

Synthesis and Characterization of Nickel(II) and Copper(II) Complexes with Non-symmetric Tetraaza[14]annulene Derivatives. X-ray Crystal Structure of Copper(II) Complex

D. I. KIM¹, E. H. KIM¹, Z. U. BAE¹, H. G. NA², J. H. CHOI^{3*} and Y. C. PARK^{1*}

¹Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea; ²Department of Chemistry, Daejin University, Pochon 487-800, Korea; ³Department of Chemistry, Andong National University, Andong 760-749, Korea

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Abstract

The complexes 13,14-([X]benzo)-3-(*p*-[Y]benzoyl)-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraenato(2-)-nickel(II), wherein Y = CH₃, H, Cl, NO₂ or OCH₃, X = CH₃ or Cl, have been synthesized and characterized. IR spectra of the benzoylated complexes show intense bands in the regions 1641–1654 cm⁻¹ attributable to the stretching modes of C=O. Hammett plots of the 1/λ_{max} of π → π* have positive slopes of 0.251 for **A** series (X = CH₃) and 0.233 for **B** series (X = Cl), respectively, which are quite similar to those based on the NMR resonances of methine protons. The cyclic voltammograms of the complexes show two one-electron irreversible oxidation processes in the potential range of +0.1 to +0.8 V and two, three or four reduction peaks between -1.2 and -2.8 V depending on the substituents. Hammett plots of first and second oxidation potentials are linear with the positive slopes (0.039 and 0.057 V for **A** series, 0.036 and 0.047 V for **B** series). The structure of the copper(II) complex (orthorhombic, C222₁, *a* = 8.0994(11), *b* = 8.3187(10), *c* = 24.561(5) Å, α(=β=γ) = 90.0°, *Z* = 4, *R*₁ = 0.0474 and *wR*₂ = 0.1219) was characterized using single crystal X-ray diffraction method.

Introduction

The reactivity of tetraaza[14]annulene derived complexes with various reagents can be employed to introduce a number of substituents into the macrocyclic ligand [1]. The prepared complexes have been treated as models of biologically significant macrocyclic systems such as heme proteins, chlorophylls and metalloenzymes [2, 3]. Thus, the two methine sites of nickel(II) complexes with tetraaza[14]annulene have been found to be reactive nucleophilic centers [1]. There are some examples for the electrophilic substitution reaction (*p*-substituted benzoyl chloride, acetyl chloride, glutaryl chloride, etc.) of the symmetrical tetraaza[14]annulene nickel(II) complexes [4, 5].

Previously [6–8] we reported a series of asymmetrical tetraaza[14]annulene nickel(II) complexes and investigated the effect of various substituents (CH₃, H, Cl and NO₂) on macrocycle ring and on dibenzoyl group pended at methine sites. In this article, we report the synthesis of new asymmetrical 14-π tetraazaannulene nickel(II) complexes bearing one substituted benzene group (X = CH₃ and Cl) in macrocycle and *p*-substituted benzoyl group (Y = OCH₃, CH₃, H, Cl and NO₂)

at methine site by using the modified method described in the literature [7–9]. We studied the substituent effect on benzoyl group using UV–Visible, IR, ¹H NMR and EI mass spectra. The redox potentials of the synthesized new nickel(II) complexes are measured using glassy carbon electrodes. These new complexes may be helpful to understand the catalytic activities of asymmetrical tetraaza[14]annulenes. As it is not easy to prepare an asymmetrical free-based ligand in comparison to a symmetrical free-based ligand we synthesized asymmetrical 14-π tetraaza[14]annulene copper(II) complex by demetallating the nickel(II) complex **3** and report the crystal structure of free ligand **L** recognized by X-ray diffraction analysis.

Experimental

Materials and measurements

Ni(OAc)₂·4H₂O, (1,2-[X]phenylenediamine (X = CH₃ and Cl), *p*-[Y]benzoyl chloride (Y = CH₃, H, Cl, NO₂ and OCH₃), Cu(OAc)₂·H₂O, 1,2-diaminoethane, 2,4-pentanedione, triethylamine were purchased from Aldrich. Solvents CH₃CN, CH₂Cl₂, etc. were refluxed over calcium hydride under nitrogen, and checked for

* Authors for correspondence. E-mail: ychpark@bh.knu.ac.kr

their purities by GC just before use. Dimethylsulfoxide (DMSO) was purchased from Merck and used without further purification. Tetraethylammonium perchlorate (TEAP) used as a supporting electrolyte was prepared and purified by the method described by Kolthoff and Coetzee [10]. Elemental analyses of the complexes prepared were carried out on a Carlo-Erba, EA 1108 instrument. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer in CHCl_3 . Infrared spectra were recorded on a Galaxy 7020 A (Mattson Instruments, Inc.) using KBr pellets. $^1\text{H-NMR}$ (300 MHz) spectra were recorded with a Bruker instrument in CDCl_3 with tetramethylsilane (TMS) as an internal reference. 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 at room temperature using a Bioanalytical System (BAS) CV-50W electrochemical analyzer and a C2 cell stand. A three electrode system for the electrochemical measurements composed of a glassy carbon electrode as a working electrode, Ag/Ag^+ (0.01 M AgNO_3 in 0.1 M TEAP–DMSO solution) as a reference electrode, and a platinum wire as an auxiliary electrode were used.

