Synthesis of Binuclear Ligands Possessing Two Discrete Multidentate N-Heterocyclic Podand Coordination Sites and Their Bimetallic Nickel(II) Complexes

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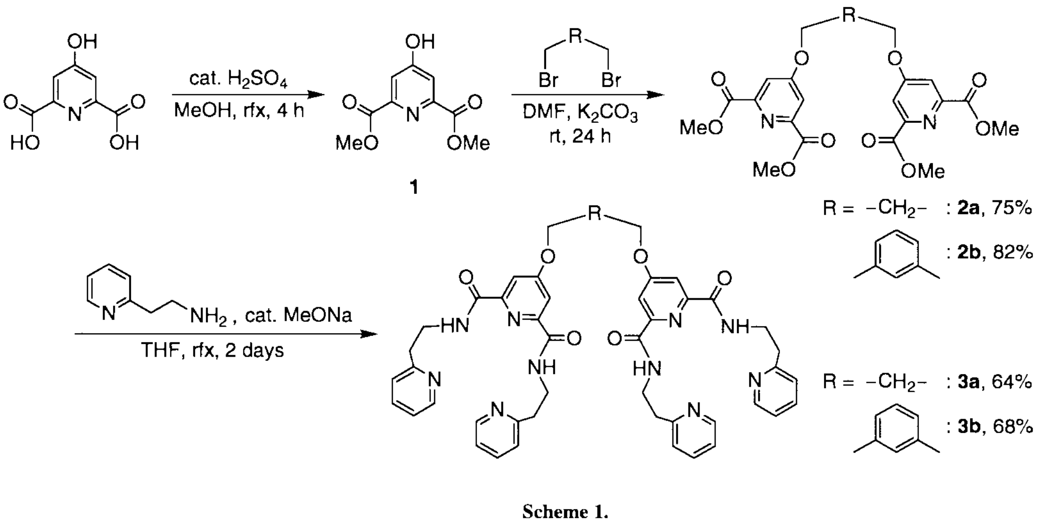
Binuclear ligands possessing two discrete multidentate N-heterocyclic podand coordination sites connected by a flexible propylene spacer and a rigid *m*-xylene spacer were synthesized. Treatment of the binuclear ligands with $Ni(OAc)_2$ afforded the bimetallic nickel(II) complexes with two discrete nickel centers. The single-crystal X-ray structure determination of the bimetallic nickel(II) complex with a propylene spacer revealed a little distorted square planar geometry at each nickel center.

Amido-N ligands, which possess σ-donor properties of the deprotonated nitrogen, are known to afford stable complexes with transition metals.[1] We have demonstrated that the efficient catalytic systems for oxygenation reaction with molecular oxygen are achieved by utilization of transition metal complexes with the multidentate N-heterocyclic podand ligands composed of 2,6-pyridinedicarboxamide unit.[2] An intramolecular axial coordination of the podand N-heterocyclic moiety by virtue of the flexibility of the podand moieties appears to participate in forming an efficient catalytic system. Flexible podand ligands are considered to confer to complexes possessing various metal geometry under different modes of coordination.[3] On the other hand, two metal centers in close proximity cooperatively activate oxygen in oxygenases like tyrosinase and methane monooxygenase.[4] A bimetallic system is considered to be important from the viewpoints of biomimetic models and synthetic catalysts.[5] We herein report the synthesis of binuclear ligands possessing two discrete multidentate N-heterocyclic podand coordination sites and characterization of the bimetallic nickel(II) complexes.

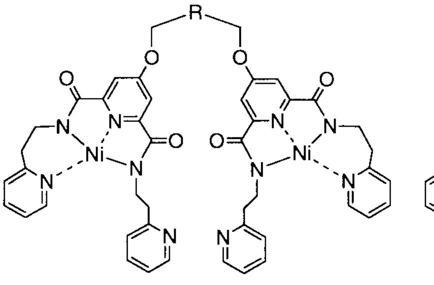
Binuclear ligands **3** composed of a flexible propylene spacer and a rigid *m*-xylene spacer were prepared conveniently from chelidamic acid according to the path shown in Scheme 1, instead of using 4-chloro-2,6-pyridinedicarbonyl dichloride as a starting compound. Chelidamic acid was converted into the methyl ester **1**, two molecules of which were linked by treatment with 1,3-dibromopropane or 1,3-bis(bromomethyl)benzene in the presence of potassium carbonate to give **2** in good yields. Amidation of **2** with 2-(2-aminoethyl)pyridine afforded the desired binuclear ligands **3** in moderate yields (**3a**, 64%; **3b**, 68% based on **2**). The thus-obtained binuclear ligands **3** were fully characterized by spectral data and elemental analyses.[6] Only one set of well-resolved signals for protons of podand coordination moieties was observed in ^{1}H NMR, indicating that both podand coordination moieties adopt the symmetrical conformation.

