Atmospheric CO_2 Fixation by Dinuclear Ni(II) Complex, [TPANi(II)(μ-OH)$_2$Ni(II)TPA](ClO_4)$_2$ (TPA = Tris(pyridylmethyl)amine)

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The dinuclear Ni(II) complex [TPANi(II)(μ-OH)$_2$Ni(II)TPA](ClO_4)$_2$ (TPA = tris(pyridylmethyl)amine) (**2**) can react with atmospheric CO_2 readily, and forms corresponding μ-carbonate complex, [TPANi(II)(μ-CO_3)Ni(II)TPA](ClO_4)$_2$ (**3**).

The atmospheric CO_2 fixation is of special interest from the point of view of environmental chemistry.[1] The increase of atmospheric CO_2 will cause serious environmental problem in the near future. Thus, the development of effective chemical method to eliminate CO_2 is an urgent matter.

Many CO_2 insertion reactions to the metal-anion ligand bonds are known.[2] However most of the complexes having such reactivity are dioxygen reactive, therefore they can not be the appropriate means for atmospheric CO_2 fixation. Here we will describe the atmospheric CO_2 fixation by using Ni(II) complex. Some reports have presented the reaction of the metal-hydroxy complex with CO_2 affording metal carbonato or bicarbonato complex.[3] Our research goal is to develop effective system for atmospheric CO_2 fixation by using such metal hydroxy complex. To design the suitable ligand for the metal hydroxy complex, it is necessary to investigate the reactivity of the complex toward CO_2 systematically by using various ligands. We believe this type of research will contribute to solve such a serious environmental problem.

[TPANi(II)(μ-OH)$_2$Ni(II)TPA](ClO_4)$_2$ (**2**)[4] was obtained immediately as a blue solid by the treatment of 10 ml aqueous solution of [TPANi(II)(μ-Cl)$_2$Ni(II)TPA](ClO_4)$_2$ (**1**) (300 mg)[5] with 0.1 N NaOH aqueous solution (10 ml), (yield ca. 88%). Single crystals suitable for the X-ray measurement could be obtained by the Et_2O slow diffusion of methanolic solution of **2**. The X-ray structure is shown in Figure 1.[6] The crystal system indicates the center of imposed symmetry. Each nickel shows slightly distorted octahedral with N_4O_2 donor set. The distances between bridging hydroxy group and nickel are 1.990 Å and 2.034 Å. These are typical values of those found in high spin nickel(II) complex.[3c] The UV-visible spectra in methanol shows the bands at 585, 770(sh) and 890 nm. These bands can be assigned as typical d-d transition bands in high spin Ni(II) octahedral system ($^3A_{2g} \rightarrow {}^3T_{1g}$ (585 nm), $^3A_{2g} \rightarrow {}^3T_{2g}$(770 and 890 nm)) respectively.

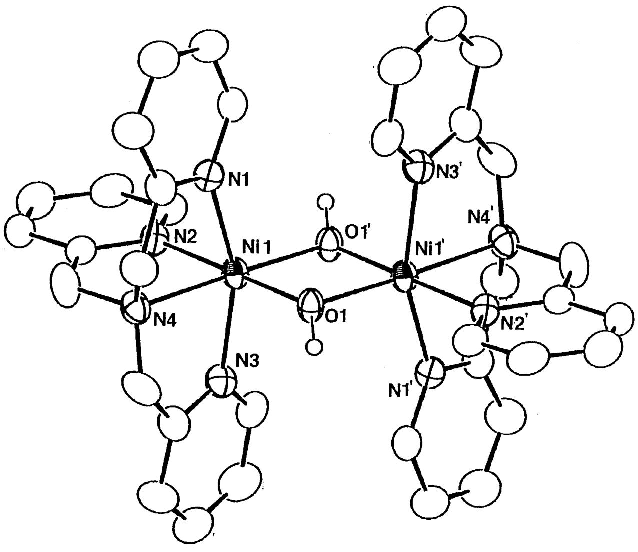

Figure 1. The ortep view of complex **2.** The counter ions (perchlorate) are omitted for clarity. Selected distances (Å) and angles(deg):
NI(1)O(1) 2.034(4); NI(1)O(1) 1.990(4); NI(1)N(1) 2.118(6);
NI(1)N(2) 2.090(5); NI(1)N(3) 2.113(5); NI(1)N(4) 2.114(5);
O(1)NI(1)O(1) 82.1(2); O(1)NI(1)N(1) 94.5(2); O(1)NI(1)N(2) 178.2(2);
O(1)NI(1)N(3) 90.4(2); O(1)NI(1)N(4) 96.5(2); O(1) NI(1) N(1) 99.2(2);
O(1)NI(1) N(2) 99.4(2); O(1)NI(1)N(3) 102.6(2); O(1) NI(1) N(4) 178.1(2);
N(1)NI(1) N(2) 86.3(2); N(1)C(5)C(4) 121.5(7); N(1)NI(1)N(3) 158.1(2);
N(1)NI(1)N(4) 79.5(2); N(2) NI(1) N(3) 88.3(2); N(2) NI(1) N(4) 81.9(2);
N(3)NI(1)N(4) 78.7(2).