Synthesis

13,14-([Methyl]benzo)-3-(p-[Y]benzoyl)-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraenato(2-)-nickel(II): $Y = \text{CH}_3$ (A_1), H (A_2), Cl (A_3), NO_2 (A_4), OCH_3 (A_5)

Complex **1** (0.001 mol), prepared according to [7, 8], was dissolved in benzene (60 cm^3) containing triethylamine (0.001 mol) and *p*-[Y]benzoyl chloride (0.001 mol). The mixture was refluxed for 5 h with stirring and bubbling dry nitrogen gas. In all the synthesis the reaction mixtures were left to stand at room temperature for 18 h and filtered to remove triethylamine hydrochloride. The filtrates were evaporated to dryness and the resulting solids were chromatographed onto activated aluminum oxide and eluted with chloroform. The dark red products were obtained by recrystallizing from dichloromethane:methyl alcohol (1:3). For $\text{C}_{27}\text{H}_{30}\text{N}_4\text{O-Ni}$ (A_1): Yield 33%. Anal. Calcd. (%): C, 66.83; H, 6.23; N, 11.55. Found: C, 66.83; H, 6.52; N, 11.57. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1550; $\nu(\text{C}=\text{N})$, 1631; $\nu(\text{aromatic})$, 760 and 840; $\nu(\text{C}=\text{O})$, 1641. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) in chloroform 376 and 28,500, and 510 and 3550. EIMS: m/z 484 $[\text{M}]^+$. For $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O-Ni}$ (A_2): Yield 35%. Anal. Calcd. (%): C, 66.29; H, 5.99; N, 11.89. Found: C, 66.18; H, 6.09; N, 11.67. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1549; $\nu(\text{C}=\text{N})$, 1631; $\nu(\text{aromatic})$, 723 and 805; $\nu(\text{C}=\text{O})$, 1641. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) 376 and 26,250, and 504 and 3950. EIMS: m/z 470 $[\text{M}]^+$. For $\text{C}_{26}\text{H}_{27}\text{N}_4\text{OCINi}$ (A_3): Yield 35%. Anal. Calcd. (%): C, 61.75; H, 5.38; N, 11.08. Found: C, 61.62; H, 5.50; N, 10.83. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1548; $\nu(\text{C}=\text{N})$, 1630; $\nu(\text{aromatic})$, 765 and 847; $\nu(\text{C}=\text{O})$, 1641. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$)

375 and 28,000, and 502 and 4150. EIMS: m/z 504 $[\text{M}]^+$. For $\text{C}_{26}\text{H}_{27}\text{N}_5\text{O}_3\text{Ni}$ (A_4): Yield 40%. Anal. Calcd. (%): C, 60.49; H, 5.27; N, 13.57. Found: C, 60.56; H, 5.34; N, 13.78. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1550; $\nu(\text{C}=\text{N})$, 1630; $\nu(\text{aromatic})$, 725 and 849; $\nu(\text{C}=\text{O})$, 1641; $\nu(\text{NO}_2)$, 1345. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) 373 and 26,500, and 518 and 5250. EIMS: m/z 515 $[\text{M}]^+$. For $\text{C}_{27}\text{H}_{30}\text{N}_4\text{O}_2\text{Ni}$ (A_5): Yield 37%. Anal. Calcd. (%): C, 64.69; H, 6.03; N, 11.18. Found: C, 64.59; H, 6.27; N, 11.14. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1550; $\nu(\text{C}=\text{N})$, 1631; $\nu(\text{aromatic})$, 773 and 847; $\nu(\text{C}=\text{O})$, 1641. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) 377 and 26,000, and 522 and 3250. EIMS: m/z 500 $[\text{M}]^+$.

