

## Synthesis and Structure of 3,10-Di(*p*-chlorobenzoyl)-4,9-dimethyl-2,11-diphenyl-1,5,8,12-monobenzotetraazacyclo[14]annulenenickel(II)

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Tetraazacyclo[14]annulene complexes have been interested due to usefulness as model compounds for largely the interaction between substrates and metal centers in biological systems such as hemoproteins and metalloenzymes.<sup>1-6</sup> The reactions of tetraazacyclo[14]annulenenickel(II) complexes with electrophiles such as perfluorobenzoyl, azobenzene and benzoyl groups are also studied.<sup>7-12</sup> The aim of introducing these substituents to the macrocycle compounds is to prepare new compounds with additional active functional groups.<sup>8</sup> In previous papers, we reported several crystal structures and electroproperties of asymmetrical tetraazacyclo[14]annulenenickel(II) complexes, their catalytic activities for the oxidation of styrene derivatives, substituent effects on the reaction of the complexes with benzoyl chloride derivatives, and synthesis of free ligands such as tetraazacyclo[14]tetradecines by demetallation.<sup>13-17</sup>

In this study, we report the synthesis and characterization of new asymmetrical tetraazacyclo[14]annulenenickel(II) complexes, **1** and **2** (Scheme 1) and the structural characteristics of the complex **2** using X-ray diffraction analysis.

### Experimental Section

**Materials and measurements.** Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, 1,2-phenylenediamine, 1,2-diaminoethane, 1-benzoylacetone, *p*-chlorobenzoylchloride and triethylamine were purchased from Aldrich and Fluka. The solvents such as *n*-butanol, *n*-

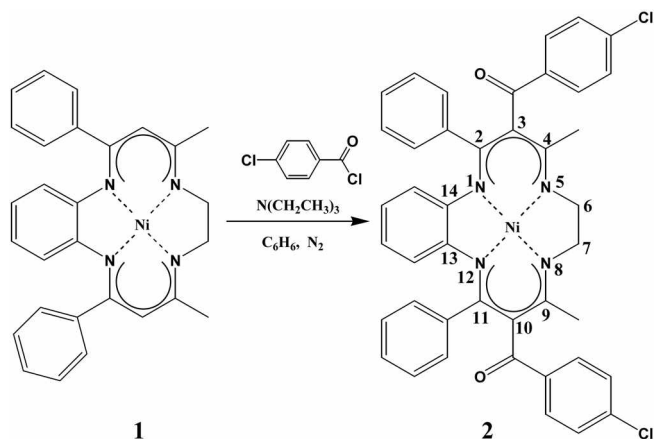
hexane, benzene and CH<sub>2</sub>Cl<sub>2</sub> were refluxed over calcium hydride under nitrogen, and checked for purities by GC just before use.

Elemental analyses (C, H, N) of the compounds prepared were carried out on a Carlo-Ebra, EA 1108 instrument. Infrared spectra were recorded on a Matteson Instruments, Inc. Galaxy 7020 A using KBr disc. <sup>1</sup>H-NMR (400 MHz) spectra were recorded on a AVANCE digital 400 Bruker instrument at room temperature and chemical shifts in CDCl<sub>3</sub> were given in ppm relative to tetramethylsilane as internal reference. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer.