A synthetically useful catalytic epoxidation of olefins by nickel(II) complexes in the presence of aldehydes under molecular oxygen has been investigated extensively.[7] In this context, we embarked upon the preparation of the bimetallic nickel(II) complex with the binuclear ligand **3** although complexation with five- or six-coordinated transition metal is possible. Complexation of **3a** and **3b** with $Ni(OAc)_2$ led to the selective formation of the bimetallic nickel(II) complexes **4a** and **4b**, respectively.[8] The single-crystal X-ray structure determination of **4a** revealed that the nickel center is coordinated by four nitrogens of the deprotonated amide moieties, central pyridine, and one of the podand pyridines as shown in Figure 1.[9] A little distorted square planar geometry was observed at each nickel center substituted with two amide nitrogens of **3a** (N(2)-Ni(1)-N(3), 164.0°; N(7)–Ni(2)–N(8), 163.8°). The two deprotonated amido moieties and central pyridine ring are coplanar to form two five-membered chelate rings with extended conjugation, resulting in the significant deviation from 90° of the bond angles involving

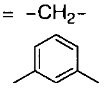


Scheme 1.

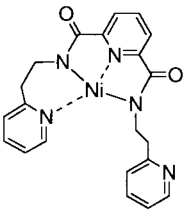
the chelation (N(1)–Ni(1)–N(2), 82.6°; N(1)–Ni(1)–N(3), 83.2°; N(6)–Ni(2)–N(7), 82.6°; N(6)–Ni(2)–N(8), 82.8°). The lengths of two nickel-amide nitrogen bonds are different, probably due to the formation of six-membered chelate ring with one of the podand pyridine moiety (Ni(1)–N(2), 1.97 Å; Ni(1)–N(3), 1.90 Å; Ni(2)–N(7), 1.95 Å; Ni(2)–N(8), 1.90 Å).



R = $-CH_2-$: **4a**



: **4b**



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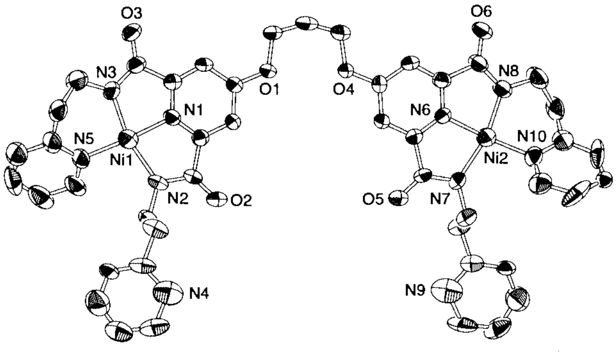

Figure 1. ORTEP view of the X-ray crystal structure of **4a**: (40% probability ellipsoids). Hydrogen atoms are omitted for clarity.

The catalysis of bimetallic nickel(II) complexes **4** was examined in the catalytic epoxidation reaction of *trans*-1-phenylprop-1-ene. Treatment of *trans*-1-phenylprop-1-ene with a catalytic amount of **4** in the presence of pivalaldehyde under molecular oxygen led to the selective formation of the corresponding *trans*-epoxide in a moderate yield (**4a**: 60%, **4b**: 76%).[10] The bimetallic nickel(II) complex **4b** exhibited a higher catalytic activity than the mononuclear nickel(II) complex **5** (53%). The reason still remains obscure why the more enhanced epoxidation reaction was observed with **4b**. The two metal centers of **4b**, which are orientated by a rigid *m*-xylene spacer, are supposed to operate cooperatively in the epoxidation reaction; one metal center of **4b** binds to the substrate or two metal centers activate molecular oxygen.