13,14-([Chloro]benzo)-3-(p-[Y]benzoyl)-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraenato(2-)-nickel(II): $Y = \text{CH}_3$ (B_1), H (B_2), Cl (B_3), NO_2 (B_4), OCH_3 (B_5)

The complexes **B** series were prepared from a mixture of complex **2** (0.001 mol) prepared by the method reported in the literature [7, 8], triethylamine and *p*-[Y]benzoyl chloride according to the procedure described above. The dark red products were obtained by recrystallization from dichloromethane and methyl alcohol 1:3 mixture. For $\text{C}_{26}\text{H}_{27}\text{N}_4\text{OCINi}$ (B_1): Yield 50%. Anal. Calcd. (%): C, 61.75; H, 5.38; N, 11.07. Found: C, 62.06; H, 5.49; N, 11.21. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1560; $\nu(\text{C}=\text{N})$, 1603; $\nu(\text{aromatic})$, 756 and 840; $\nu(\text{C}=\text{O})$, 1644. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) 379 and 29,000, and 516 and 3700. EIMS: m/z 504 $[\text{M}]^+$. For $\text{C}_{25}\text{H}_{25}\text{N}_4\text{OCINi}$ (B_2): Yield 52%. Anal. Calcd. (%): C, 61.07; H, 5.13; N, 11.40. Found: C, 60.85; H, 5.23; N, 11.66. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1558; $\nu(\text{C}=\text{N})$, 1637; $\nu(\text{aromatic})$, 726 and 808; $\nu(\text{C}=\text{O})$, 1646. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) 377 and 31,500, and 514 and 5500. EIMS: m/z 490 $[\text{M}]^+$. For $\text{C}_{25}\text{H}_{24}\text{N}_4\text{OCl}_2\text{Ni}$ (B_3): Yield 58%. Anal. Calcd. (%): C, 57.08; H, 4.60; N, 10.65. Found: C, 57.11; H, 4.87; N, 10.58. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1584; $\nu(\text{C}=\text{N})$, 1640; $\nu(\text{aromatic})$, 761 and 848; $\nu(\text{C}=\text{O})$, 1654. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) 377 and 33,200, and 501 and 4240. EIMS: m/z 525 $[\text{M}]^+$. For $\text{C}_{25}\text{H}_{24}\text{N}_5\text{O}_3\text{ClNi}$ (B_4): Yield 60%. Anal. Calcd. (%): C, 55.95; H, 4.51; N, 13.05. Found: C, 55.65; H, 4.66; N, 12.99. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1545; $\nu(\text{C}=\text{N})$, 1621; $\nu(\text{aromatic})$, 728 and 851; $\nu(\text{C}=\text{O})$, 1640; $\nu(\text{NO}_2)$, 1349. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) 375 and 33,800, and 512 and 5550. EIMS: m/z 535 $[\text{M}]^+$. For $\text{C}_{26}\text{H}_{27}\text{N}_4\text{O}_2\text{ClNi}$ (B_5): Yield 50%. Anal. Calcd. (%): C, 57.56; H, 5.23; N, 10.74. Found: C, 57.79; H, 5.33; N, 10.45. IR (cm^{-1}): $\nu(\text{C}=\text{C})$, 1562; $\nu(\text{C}=\text{N})$, 1597; $\nu(\text{aromatic})$, 766 and 847; $\nu(\text{C}=\text{O})$, 1643. UV–vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) 378 and 33,400, and 517 and 3610. EIMS: m/z 520 $[\text{M}]^+$.

13,14-Benzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene (L)

Complex **3** [7, 8] (0.015 mol) was dissolved in absolute ethanol (50 cm^3) and treated with an excess of gaseous HCl until the blue-colored hydrochloride precipitated.

The reaction mixture was further stirred at room temperature for 15 h. To the solid was collected, dissolved in water (300 cm³) and sodium cyanide (0.2 mol) was added (under efficient hood). The yellow precipitate was recovered, washed with water, and dried *in vacuo*. For C₁₈H₂₄N₄: Yield 25%. Anal. Calcd. (%): C, 72.94; H, 8.16; N, 18.90. Found: C, 72.78; H, 8.22; N, 18.93. IR (cm⁻¹): ν(C=C), 1502; ν(C=N), 1562; ν(C₆H₆), 746. UV-vis: λ_{max} (nm) and ε_{max} (M⁻¹ cm⁻¹) 322 and 36,000. ¹H-NMR (CDCl₃): 1.972, 2.101(s) (methyl); 4.757(s) (methine); 3.443(s) (ethylene); 6.945(m) (aromatic); 11.873 (br) (N-H). EIMS: *m/z* 296 [M]⁺.