#### Synthesis.

**4,9-Dimethyl-2,11-diphenyl-1,5,8,12-monobenzotetraazacyclo[14]annulenenickel(II) (1):** Under a nitrogen atmosphere, 1,2-phenylenediamine (2.16 g, 0.02 mol) and ethylenediamine (1.2 g, 0.02 mol) was added to *n*-butanol (100 mL) solution of nickel(II) acetate tetrahydrate (5.0 g, 0.02 mol). To the hot (100 °C) mixture were added 0.04 mol of 1-benzoylacetone. The solution was refluxed until precipitation of the product. After cooling at room temperature, the solution was filtered, washed with *n*-butanol, and air-dried. The product was recrystallized from dichloromethane and *n*-hexane (1 : 2) mixture to obtain dark red crystal. Yield; 40%. Found: C, 70.69; H, 5.30; N, 11.52%. Calc. For C<sub>28</sub>H<sub>22</sub>N<sub>4</sub>Ni: C, 70.59; H, 5.46; N, 11.76%. IR (KBr disc, cm<sup>-1</sup>): ν(C=C), 1518; ν(C=N), 1559; ν(aromatic),<sup>13,16</sup> 747 and 783. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 2.17 (s, methyl, 6H), 3.49 (s, ethylene, 4H), 5.23 (s, methine, 2H), 6.08-6.12 (m, aromatic on 13 and 14, 4H), 7.31-7.38 (m, aromatic on 2 and 11, 10H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, δ): 20.930 (methyl), 53.185 (ethylene), 105.869 (methine), 156.267, 159.116 (diiminate), 128.639, 140.953, 145.071 (aromatic on 13 and 14), 118.437, 120.959, 128.215, 128.464 (aromatic on 2 and 11).

**3,10-Di(*p*-chlorobenzoyl)-4,9-dimethyl-2,11-diphenyl-1,5,8,12-monobenzotetraazacyclo[14]annulenenickel(II) (2):** The complex **1** (0.477 g, 0.001 mol) was dissolved in benzene (50 cm<sup>3</sup>) containing triethylamine (0.202 g, 0.002 mol) and added the corresponding *p*-chlorobenzoyl chloride (0.350 g, 0.002 mol) in benzene (30 cm<sup>3</sup>) using dropping funnel. The mixture was heated under reflux for 24 h with stirring and bubbling nitrogen gas for protecting from moisture. The reaction mixture was standing for 24 h at



Scheme 1

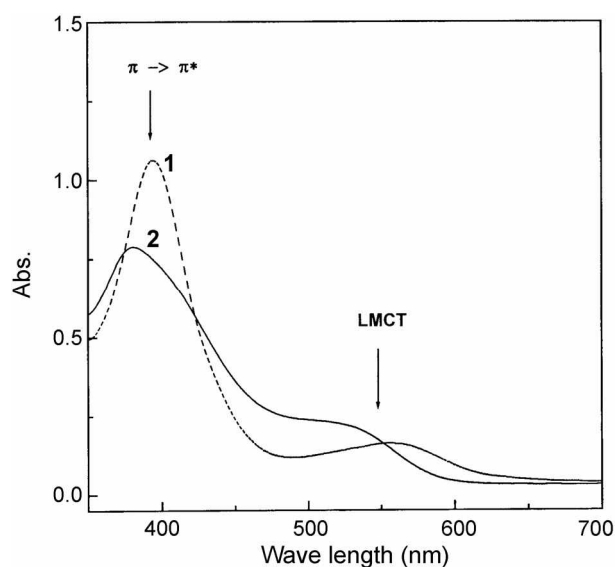
room temperature and filtered. The filtrate was evaporated to dry under reduced pressure and the resulting solid was recrystallized from a mixture 1 : 2 of dichloromethane and *n*-hexane to obtain dark red crystal. Yield; 20%. Found: C, 66.94; H, 4.38; N, 7.22. Calc. For  $C_{42}H_{32}N_4O_2Cl_2Ni$ : C, 66.90; H, 4.24; N 7.43%. IR (KBr disc,  $cm^{-1}$ ):  $\nu(C=C)$ , 1541;  $\nu(C=N)$ , 1576;  $\nu(C=O)$ , 1645;  $\nu(\text{aromatic})$ , 746, 787, 841.  $^1H$ -NMR ( $CDCl_3$ ,  $\delta$ ): 2.297 (s, methyl, 6H), 3.660 (s, ethylene, 4H), 5.947-5.996 (m, aromatic on 13 and 14, 4H), 7.31-7.38 (m, aromatic on 2 and 11, 10H), 7.489, 7.510 (d) 7.165, 7.186 (d) (aromatic of benzoyl group).  $^{13}C$ -NMR ( $CDCl_3$ ,  $\delta$ ): 18.594 (methyl), 53.204 (ethylene), 117.318 (methine), 156.962, 159.135 (diiminate), 120.023, 140.664, 145.767 (aromatic on 13 and 14), 120.023, 121.225, 137.516, 138.308 (aromatic on 2 and 11), 127.974, 128.259, 130.559, 130.765 (aromatic of benzoyl group), 198.544 (C=O).