In conclusion, the binuclear ligands composed of two discrete multidentate N-heterocyclic podand coordination sites were synthesized. The thus-obtained binuclear ligands were found to form the bimetallic nickel(II) complexes **4** with two discrete nickel centers. The bimetallic nickel(II) complex **4b** exhibited the enhanced catalytic activity in the epoxidation reaction of *trans*-1-phenylprop-1-ene probably due to bimetallic catalysis. Further investigation on the catalytic reaction including mechanistic study is now in progress.

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6 **3a**: mp 107–108 °C (uncorrected); IR (KBr): 3337, 1673 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ 8.45 (ddd, 4H, *J* = 5.0, 1.8, 0.7 Hz), 7.74 (s, 4H), 7.73 (td, 4H, *J* = 7.7, 1.8 Hz), 7.34 (ddd, 4H, *J* = 7.7, 1.2, 0.7 Hz), 7.26 (ddd, 4H, *J* = 7.7, 5.0, 1.2 Hz), 4.39 (t, 4H, *J* = 6.0 Hz), 3.77 (t, 8H, *J* = 7.2 Hz), 3.11 (t, 8H, *J* = 7.2 Hz), 2.38 (t, 2H, *J* = 6.0 Hz); FABMS *m*/*z* 823 (M^++1); Anal. Calcd for $C_{45}H_{46}N_{10}O_6{\cdot}CH_2Cl_2$: C, 60.86; H, 5.33; N, 15.43%. Found: C, 60.92; H, 5.70; N, 15.62%. **3b**: mp 81–82 °C (uncorrected); IR (KBr): 3335, 1675 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ 8.45 (ddd, 4H, *J* = 5.1, 1.8, 0.7 Hz), 7.78 (s, 4H), 7.73 (td, 4H, *J* = 7.7, 1.8 Hz), 7.59 (br s, 1H), 7.44–7.48 (m, 3H), 7.34 (ddd, 4H, *J* = 7.7, 1.1, 0.7 Hz), 7.26 (ddd, 4H, *J* = 7.7, 5.1, 1.1 Hz), 5.31 (s, 4H), 3.77 (t, 8H, *J* = 7.3 Hz), 3.11 (t, 8H, *J* = 7.2 Hz); FABMS *m*/*z* 885 (M^++1); Anal. Calcd for $C_{50}H_{48}N_{10}O_6{\cdot}CH_2Cl_2$: C, 63.29; H, 5.00; N, 14.47%. Found: C, 63.26; H, 5.18; N, 14.51%.

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8 **4a**: mp 253–254 °C (decomp.); IR (KBr): 1600 cm^{-1}; FABMS *m*/*z* 937 (M^++1); Anal. Calcd for $C_{45}H_{42}N_{10}O_6Ni_2{\cdot}2MeOH$: C, 56.43; H, 5.04; N, 14.00%. Found: C, 56.77; H, 5.17; N, 13.97%. **4b**: mp 208–209 °C (decomp.); IR (KBr): 1597 cm^{-1}; FABMS *m*/*z* 999 (M^++1); Anal. Calcd for $C_{50}H_{44}N_{10}O_6Ni_2{\cdot}MeOH$: C, 59.45; H, 4.70; N, 13.59%. Found: C, 59.68; H, 4.49; N, 13.50%.

9 Crystal data for **4a**: $C_{45}H_{42}N_{10}O_6Ni_2{\cdot}CH_3OH$, M = 968.33, triclinic, space group $P\bar{1}$ (No. 2), a = 16.781(3) Å, b = 16.741(2) Å, c = 10.5593(8) Å, α = 101.264(7)°, β = 101.38(1)°, γ = 109.23(2)°, V = 2635.0(8) $Å^3$, Z = 2, D_{calcd} = 1.220 g cm^{-3}, R = 0.114, R_w = 0.311. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-165879 for **4a**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

10 To a solution of **4** (0.01 mmol) or **5** (0.02 mmol) in 1,2-dichloroethane (1 mL) was added *trans*-1-phenylprop-1-ene (52 μL, 0.40 mmol) and pivalaldehyde (87 μL, 0.80 mmol), and then the resulting mixture was stirred at 20 °C for 12 h under an atmospheric pressure of oxygen. The formation of the *trans*-epoxide was detected by ^1H NMR and GLC.