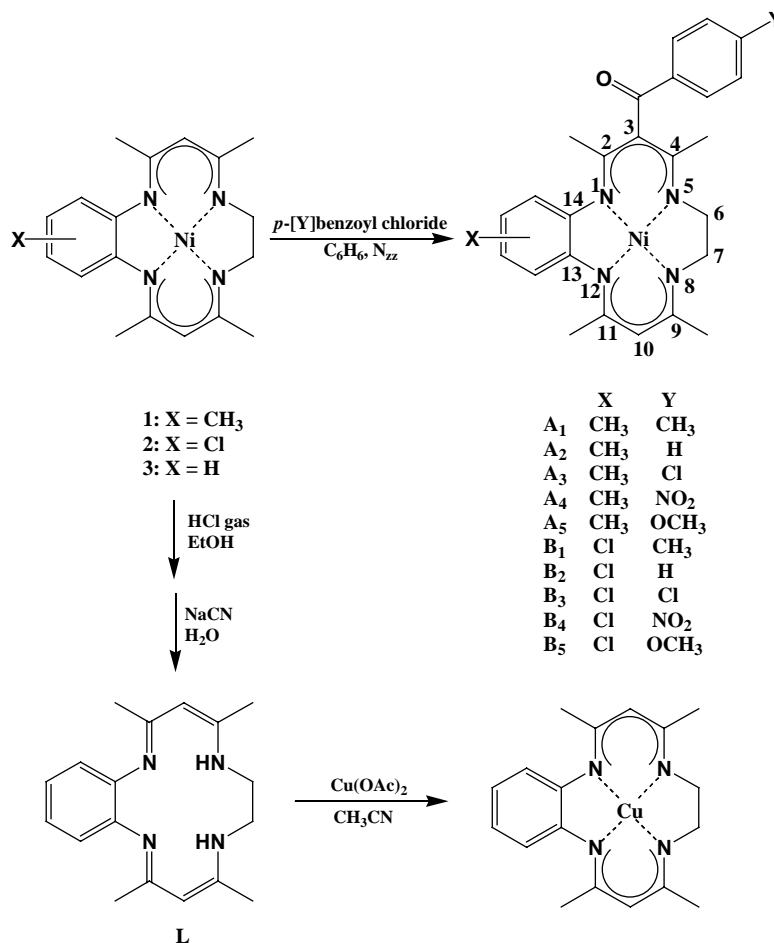
13,14-Benzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraenato(2-)copper(II)

Cu(OAc)₂·H₂O (0.001 mol) and free ligand (L) (0.001 mol) were dissolved in acetonitrile (80 cm³). The mixture was heated under reflux for 2 h with stirring and bubbling dry nitrogen gas. The reaction mixture was left to stand in refrigerator for 12 h. The solid was filtered and washed with acetonitrile. The product was chromatographed on aluminum oxide using chloroform as an eluent. The green eluate was collected, evaporated *in vacuo* and dried. The powder has green color. A dark

blue crystal was obtained by recrystallization from dichloromethane:methyl alcohol (1:1). For C₁₈H₂₂CuN₄: Yield 47%. Anal. Calcd. (%): C, 60.40; H, 6.20; N, 15.65. Found: C, 60.38; H, 6.20; N, 15.60. IR (cm⁻¹): ν(C=C), 1522; ν(C=N), 1563; ν(aromatic), 745. UV-vis: λ_{max} (nm) and ε_{max} (M⁻¹ cm⁻¹) 360 and 26,900, 606 and 850. EIMS: *m/z* 357 [M]⁺.

X-ray crystallographic analysis

Preliminary examination and data collection for crystal of Cu(II) complex were performed with MoK_α radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer controlled κ-axis diffractometer equipped with a graphite crystal as 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 and Lorentz-polarization and absorption corrections were applied to the data. The structure was solved by direct methods using SHELXS-97 [11] and refined by full-matrix least-squares calculations with SHELXL-97 [12]. The final cycle of the refinement converged with R = 0.047 and wR = 0.1219.



Scheme 1

Table 1. ¹H-NMR data for asymmetrical nickel(II) complexes, **A** and **B** series^a