**X-ray crystallographic analysis:** The crystallographic data for the complex **2**;  $C_{43}H_{34}Cl_4N_4O_2Ni$   $FW = 839.25$ , monoclinic, space group  $P2_1/c$ ,  $a = 10.8314(18)$  Å,  $b = 27.103(5)$  Å,  $c = 12.919(2)$  Å,  $\beta = 100.517(3)^\circ$ ,  $V = 3728.8(11)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.495$  Mg/m<sup>3</sup>, crystal dimensions  $0.50 \times 0.18 \times 0.05$  mm,  $F(000) = 1728$ , 22600 reflections collected, 8811 independent reflections,  $R_1[I > 2\sigma(I)] = 0.0558$ ,  $wR_2[I > 2\sigma(I)] = 0.1148$ . Diffraction studies were performed using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on an Enraf-Nonius CAD4 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 and refined by full-matrix least-squares calculations with SHELX-97.<sup>18,19</sup>

## Results and Discussion

The IR spectra of a new complex **2** showed a very strong band at the  $1645\text{ cm}^{-1}$  attributed to the stretching modes of C=O, reflecting benzoylation at methine sites, which are supported by similar observations for nickel(II) complexes of asymmetrical dibenzoylated tetraazacyclo[14]annulenes.<sup>15</sup> The IR spectra of C=C and C=N showed bands at around  $1518$  and  $1559\text{ cm}^{-1}$ , and  $1541$  and  $1576\text{ cm}^{-1}$ , respectively. The  $^1H$ -NMR peaks of methyl and ethylene for complex **2** were shifted to down field  $0.12$  ppm and  $0.16$  ppm, and the methine peak was disappeared due to benzoylations. The  $^{13}C$ -NMR peak of methine was moved to down field  $12$  ppm by benzoylation, while the methyl peak was moved to upfield around  $2$  ppm. These results were explained that two benzoyl groups were not located at the same plane with macrocycle ring.

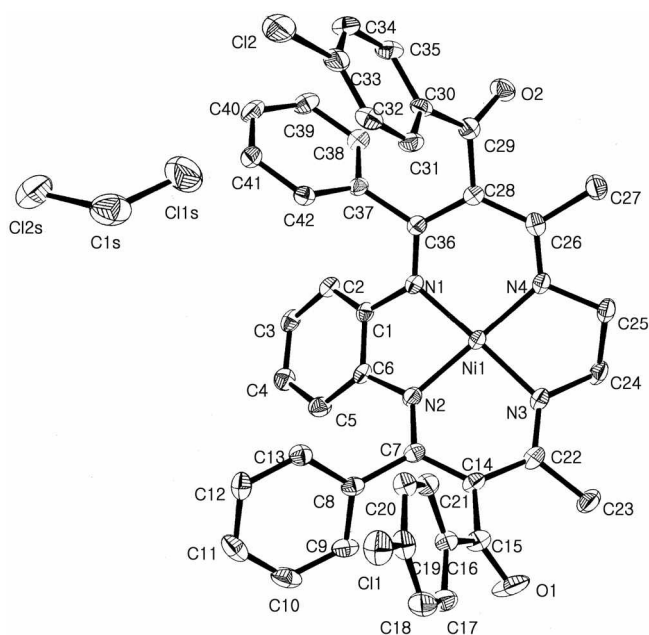
In Figure 1, the UV-visible spectra of complexes **1** and **2** exhibited a peak at  $395\text{ nm}$  ( $\epsilon_{max} = 21,200\text{ M}^{-1}\text{ cm}^{-1}$ ) and  $380\text{ nm}$  ( $\epsilon_{max} = 15,800\text{ M}^{-1}\text{ cm}^{-1}$ ), respectively, due to  $\pi \rightarrow \pi^*$  transition and a peak in visible region by ligand to metal charge transfer (LMCT) at  $560\text{ nm}$  ( $\epsilon_{max} = 3,240\text{ M}^{-1}\text{ cm}^{-1}$ )



