Characterization and X-ray Crystal Structure of 5,9-Dihydro-2,4,10,12-tetramethyl-1,5,9,13-monobenzotetraazacyclotetradecine

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The tetraaza[14]annulene rings have been attracted much attention for their utilities as model compounds in biological system when coordinated to transition metal centered.[1-4] The most attentions have been given to the 14-membered symmetrical 5,14-dihydrodibenzotetraazacyclotetradecine ligands and their tetrasubstituted symmetric derivatives.[5,6] Crystal structures for these macrocycle ligands and their metal complexes have been reported.[7-11] Previously, we reported the spectral and electrochemical properties of a series of asymmetrical tetraaza[14 or 15]annulene nickel(II) complexes.[12,13] But the asymmetrical tetraaza[15]annulene as free ligand has not been characterized and its structure also not analyzed until now.

In this paper, we attempted to synthesize a new ligand monobenzotetraazacyclo[15]tetradecine from the reaction of asymmetrical monobenzotetraazacyclo[15]tetradecinato(2-)-nickel(II) complex with anhydrous hydrochloric acid gas in ethanol. We studied spectral and electrochemical properties of the new free ligand by means of infrared, UV-visible, mass, ^{1}H-nmr and ^{13}C-nmr spectra, and cyclic voltammograms. The crystal structure of the ligand, 5,9-dihydro-2,4,10,12-tetramethyl-1,5,9,13-monobenzotetraazacyclo[15]tetradecine, was identified by X-ray diffraction analysis.

Experimental Section

Materials. $Ni(OAc)_2 \cdot 4H_2O$, 1,2-phenylenediamine, 1,3-diaminopropane, NaCN and 2,4-pentandione were purchased from Aldrich and Fluka. The solvents such as CH_3OH, CH_3CH_2OH, CH_2Cl_2 were refluxed over calcium hydride under nitrogen, and checked for their purities by GC just before use. Dimethylsulfoxide (DMSO) was purchased from Merck and used without purification further. Tetraethylammonium perchlorate (TEAP) used as supporting electrolyte was prepared and purified by using the processes described in the literature.[14]

Measurements. Elemental analysis of free ligand prepared was carried out on a Carlo-Ebra, EA 1108 instrument. Infrared spectra were recorded on a Matteson Instruments, Inc. Galaxy 7020 A using KBr Pellets. ^{1}H-NMR and ^{13}C-NMR (300 MHz) spectra were recorded on a Brucker instrument at room temperature and chemical shifts in $CDCl_3$ were given in ppm relative to tetramethylsilane as internal reference. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer. EI mass spectra were determined with a JEOL MS-DX 300 gas chromatograph mass spectrometer at 70 eV using a direct inlet system.

Cyclic voltammetry was performed using a Bioanalytical System (BAS) CV-50W electrochemical analyzer and C2 cell stand at room temperature. The three-electrode system composed of the glassy carbon electrode as a working electrode, and Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TEAP-DMSO solutions) as a reference electrode, and a platinum wire as an auxiliary electrode for the electrochemical measurement was used.

Synthesis: 5,9-Dihydro-2,4,10,12-tetramethyl-1,5,9,13-monobenzotetraazacyclo[15]tetradecine. The ligand was prepared by modifying the method of L'Eplattenier and Pugin.[15] A mixture of asymmetrical monobenzotetraaza[15]-annulene nickel(II) complex (5.52 g, 0.015 mol) prepared by the method described in the literatures[16,17] was dissolved in absolute ethanol (50 cm^3) and was treated excess anhydrous hydrochloric acid until the blue colored ligand salt precipitates. The reaction mixture was continually stirred at room temperature for 18 h. The solid was filtered, dissolved in water (300 cm^3) and neutralized by adding solid sodium cyanide under fume hood. The bright yellow precipitate was recovered, washed with water, and then dried in *vacuo*. The red single crystal was obtained by recrystallizing from a mixture of dichloromethane and methyl alcohol. Yield 0.93 g (20%). Anal. Calcd. (%) for $C_{19}H_{26}N_4$: C, 73.51; H, 8.44; N, 18.05; Found: C, 73.50; H, 8.40; N, 18.05. IR (KBr disc, cm^{-1}): ν (C=C), 1552; ν (C=N), 1574; ν (C_6H_6), 723. UV-vis: λ_{max} (nm) and ε_{max} ($M^{-1}\,cm^{-1}$) in $CHCl_3$ 316 and 37000. ^{1}H NMR ($CDCl_3$): 1.868, 1.934 (s) (methyl); 4.613 (s) (methine); 2.152 (s), 3.415 (t) (propylene); 6.812-6.965 (m) (aromatic); 11.220 (br) (N-*H*). ^{13}C NMR ($CDCl_3$): 19.721, 20.573 (s) (methyl); 95.378 (s) (methine); 157.291, 162.421 (s) (C-N & C=N); 30.474, 45.841 (s) (propylene); 121.512, 122.370, 141.253 (s) (aromatic). EIMS: m/z 310 $[M]^+$.