Compd	Methyl	Methine	Ethylene	X (methyl)	Y	Aromatic (macrocycle)	Aromatic (benzoyl)
A ₁	2.275(s), 1.859(s), 2.414(s), 2.081(s)	5.057(s)	3.322(t), 3.507(t)	2.275(s)	2.414(s) (methyl)	6.507–6.992(m)	7.219(d), 7.792(d)
A ₂	2.297(s), 1.852(s), 2.413(s), 2.079(s)	5.057(s)	3.322(t), 3.508(t)	2.273(s)		6.509–6.989(m)	7.404–7.976(m)
A ₃	2.297(s), 1.839(s), 2.410(s), 2.080(s)	5.058(s)	3.319(t), 3.515(t)	2.275(s)		6.515–6.987(m)	7.387(d), 7.809(d)
A ₄	2.361(s), 1.818(s), 2.409(s), 2.083(s)	5.067(s)	3.325(t), 3.544(t)	2.280(s)		6.531–6.983(m)	7.968(d), 8.254(d)
A ₅	2.270(s), 1.872(s), 2.415(s), 2.080(s)	5.057(s)	3.347(t), 3.503(t)	2.270(s)	3.873(s) (methoxy)	6.506–6.993(m)	6.870(d), 7.880(d)
B ₁	2.249(s), 1.879(s), 2.437(s), 2.096(s)	5.103(s)	3.341(t), 3.519(t)		2.416(s) (methyl)	6.646–6.968(m)	7.149(d), 7.793(d)
B ₂	2.257(s), 1.873(s), 2.404(s), 2.096(s)	5.103(s)	3.342(t), 3.529(t)			6.650–7.156(m)	7.439–7.907(m)
B ₃	2.258(s), 1.859(s), 2.401(s), 2.095(s)	5.104(s)	3.358(t), 3.538(t)			6.663–7.153(m)	7.399(d), 7.813(d)
B ₄	2.319(s), 1.836(s), 2.400(s), 2.099(s)	5.112(s)	3.345(t), 3.554(t)			6.669–7.151(m)	7.977(d), 8.265(d)
B ₅	2.232(s), 1.892(s), 2.405(s), 2.096(s)	5.102(s)	3.344(t), 3.518(t)		3.876(s) (methoxy)	6.674–6.955(m)	7.150(d), 7.881(d)

^a Chemical shifts in ppm from TMS internal reference measured in CDCl₃ at 300 MHz; multiplicity of a proton signal is given in parentheses after δ -value; s = singlet, d = doublet, t = triplet, m = multiplet.

Results and discussion

The asymmetrical nickel(II) complexes (series **A** and **B**), and a free ligand **L** and its copper(II) complex were prepared by procedures shown in Scheme 1. The condensation reaction of complex **1** (or **2**) and *p*-[**Y**]benzoyl chloride in a 1:1 molar ratio in the presence of triethylamine was performed in refluxing benzene. Purifications of the crude products were achieved by column chromatography on activated aluminum oxide and recrystallized from dichloromethane and methyl alcohol 1:3 mixture. The products obtained as pure compounds or mixtures of isomers were characterized by elemental analyses, EI mass, IR and electronic spectra (see Experimental part), ¹H NMR (Table 1) and electrochemical methods (Table 2). Although the studied products are mixtures of isomers no splitting of the signals was observed.

IR and electronic spectra

IR spectra of all new complexes exhibited very intense bands in the regions 1640–1654 cm⁻¹ attributable to the stretching modes of C=O reflecting benzoylation at methine site, which are supported by similar observations for nickel(II) complex of dibenzoylated tetraaza[14]annulene [9]. The aromatic bands had two characteristic modes at around 750 (macrocycle) and 850 cm⁻¹ (benzoyl group). The NO₂ of benzoyl group exhibited a strong band at around 1345 cm⁻¹. The bands

Table 2. Redox potential data for asymmetrical nickel(II) complexes^a

Comp.	<i>E</i> _{p(1)} (mV)	<i>E</i> _{p(2)} (mV)	<i>E</i> _n (mV)
A ₁	+150	+690	-2350, -2650
A ₂	+150	+700	-2280, -2660
A ₃	+160	+710	-2090, -2290, -2680
A ₄	+180	+740	-1770, -1230, -2720
A ₅	+140	+680	-2420, -2660
B ₁	+230	+730	-2330, -2690
B ₂	+240	+740	-2250, -2670
B ₃	+250	+750	-2070, -2250, -2640, -2800
B ₄	+270	+770	-1220, -1740, -2570, -2700,
B ₅	+230	+720	-2390, -2700

^a All data are measured in 0.1 M TEAP-DMSO solutions vs Ag/Ag⁺ (0.01 M AgNO₃ in DMSO) at 25 °C.

for C=C and C=N are at around 1560 and 1630 cm⁻¹, respectively, for all complexes.

