{-1}$) typical of singlet ground-state **Ni(II)**[7]. There is little tendency to add water

Table 1. Spectral Data of Ni(II) and Cu(II) Complexes of L^3

Compound	IR spectra, cm^{-1}		d-d band[a]	Reference
	ν(C=N)	$\nu(ClO_4)$	λ_{max}, (ε)[b]	
$[NiL^2](ClO_4)_2$	1650		448(111)	4
$[NiL^3](ClO_4)_2$	1650	1092, 624	455(134)	this work
$[CuL^2](ClO_4)_2$	1650		526(179)	4
$[CuL^3](ClO_4)_2$	1663	1107, 625	532(207)	this work

[a] In H_2O solutions at 25℃. [b] nm ($dm^3mol^{-1}cm^{-1}$)

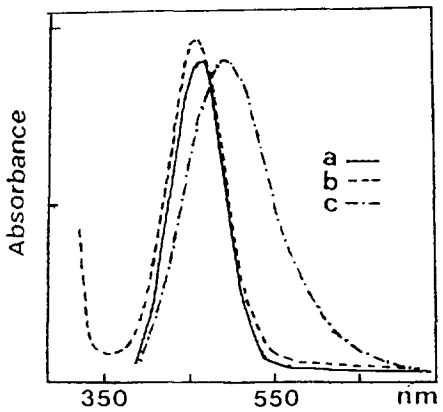


Figure 1. Visible absorption spectra of (a) $[NiL^3]^{2+}$ in CH_3NO_2, (b) $[NiL^3]^{2+}$ in CH_3CN, and (c) $[CuL^3]^{2+}$ in CH_3NO_2 at 25℃. [Notice the absence of the characteristic octahedral Ni(II) band of around 350 nm in CH_3CN solution.]

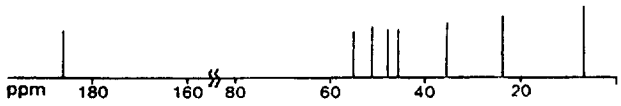


Figure 2. The ^{13}C NMR spectrum of $[NiL^3](ClO_4)_2$ in Me_2SO-d_6 solution with solvent peaks omitted.

or CH_3CN ligands in the axial position to give octahedral species (see Figure 1) as is frequently observed with macrocyclic tetra-aza nickel(II) complexes. The reason might be due to the steric crowding of the axial sites increased by N-ethyl groups on two nitrogen atoms. The electronic spectra of Ni(II) and Cu(II) complexes of L^3 show the 6-7 nm shift of λ_{max} longer wavelengths than those of L^2, indicating that N-ethyl complexes weaken the ligand field strength of complex further than N-methyl complexes do[8]. Two nitrogen atoms with R_2(ethyl group) in L^3 tend to form sp^2 rather than sp^3 hybridization as suggested by the X-ray data of the Ni-N bonds length in similar complexes[9]. The ^1H NMR spectrum[10] of $[NiL^3](ClO_4)_2$ in Me_2SO-d_6 solution shows a sharp singlet at $\delta=2.08$ ppm which is assigned to the imine methyl groups. The methyl triplet and methene quartet of N-ethyl occur at $\delta=1.15$ and $\delta=2.74$ ppms, respectively. The three peaks mentioned just before as well as other ones do not show any broadening, indicating that this complex maintains the square-planar geometry and is diamagnetic even in coordinating solvent of Me_2SO[11].

The ^{13}C NMR spectrum of $[NiL^3](ClO_4)_2$ is shown to be 8 resonances rather than 16 ones, indicating that the ligand contains eight pairs of nonequivalent carbon atoms (Figure 2). This observation supports the symmetric arrangements of this complex. Namely, there is the possibility of two stereoisomers, *i.e.*, one N-meso form and the other racemic form[12]. We are currently doing X-ray analysis in order to tell in which form the complex exists. In conclusion, we have synthesized N-ethyl 14-tetra-aza diene (L^3) by the non-template reaction and its Ni(II) and Cu(II) complexes.

