Preparation and Structure of Tetrakis(indolo[2,3-*b*]quinoxalinato)dinickel(II)

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Treatment of 6*H*-indolo[2,3-*b*]quinoxaline (**1**) with $NaBH_4$ in ethanol at 82 °C for 10 min under argon gives the reactive anion species **2** (generated by deprotonation of N-6 position of **1**), which upon reaction with $Ni(OAc)_2{\cdot}4H_2O$ in ethanol at 82 °C for 6 h under argon forms the title dinuclear nickel(II) complex **3**. The molecular structure of the novel complex **3**, indicating the Ni-Ni distance of 2.618(1) Å, is reported.

Although the chemistry of 6*H*-indolo[2,3-*b*]quinoxaline (**1**) and its derivatives has been studied to a great extent and the physical and chemical properties[1] and the biological activities[2] for numerous these compounds have been well documented, nothing has so far been established for preparation of the metal complexes with indolo[2,3-*b*]quinoxalines as ligands. On the other hand, the dinuclear nickel(II) complexes have been of interest because of the magnetic and electronic properties.[3] As a series of basic studies on the creation of novel functional materials with delocalized electron systems and on their potential utility, we have been particularly interested in the molecular structure and the characteristic properties of a dinuclear nickel(II) complex possessing **1** as ligand. We now wish to describe on a facile preparation and the molecular structure of a novel dinuclear nickel(II) complex, tetrakis(indolo[2,3-*b*]quinoxalinato)dinickel(II) (**3**), which enabled us to determine the crystal structure by means of X-ray diffraction.

The target complex **3** was prepared according to the following method. A solution of 6*H*-indolo[2,3-*b*]quinoxaline (**1**)[4] (100 mg, 456 μmol) and $NaBH_4$ (40 mg, 1.1 mmol) in ethanol (60 mL) was refluxed at 82 °C for 10 min under argon. After cooling to room temperature, the insoluble $NaBH_4$ was removed by using a centrifugal separator. To the resulting orange solution of the reactive anion species **2**[5] was added $Ni(OAc)_2{\cdot}4H_2O$ (60 mg, 241 μmol), and the mixture was refluxed at 82 °C for 6 h under argon. The ethanol containing the precipitated dinuclear nickel(II) complex **3** was centrifuged. The crude reddish-orange solid **3** obtained was washed with ethanol and recrystallized from dichloromethane-ethanol (2:1, vol/vol) to provide pure complex **3** (30 mg, 30 μmol, 67% yield)[7] (the recovered starting material **1**: 60 mg, 273 μmol, conversion: 40%), whose structure was established on the basis of the elemental analysis, the spectroscopic data [UV-visible, FT-IR, FAB-MS, and ^1H-NMR[8] including its 2D NMR (H-H COSY)],[9a] and the X-ray crystallographic analysis.[9b]

Complex **3** was dark reddish-orange blocks. The TGA/DTA (thermal analysis) indicated that **3** contained 3.933% of CH_2Cl_2 in the crystals (calculated from the height of the TGA mass step below 205.3 °C) and decomposed around 420 °C. The UV-visible spectrum [λ_{max} (CH_2Cl_2) nm (log ε) for dimer] appeared at 244(5.11), 277(5.27), 292sh(4.89), 350(4.71), 366sh(4.58), and 470(4.05). The bathochromic shifts of all characteristic absorption bands were observed as compared with those of **1**.[4] The absorption maximum (λ_{max} 470 nm) seems to be the corresponding *intra*-ligand π-π* transition. The IR(KBr) spectrum suggested the presence of C=N[4] (ν_{max} 1562 cm^{-1}, st) coordinated to a nickel(II) atom. The molecular formula $C_{56}H_{32}N_{12}Ni_2$ was determined by the exact FAB-MS (negative) spectrum (Found: *m/z* 988.1606; Calcd for $C_{56}H_{32}N_{12}Ni_2$: M^-, *m/z* 988.1580.). The elemental analysis confirmed the molecular formula $C_{113}H_{66}N_{24}Ni_4Cl_2$ (Found: C, 65.26; H, 3.48; N, 16.00%. Calcd for $C_{113}H_{66}N_{24}Ni_4Cl_2$ [$2C_{56}H_{32}N_{12}Ni_2{\cdot}CH_2Cl_2$]: C, 65.33; H, 3.20; N, 16.18%.). The 500 MHz ^1H-NMR (CD_2Cl_2) spectrum showed signals, indicating all the four ligands are equivalent, at δ 7.03 (4H, ddd, *J* = 7.5, 7.5, 1.0 Hz, H-9), 7.68 (4H, ddd, *J* = 8.5, 7.0, 1.5 Hz, H-2), 7.73 (4H, ddd, *J* = 8.0, 7.5, 1.0 Hz, H-8), 7.81 (4H, dd, *J* = 7.5, 1.0 Hz, H-10), 7.95 (4H, dd, *J* = 8.5, 1.5 Hz, H-1), 8.51 (4H, ddd, *J* = 8.0, 7.0, 1.5 Hz, H-3), 9.17 (4H, dd, *J* = 8.0, 1.0 Hz, H-7), and 12.11 (4H, dd, *J* = 8.0, 1.5 Hz, H-4). The larger down field shifts for H-4 (+ 4.02 ppm) and H-7 (+ 1.61 ppm) protons of the four ligands were observed as compared with those of **1**,[4] suggesting some specific *intra*-molecular interaction between the ligand and nickel(II) atom. The elemental analysis and the spectroscopic data led to the structure tetrakis(indolo[2,3-*b*]quinoxalinato)dinickel(II).