X-ray crystallographic analysis. Preliminary examination and data collection for crystal of asymmetrical tetraaza-cyclo[15]annulene ligand were performed with Mo-Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4

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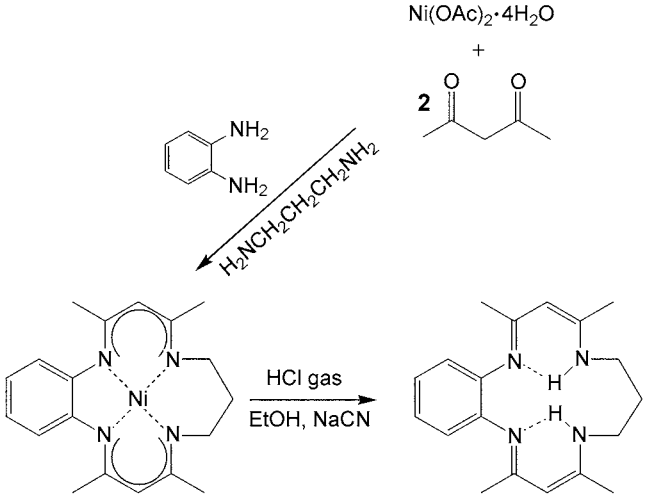
computer controlled *k*-axis diffractometer equipped with a graphite crystal, incident-beam monochromator. Cell constants and orientation matrices for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The data were collected for Lorentz-polarization and absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-86[18] and refined by full-matrix least-squares calculations with SHELX-97.[19] Hydrogen atoms were included in calculated positions, except for those involving hydrogen bonding specifically for the hydrogen atoms bonded to the nitrogen atoms, which were refined with isotropic thermal parameters.

The crystallographic data for the free ligand; $C_{19}H_{26}N_4$ *FW* = 310.44, monoclinic, space group $P2_1/c$, a = 11.7526(13) Å, b = 9.3961(10) Å, c = 16.7167(18) Å, β = 107.130(2)°, V = 1764.1(3) Å^3, Z = 4, D_c = 1.169 Mg/m^3, μ(Mo Kα) = 0.071 mm^{-1}, crystal dimensions 0.53 × 0.20 × 0.05 mm, 10714 reflections collected, 4243 independent reflections, $R_1[I > 2\sigma(I)]$ = 0.0437, $wR_2[I > 2\sigma(I)]$ = 0.0984. The selected bond distances and angles were presented in Table 1.

Results and Discussion

The free ligand was prepared according to the processes illustrated in Scheme 1. Purification of the crude product was achieved by recrystallizing from mixtures of dichloromethane and methyl alcohol. Elemental analysis and mass spectrum given in the Experimental section were consistent with those for the formula of asymmetrical monobenzotetraazacyclo[15]tetradecine synthesized.

The UV-visible spectrum of free ligand exhibited only one peak in the near UV region at 316 nm (ε_{max} = 37000 M^{-1} cm^{-1}) due to $\pi \rightarrow \pi^*$ transition, while that of its nickel(II) complex showed a band of ligand at 379 nm (ε_{max} = 22800 M^{-1} cm^{-1}).[12] The stretching modes of the C=C and C=N bonds for the compound appeared at 1552 and 1574 cm^{-1}, respectively. The ^{1}H-NMR peaks of methyl and methine protons were shifted to upfield around 0.2 ppm compared to the nickel(II) complex with monobenzotetraazacyclo[15]-tetradecine. The amine proton peak was shown at 11.220 ppm, which did not find in the nickel(II) complex.



Scheme 1

The cyclic voltammograms of the free ligand and its nickel complex in 0.1 M TEAP-DMSO solutions *vs* Ag/Ag$^+$ (0.01 M) at 25 °C and scan rates of 100 mV s^{-1} were shown in Figure 1. The free ligand had one electron, two appreciably irreversible waves corresponding to oxidation of macrocycle (Mc), Mc $\rightarrow$ Mc$^{\cdot+}$ and Mc$^{\cdot+}$ $\rightarrow$ Mc^{2+} at +169 mV and +569 mV, respectively. The oxidation potentials of the free ligand were shifted to less positive values relative to those of its metal complex as shown in Figure 1. The observation might be attributed to a change of electron density on the macrocycle ring. Such discussion is supported by similar observations for nickel(II) and palladium(II) complexes with other asymmetrical tetraazaannulenes.[20,21]

The molecular structure of 5,9-dihydro-2,4,10,12-tetramethyl-1,5,9,13-monobenzotetraazacyclo[15]tetradecine was illustrated in Figure 2. As shown in Figure 2(a), the free ligand geometry of a saddle-shaped conformation was tilted to opposite sides of the plane defined by four nitrogen atoms, being sterically more stable structure. The free ligand showed two N–H $\cdots$N hydrogen bonds in the central part of the molecule, in which the hydrogens were geometrically connected with not *trans* but *cis* form (two nitrogens of propylene group) to each other in the tetraaza plane. The two H-atoms (H(3n) and H(4n)) might be weakly participated in interactions with both the N(1) and N(2) atoms, respectively. The N(3)-H(3n) and N(4)-H(4n) distances (0.94 and 0.90 Å), respectively, were about 0.35 Å shorter than those of