The electronic absorption spectra of the new complexes showed intense bands between 370 and 530 nm. The bands in the near UV region (370–400 nm) with molar absorptivities of 26,000–34,000 M⁻¹cm⁻¹ could be attributed to $\pi \rightarrow \pi^*$ transitions. Spectra in the visible region showed bands at 498–526 nm ($\epsilon_{\text{max}} = 3000\text{--}6000 \text{ M}^{-1} \text{ cm}^{-1}$) attributed to ligand–metal charge transfer (LMCT) from the highest occupied ligand molecular orbital to the lowest empty *d*-orbital of nickel. The maximum wavelengths (λ_{max}) and molar absorptivities

are similar to those of dibenzoylated nickel(II) complexes [9]. The $1/\lambda_{\max}$ ($\pi \rightarrow \pi^*$) of **A** series was linearly and positively dependent on the electron-withdrawing residue (Y) [13] of the benzoyl group. The slopes of $1/\lambda_{\max}$ plots against σ_p for **A** and **B** series are 0.251 and 0.233, respectively. The substituent (X) effects of [X]benzo macrocycles for dibenzotetraaza[14]annulene complexes ($\rho = -0.72$) [14] and dibenzoylated monobenzotetraaza[14]annulene complexes ($\rho = -0.83$) [9] are negatively linear. From such results found for asymmetrical benzoylated monobenzotetraaza[14]annulenes complexes it could be deduced that the energies of $\pi \rightarrow \pi^*$ transition are correlated with inductive effects of the substituents on benzoyl group in the order: $\text{NO}_2 > \text{Cl} > \text{H} > \text{CH}_3 > \text{OCH}_3$.

¹H-NMR spectra and Hammett plot

¹H-NMR chemical shifts and their assignments are listed in Table 1. The assignments were accomplished based on comparisons with those for complexes reported earlier [8, 15, 16]. The proton peaks of the 2- and 4-methyl groups are shifted upfield (0.1–0.3 ppm) compared to those of 9- and 11-methyl groups. This reflects the shielding effect caused by the magnetic anisotropy of the benzoyl group at methine site distorted out of the plane of macrocycle. Due to the same effect the ethylene protons are revealed as two triplets. Opposite to the benzoyl group the methine proton peak is a little affected by substituents on benzoyl group [13, 14]. Substituent effects on the resonances of methine protons for these complexes were also examined by means of a Hammett plot. As shown in Figure 1, the relationships between $\Delta\rho$ ($\delta_Y - \delta_H$; δ_Y = chemical shifts of substituent) and σ_p are linear with almost the same slope of 0.010 for **A** and **B** series.

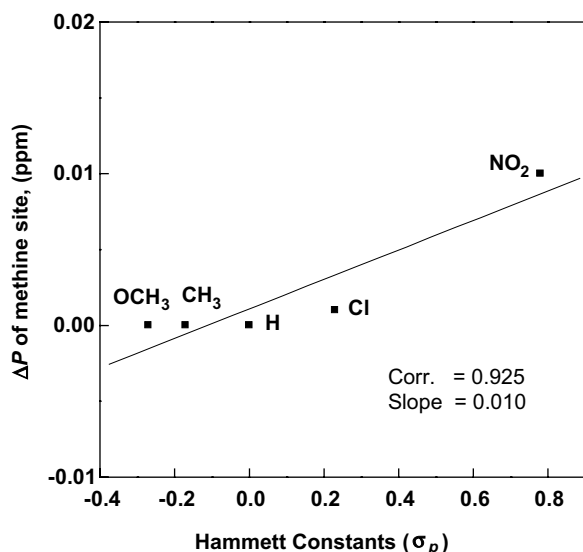


Figure 1. Correlation between differences of chemical shifts (ΔP) and Hammett constants (σ_p) for the **A** series. ΔP (ppm) = $\delta_Y - \delta_H$; δ_Y = chemical shifts of substituent.

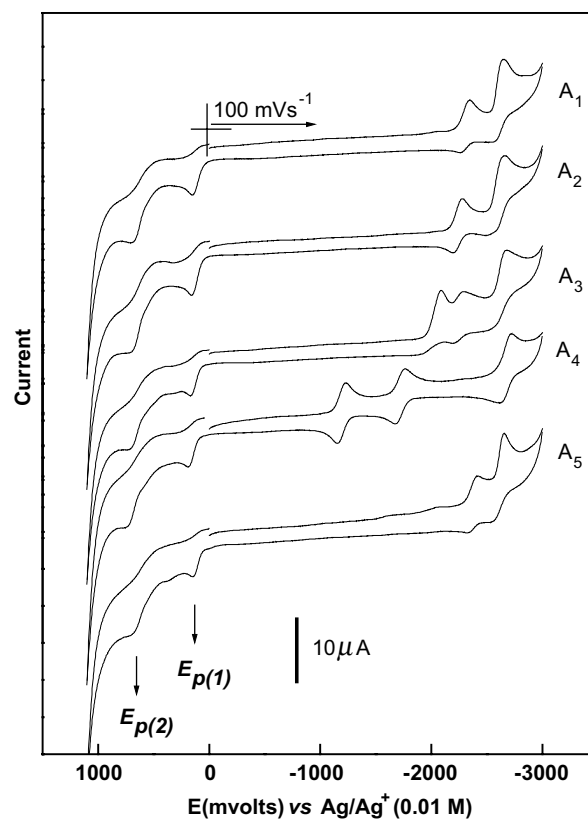


Figure 2. Cyclic voltammograms of **A** series (0.001 M) in 0.1 M TEAP-DMSO solutions vs Ag/Ag^+ (0.01 M) at 25°C and scan rate of 100 mV s^{-1} .