The crystal structure of **3** was then determined by means of X-ray diffraction.[10] The molecular structure of **3** based on the ORTEP drawing is shown in Figure 1a, indicating the formation of the title dinuclear nickel(II) complex. The four indolo[2,3-*b*]quinoxalinato ligands symmetrically coordinated to the two nickel(II) atoms [Ni-Ni distance 2.618(1) Å, which is characteristically longer than the distances observed for the Ni-Ni of $Ni_2(form)_4$ (2.485(2) Å),[11a] $Ni_2(napy)_4Br_2B(C_6H_5)_4$ (2.415(4) Å),[11b] $Ni_4(\mu_4\text{-phdpda})_4$ (2.3010(6)-2.3280(6) Å)[11c] and $Ni_7(\mu_4\text{-teptra})_4Cl_2$ (2.215(2)-2.383(1) Å)[11c]], affording the neutral complex **3** which has two square-planer coordination geometries formed by the atoms N(5), N(6'), N(6''), N(5''') and Ni, and N(6), N(5'), N(5''), N(6''') and Ni; the bond lengths between Ni and N atoms [Ni-N(5) 1.929(4) Å, Ni-N(6') 1.905(4) Å, Ni-N(6) 1.913(4) Å, and Ni-N(5') 1.911(4) Å] are within a close range of the average Ni-N bond distances for $Ni_2(form)_4$ and $Ni_4(\mu_4\text{-phdpda})_4$. Interestingly, the four ligands of $Ni_2(napy)_4Br_2B(C_6H_5)_4$ without π stacking structure in the single crystal symmetrically twist by 25° from the dinickel chain and further both $Ni_4(\mu_4\text{-phdpda})_4$ and $Ni_7(\mu_4\text{-teptra})_4Cl_2$ form a respective unique helical structure; however, the four ligands of complex **3** do not twist. Thus, the two different views for the packing (molecular) structure of **3** revealed that this molecule formed a unique accumulation (π stacking structure) in the single crystal (Figures 1b,c) and the *inter*-plane distances between the overlapping molecules were 3.47–3.57 Å (Figure 1b), suggesting the *inter*-ligand π-π* transition (*inter*-molecular photo-induced electron transfer) can be generated.[12]

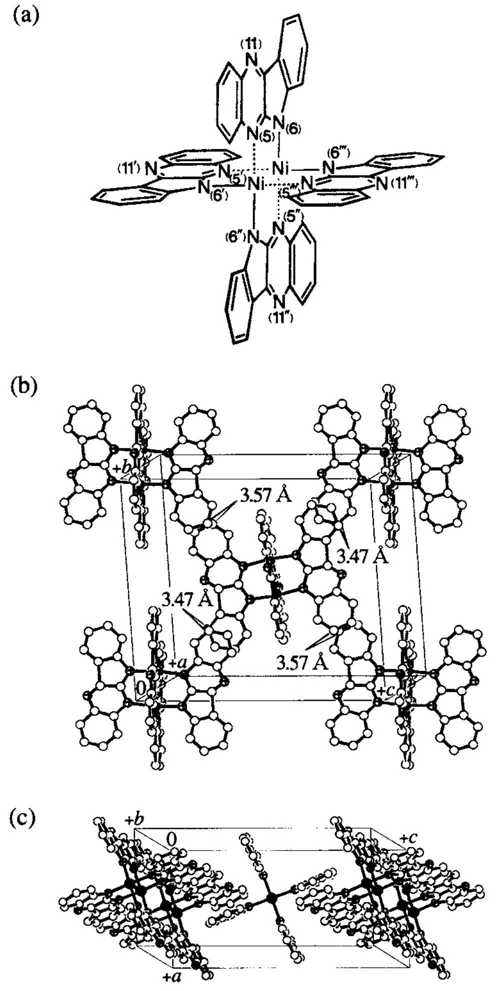

Figure 1. The molecular structure of complex **3** (a) based on the ORTEP drawing and the two different views (b and c) for the packing (molecular) structure of complex **3**; hydrogen atoms and solvent (CH_2Cl_2) are omitted for reasons of clarity.