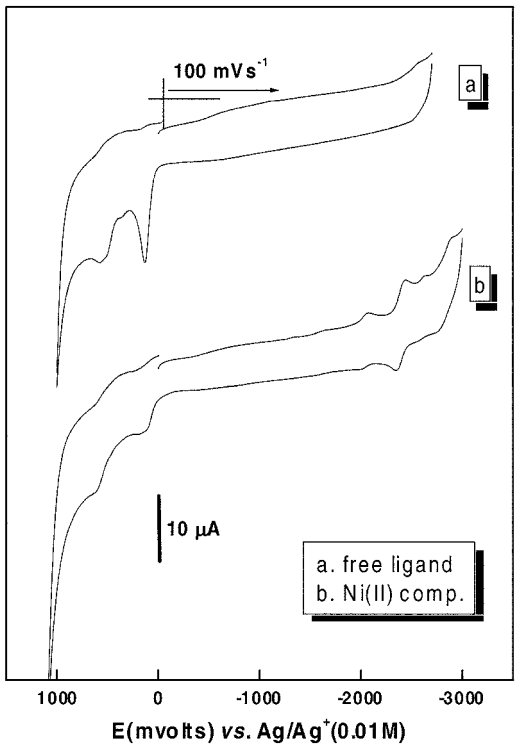


Figure 1. Cyclovoltammograms of free ligand and its nickel complex.

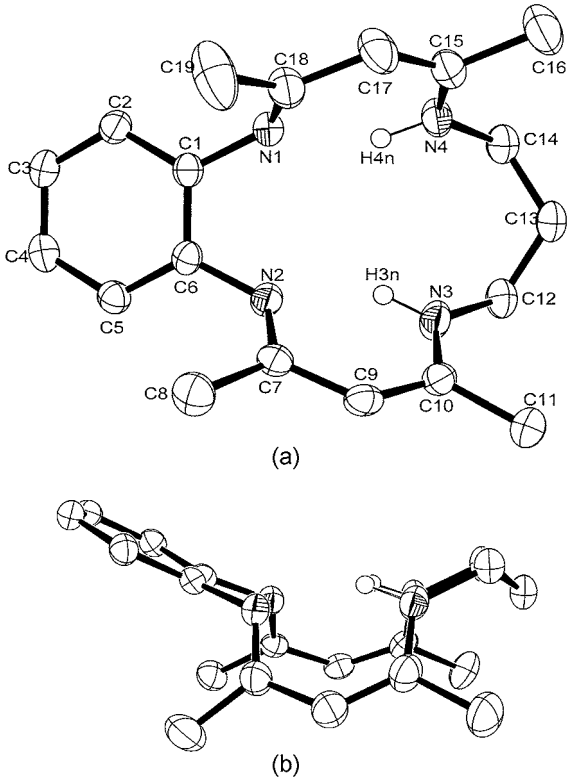


Figure 2. The molecular structure (a) and its side view (b) of free ligand.

Table 1. Selected bond distances [Å] and angles [°] for free ligand

N(1)-C(1)	1.4084(19)	N(3)-C(10)	1.340(2)
N(1)-C(18)	1.286(2)	N(3)-C(12)	1.454(2)
N(2)-C(7)	1.2987(19)	N(4)-C(15)	1.345(2)
N(2)-C(6)	1.4077(19)	N(4)-C(14)	1.452(2)
C(1)-C(6)	1.410(2)	C(13)-C(14)	1.531(3)
C(7)-C(9)	1.429(2)	C(15)-C(17)	1.370(2)
C(9)-C(10)	1.376(2)	C(17)-C(18)	1.443(2)
C(12)-C(13)	1.529(3)		
C(1)-N(1)-C(18)	123.48(13)	C(10)-N(3)-C(12)	127.21(15)
C(6)-N(2)-C(7)	123.28(13)	C(14)-N(4)-C(15)	126.09(15)

symmetrical tetraaza[14]annulene.[7,11] The position of hydrogen atoms could be attributed to different basicities between propylenediamine and phenylenediamine.[22] The imino C=N bond lengths (N(1)-C(18) 1.286 Å and N(2)-C(7) 1.2987 Å) were about 0.05 Å shorter than the amino C-N type (N(3)-C(10) 1.340 Å and N(4)-C(15) 1.345 Å). The average value (about 123.38°) of C-N-C bond angles of imino types typically was smaller than that (126.65°) of amino groups, reflecting more sp^2 character.

Supplementary material. Crystallographic data for the structural analysis have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 222452. Copies of this information can be obtained free of charge *via* E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk; Tel: +44-1233-336031; Fax: +44-1223-336033.

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