Electrochemical behaviors and Hammett plot

The redox potentials of nickel(II) complexes measured in 0.1 M TEAP-DMSO solutions versus Ag/Ag^+ (0.01 M) at 25°C and at sweep rate of 100 mV s^{-1} are collected in Table 2. Typical voltammograms in the potential range from +1.1 to -3.0 V versus Ag/Ag^+ are shown in Figure 2. The cyclic voltammograms of the complexes **A** (or **B**) series show two irreversible oxidation processes in the potential range of +0.1 to +0.8 V and two to four reduction peaks in the range of -1.2 to -2.8 V . The reduction peaks for the complexes must be associated with the benzoyl group and its substituents [17–19]. The asymmetrical tetraaza[14]annulene nickel(II) complexes without benzoyl group show one reversible reduction peak at around -2.6 V due to metal ion [9]. Thus the first-, second- or third-reduction peaks could be attributed to tetraaza[14]annulene.

The relationships between E_p (V) and σ_p are linear with positive slopes of 0.039 and 0.057 V for the first and the second oxidation peaks of **A** series, respectively (Figure 3). The corresponding slopes for the complexes **B** series are 0.036 and 0.047 V. These slopes are similar to the oxidation potentials for metalloporphyrins with β substituents located on the pyrrole residues of the porphyrin ligand [20, 21]. However, the electronic effect of substituent on the reduction wave due to the metal-

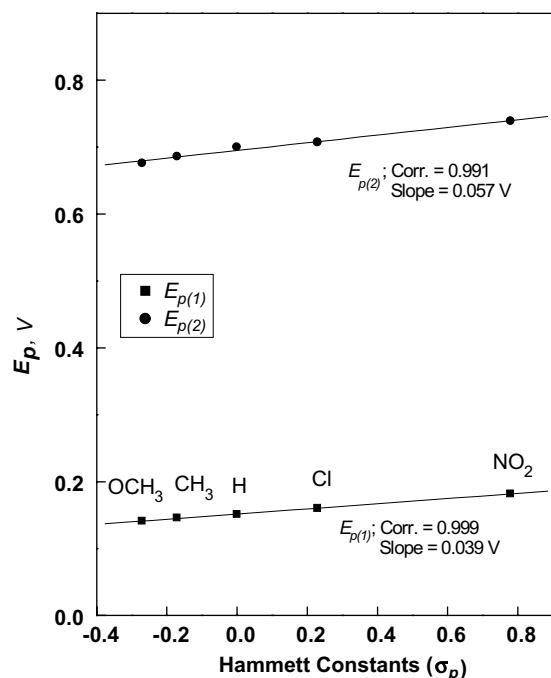


Figure 3. Hammett plots of first and second oxidation potentials vs Ag/Ag^+ (0.01 M) in 0.1 M TEAP–DMSO as function of substituent constants for A complexes (0.001 M) at 25°C and scan rate of 100 mV s^{-1} .

based ($\text{Ni}^{2+} \rightarrow \text{Ni}^{1+}$) at around -2.7 V could not be definitely found.

Crystal structure of copper(II) complex

The molecular structure of copper(II) complex with 13,14-benzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraene (**L**) is shown in Figure 4.

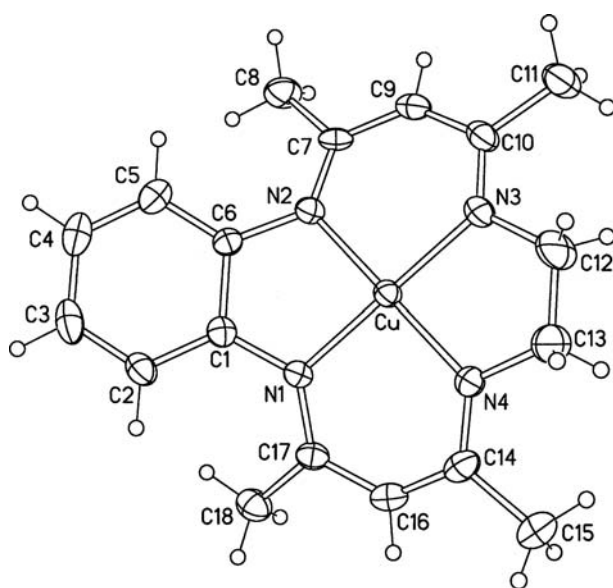


Figure 4. The ORTEP drawing of 13,14-benzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraenato(2-)-copper(II) complex.