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4 Compound **1** was prepared according to the modified Schunck's method:[1a] Reaction of isatin (300 mg, 2.0 mmol) with a 1.1 molar amount of *o*-phenylenediamine (250 mg, 2.3 mmol) in ethanol (25 mL) at reflux temperature (82 °C) for 24 h under argon quantitatively gave compound **1** (210 mg, 1.0 mmol, 67% yield)[7] (the recovered isatin: 90 mg, 0.6 mmol, conversion: 71%). **1**: yellow needles, mp > 212 °C (sublimation, determined by the TGA/DTA) (lit:[1b] mp 295–296 °C), R_f = 0.45 on silica-gel TLC (AcOEt/hexane = 2/1, vol/vol); UV-visible λ_{max} (CH_2Cl_2) nm (log ε), 260sh(4.70), 267(4.82), 337(4.32), 351(4.38), and 382(3.85); IR (KBr) ν_{max} 1616 cm^{-1} (C=N, st), 3067 (NH, st); EI-MS *m/z* 219(M^+, 100%); Found: *m/z* 219.0799, Calcd for $C_{14}H_9N_3$: M^+, 219.0796; ^1H-NMR (CD_2Cl_2) δ 7.41(1H, ddd, *J* = 7.5, 7.5, 1.0 Hz, H-9), 7.56(1H, ddd, *J* = 8.0, 1.0, 0.5 Hz, H-7), 7.69(1H, ddd, *J* = 8.0, 7.5, 1.0 Hz, H-8), 7.72(1H, ddd, *J* = 8.5, 7.0, 1.5 Hz, H-2), 7.78(1H, ddd, *J* = 8.0, 7.0, 1.5 Hz, H-3), 8.09(1H, ddd, *J* = 8.0, 1.5, 0.5 Hz, H-4), 8.28(1H, ddd, *J* = 8.5, 1.5, 0.5 Hz, H-1), 8.42(1H, ddd, *J* = 7.5, 1.0, 0.5 Hz, H-10), and 8.76(1H, brds, NH-6).

5 Reactions of various alcohols with $NaBH_4$ are well known,[6] giving a respective sodium salt of $(RO)_4B^-$. In this reaction the generated sodium salt of $(EtO)_4B^-$ served as a base for deprotonation of N-6 position of **1**, affording the reactive anion species **2**, quantitatively. **2**: reddish-orange color; visible λ_{max} (EtOH) nm, 480; exact FAB-MS(negative) (Found: *m/z* 218.0720; Calcd for $C_{14}H_8N_3$: M^-, *m/z* 218.0718).

6 a) H. J. Schlesinger, H. C. Broun, H. R. Hoekstra, and L. R. Papps, *J. Am. Chem. Soc.*, **75**, 199 (1953). b) J. C. Norrild and H. Eggert, *J. Am. Chem. Soc.*, **117**, 1479 (1995). c) S. Takekuma, H. Takekuma, T. Matsumoto, and Z. Yoshida, *Tetrahedron Lett.*, **41**, 2929 (2000).

7 The yield of the product is based on the consumed starting material.

8 The parameters were confirmed by a computer-assisted simulation analysis.

9 a) The sample dried well in a vacuum desiccator was used for the thermal, elemental and spectroscopic analyses. b) The freshly recrystallized sample, which was not dried in a vacuum desiccator, was used for the X-ray crystallographic analysis.

10 Crystallographic data for complex **3**: $C_{56}H_{32}N_{12}Ni_2 \cdot 4CH_2Cl_2$ (FW = 1330.08), dark reddish-orange block (the crystal size, 0.28 × 0.15 × 0.05 mm), monoclinic, $P2_1/c$ (#14), a = 9.271(1) Å, b = 15.950(2) Å, c = 18.812(1) Å, β = 92.436(2)°, V = 2779.1(5) $Å^3$, Z = 2, D_{calcd} = 1.589 g/cm^3, μ(Mo $K\alpha$) = 11.16 cm^{-1}, measured reflections = 6555, observed reflections = 6317, $R1$ = 0.0798, $wR2$ = 0.2284. The X-ray measurement of complex **3** was made with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) on a Quantum CCD area detector coupled with a Rigaku AFC-7 diffractometer at 200 K. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2 using the program SHELXL 97. All calculations were performed using the teXsan crystallographic software package.

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12 It should be noted that the absorption maximum (λ_{max} 470 nm) of complex **3** is near to the maximum wavelength of the solar spectrum (ca. 500 nm). Thus, the basic studies on physical and chemical functions of complex **3** are of interest from a viewpoint of potential utility of functional delocalized electron system such as photosensitive dyes.