**Figure 1.** Electronic absorption spectra of complex **1** and **2** in chloroform solution ( $5.0 \times 10^{-5}\text{ M}$ ) at room temperature.

and  $523\text{ nm}$  ( $\epsilon_{max} = 4,560\text{ M}^{-1}\text{ cm}^{-1}$ ), respectively. The two bands for complex **2** with dimethyl and diphenyl groups were shifted to shorter wave length compared to asymmetrical tetraazaannulenenickel(II) complexes with tetramethyl groups,<sup>13</sup> which might be due to an extended  $\pi$  conjugation effect by substituting two methyl groups to two phenyl ones. The benzoylation and substituted phenyl ring might also increase interaction between nickel(II) and nitrogen atoms of macrocycle ring by an expanded  $\pi$ -conjugation system of macrocycle ring.

The molecular structure of the complex **2** was drawn in Figure 2. The compound included a methylenechloride. The two phenyl rings were located between benzene on macrocycle ring and benzoyl groups at methine sites because of  $\pi$  conjugation in spite of even large steric hinderance. The average of four Ni-N bond distances was  $1.8525$  Å that is longer than the corresponding Ni-N distances ( $1.8270$  Å) for symmetrical nickel(II) complex,<sup>20</sup> while shorter than asymmetrical complex ( $1.868$  Å) with all methyl groups.<sup>21</sup> Although the basicity of ethylenediamine ( $pK_{a1}$  and  $pK_{a2}$ :  $7.08$  and  $9.89$ ) is greater than that of phenylenediamine ( $pK_{a1}$  and  $pK_{a2}$ :  $1.81$  and  $4.61$ ),<sup>22</sup> the bond lengths of four Ni-N were almost similar, which might be due to electronic effects of phenyl rings and benzoyl groups. The two benzoyl groups at methine sites and two phenyl groups at C2 and C11 were located to almost perpendicular for the macrocycle plane. The average angles of N-Ni-N of five and six membered rings were  $87.01$  and  $93.16^\circ$ , respectively and N(3)-Ni(1)-N(1) and N(4)-Ni(1)-N(2) were  $171.41$  and  $177.58^\circ$ , respectively, which are somewhat different from those of symmetrical tetraazaannulene nickel(II) complex.<sup>8</sup> The four Ni-N bonds environment around the nickel(II) atom showed tetrahedrally distorted square plane, which is appreciably different from that of tetraazacyclo[14]annulenenickel(II) with four methyl groups showing almost square planar.



**Figure 2.** The molecular structure of complex **2**. Selected bond lengths (Å) and angles (°) (standard uncertainties in parentheses); Ni(1)-N(1) 1.850(2), Ni(1)-N(2) 1.855(2), Ni(1)-N(3) 1.853(2), Ni(1)-N(4) 1.852(2), N(1)-C(36) 1.337(3), N(2)-C(7) 1.346(4), N(3)-C(22) 1.308(4), N(4)-C(26) 1.319(4), N(1)-C(1) 1.425(3), N(2)-C(6) 1.418(3), N(3)-C(24) 1.476(3), N(4)-C(25) 1.481(3), C(7)-C(14) 1.411(4), C(14)-C(22) 1.448(4), C(26)-C(28) 1.435(4), C(28)-C(36) 1.413(4), C(24)-C(25) 1.510(4), N(1)-Ni(1)-N(3) 171.41(10), N(2)-Ni(1)-N(4) 177.58(11), N(1)-Ni(1)-N(4) 93.85(10), N(1)-Ni(1)-N(2) 86.00(10), N(2)-Ni(1)-N(3) 92.47(10), N(3)-Ni(1)-N(4) 88.03(10), C(7)-C(14)-C(22) 122.0(2), C(26)-C(28)-C(36) 123.3(2).

**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 297512. Copies of this information can be obtained free of charge via E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or www: <http://www.ccdc.cam.ac.uk>; Tel: (44) 01223 762910; Fax: (44) 01223 336033; Postal

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