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References

1. R. W. Hay and G. A. Lawrence, *J. Chem. Soc., Dalton,* 1466 (1975).
2. N. F. Curtis, *J. Chem. Soc.,* 2644 (1964).
3. (a) R. Bembi, T. G. Roy, and A. K. Jhanji, *Inorg. Chem.,* **27**, 496 (1988); (b) R. W. Hay, M. A. Ali, and B. Jeragh, *J. Chem. Soc., Dalton Trans.,* 2763 (1988); (c) R. A. Kolinski and B. K. Daszkiewicz, *Inorg. Chim. Acta,* **14**, 237 (1975).
4. K. Miyamura, M. Kohzuki, R. Narushima, M. Saburi, and Yohichi, *J. Chem. Soc., Dalton Trans.,* 3093 (1987).
5. **$L^3 \cdot 2HClO_4$**: Aqueous $HClO_4$ (70%, 0.1 mol) was added dropwise to ice-salt cooled solution of N-ethyl-1,2-diaminoethane (0.1 mol) in 60 m*l* methanol. After completion of the addition, but-3-en-2-one (0.1 mol) in 12 m*l* methanol was added drop by drop in ice bath. The mixture was then stirred for 2 hr in the ice bath. The white precipitate was filtered, and washed with methanol and diethyl ether (Yield 20%). The product was not stable, and then was used *in situ* for the following reaction without further purification.
6. **$[ML^3](ClO_4)_2$**: M(II) acetate and **$L^3 \cdot 2HClO_4$** were dispersed in methanol. The suspension was heated under reflux with stirring for *ca.* 2 hr and then cooled to room temperature. The precipitate was filtered, washed with methanol and diethyl ether, and recrystallized from 90% methanol. Elemental analysis. Calcd for **$C_{16}H_{32}N_4Ni(ClO_4)_2$**: C, 35.8; H, 6.0; N, 10.4%. Found: C, 35.3; H, 6.1; N, 10.2%. Yield: 65%; ^{13}C NMR (δ Me_2SO-d_6): 6.87, 22.86, 36.40, 46.02, 47.74, 51.44, 54.20, 184.75 Calcd for **$C_{16}H_{32}N_4Cu(ClO_4)_2 \cdot 1.5H_2O$**: C, 33.7; H, 6.2: N, 9.8%. Found: C, 33.9; H, 6.2; N, 9.6%; Yield 50%.
7. G. Maki, *J. Phys. Chem.,* **28**, 615 (1958); **29**, 62 (1959).
8. N. Jubran, G. Ginzburg, H. Cohen, and Y. Koresh, *Inorg. Chem.,* **24**, 251 (1985).
9. E. K. Barefield, G. M. Freeman, and D. G. van Derveer, *Inorg. Chem.,* **25**, 552 (1986).
10. The ^1H and ^{13}C NMR spectra were recorded on Bruker FT NMR (400 MHz) with Me_2SO-d_6 as solvent.
11. R. W. Hay, D. P. Piplani, and B. Jeragh, *J. Chem. Soc., Dalton,* 1951 (1977).
12. G. H. Searle, R. W. Hay, and B. Jeragh, *Aust. J. Chem.,* **33**, 1447 (1980).

α-Methylenelactam Synthesis *via* Radical Cyclization of Propiolamide

Eun Lee and Tae Seop Kang

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-742

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Lactam synthesis *via* cyclization of radicals generated from N-substituted haloacetamides is now well documented. Typically, N-allyl and N-propargyl haloacetamides undergo cyclization under various radical-generating conditions to afford γ-lactams.[1] Synthesis of β-lactams from N-vinyl haloacetamides was also reported.[2] These reactions proceed *via* (aminocarbonyl)methyl radical intermediates. In view of the results we obtained in the synthesis of α-methylenelactones and α-methylencycloalkanones from propiolates and acetylenic ketones[3] *via* (α-alkoxycabonyl-β-stannyl)vinyl and (α-carbonyl-β-stannyl)vinyl radicals, N-substituted propiolamides appeared to be proper substrates in the synthesis of α-methylenelactams. We now report that *t*-butyl-substituted N-allyl propiolamides indeed serve well as precursors in radical cyclizations *via* (α-aminocarbonyl-β-stannyl)vinyl radicals formed by the addition of stannyl radicals to the propiolamide triple bonds.

N-*t*-Butyl propiolamide was prepared from propiolyl chloride[4] and *t*-butylamine and it was reacted with various allylic bromides under basic conditions (KOH/DMSO)[5] to form substrates **1a-g**. Radical cyclization of these substrates was