Table 3. Crystal data and structure refinement for copper(II) complex

Empirical formula	$\text{C}_{18}\text{H}_{22}\text{CuN}_4$
Formula weight	357.94
Temperature	293(2) K
Wavelength	0.71073 \AA
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimension	$a = 8.0994(11) \text{ \AA}$ $\alpha = 90^\circ$ $b = 8.3187(10) \text{ \AA}$ $\beta = 90^\circ$ $c = 24.561(5) \text{ \AA}$ $\gamma = 90^\circ$
Volume	$1654.9(4) \text{ \AA}^3$
Z, calculated density	4, 1.437 mg/m^3
Absorption coefficient	1.324 mm^{-1}
$F(000)$	748
Crystal size	$0.43 \times 0.41 \times 0.18 \text{ mm}$
Theta range for data collection	$2.59\text{--}26.49^\circ$
Limiting indices	$-1 \leq h \leq 10$, $-1 \leq k \leq 10$, $-30 \leq l \leq 1$
Reflections collected/unique	2383/2201 [$R(\text{int}) = 0.0723$]
Completeness to theta = 26.49	89.1%
Absorption correction	Empirical
Max. and min. transmission	0.3182 and 0.2123
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2201/0/209
Goodness-of-fit on F^2	1.086
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0474$, $wR_2 = 0.1219$
R indices (all data)	$R_1 = 0.0499$, $wR_2 = 0.1292$
Absolute structure parameter	$-0.01(3)$
Extinction coefficient	$0.0047(19)$
Largest diff. peak and	0.564 and $-1.179 \text{ e \AA}^{-3}$

Crystal data and refinement parameters are listed in Table 3. The selected bond distances and angles are presented in Table 4. The average for four Cu–N distances is 1.917 \AA , which is longer than the corresponding Ni–N distances of 1.870 \AA for symmetrical nickel(II) complex [22]. This difference might be due to

Table 4. The selected bond lengths [Å] and angles [$^\circ$] for copper(II) complex

Cu–N1	1.921(4)	Cu–N2	1.918(3)
Cu–N3	1.917(4)	Cu–N4	1.911(4)
N1–C1	1.402(6)	N3–C10	1.309(7)
N1–C17	1.355(6)	N3–C12	1.453(7)
N2–C6	1.412(6)	N4–C13	1.462(8)
N2–C7	1.346(5)	N4–C14	1.330(8)
C1–C6	1.428(6)	C9–C10	1.427(7)
C7–C8	1.528(6)	C10–C11	1.491(8)
C7–C9	1.368(7)	C12–C13	1.391(10)
N1–Cu–N3	179.65(19)	N2–Cu–N4	178.40(18)
N1–Cu–N2	85.12(15)	N2–Cu–N3	94.84(17)
N3–Cu–N4	85.30(15)	N1–Cu–N4	94.75(17)
Cu–N2–C7	122.1(3)	Cu–N3–C10	124.9(3)
Cu–N2–C6	111.5(3)	Cu–N3–C12	112.1(4)
N2–C6–C1	113.6(4)	N2–C6–C5	127.6(4)
C7–N2–C6	125.9(4)	C10–N3–C12	122.1(5)
N2–C7–C9	122.8(4)	N3–C10–C9	121.2(4)
C7–C9–C10	128.7(4)	N3–C12–C13	114.7(6)

larger ionic radius of copper than nickel. Also, the distances of N(2)—C(6), N(2)—C(7), N(3)—C(10) and N(3)—C(12) are 1.412, 1.346, 1.309 and 1.453 Å, respectively. The coordination environment around the central copper(II) atom is square planar, in which four Cu—N bonds are similar to those in symmetrical Cu(II) complex [23]. The average distance of C—C in the six-membered chelate rings is 1.398 Å that is similar to those of benzene (1.40 Å), reflecting some aromaticity. The average of N—Cu—N angles of five and six membered ring is 85.21° and 94.80°, respectively. The angles of N(1)—Cu—N(3) and N(2)—Cu—N(4) are 179.65° and 178.40°, respectively. These results show that the copper and the four nitrogen atoms are in almost the same plane. The distortion from planarity might be due to steric interactions of β -substituents (two methyl groups) with phenyl ring.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. On request, copies of these data can be obtained free of charge via E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>, quoting the deposition number CCDC 222446 Tel.: +44-1233-336031; Fax: +44-1223-336033.

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