The complex **2** can react with CO_2 gas at room temperature instantaneously, and color change from blue to purple was noted. Purple single crystals could be obtained by the ether diffusion of the purple methanol solution. The X-ray crystallography indicates the dinuclear nickel (μ-carbonato) complex, [TPANi(II)(μ-CO_3)Ni(II)TPA](ClO_4)$_2$ (**3**).[7,8] The ORTEP view is shown in Figure 2. The coordination geometry of each nickel atom can be described as a distorted octahedral formed by four nitrogens of TPA and two oxygens from the carbonate ion, and crystallography suggests the two nickel coordination structures are asymmetric. The trans position of O1 in Ni1 is alkyl amine nitrogen ligand, N1. In contrast, the trans position of O1 in Ni2 is pyridine nitrogen, N7. Furthermore, the differences of the bond lengths around each nickel suggested the asymmetric structure of **3**, while these bond lengths are not exceptional values as high spin Ni(II) complex.[9] For instance, Ni(1)-O(1) is 2.084(6) Å, in contrast, Ni(2)-O(1) is 2.174(6) Å. The IR band at 1570 cm^{-1} (C=O) also supports the existence of the carbonato anion in the complex.

The time dependency changes of UV-vis spectra of complex **2** under aerobic condition in methanol are shown in Figure 3. The atmospheric CO_2 fixation reaction is completed within several hours. The final spectrum confirmed the reaction proceeded quantitatively. The λ_{max} value at 585 nm in complex **2** is changed to 542 nm with three isosbestic points, 460, 570 and 700 nm.

The ligated carbonate is easily released by the treatment with aqueous base. Thus, the reaction of acetonitrile 5 mM

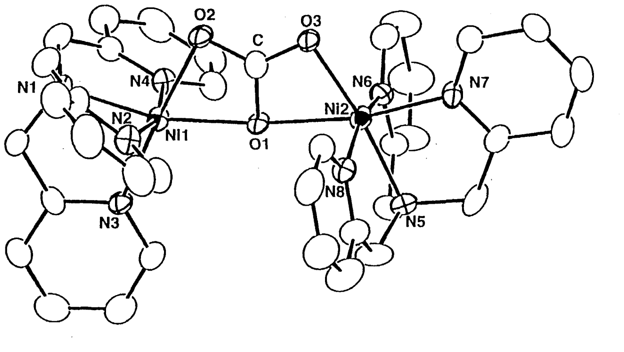

Figure 2. The ortep view of complex **3.** The counter ions (perchlorate) are omitted for clarity. Selected distances (Å) and angles(deg):
NI(1) O(1)2.084(6); NI(1) O(2)2.093(6); NI(1) N(1)2.068(7);
NI(1) N(2)2.077(8); NI(1) N(3)2.059(7); NI(1) N(4)2.056(8);
NI(2) O(1)2.174(6); NI(2) O(3)2.023(6); NI(2) N(5)2.095(7);
NI(2) N(6)2.037(7); NI(2) N(7)2.022(7); NI(2) N(8)2.041(8);
O(1)NI(1)O(2) 64.5(2); N(5) NI(2) N(8) 81.0(3); O(1)NI(1)N(1)163.3(3);
N(6)NI(2)N(7) 90.8(3); O(1)NI(1)N(2) 98.2(3); N(6)NI(2)N(8) 161.8(3);
O(1)NI(1)N(3) 112.5(3); N(7)NI(2) N(8) 93.1(3); O(1)NI(1) N(4) 95.6(3);
O(2)NI(1)N(1) 98.9(3); O(2)NI(1)N(2) 87.1(3); O(2)NI(1)N(3) 176.8(3);
O(2)NI(1)N(4) 89.9(3); N(1)NI(1)N(2) 81.3(3); N(1)NI(1)N(3) 84.2(3);
N(1)NI(1)N(4) 82.6(3); N(2)NI(1)N(3) 92.5(3); N(2)NI(1)N(4) 163.0(3);
N(3)NI(1)N(4) 91.4(3); O(1)NI(2)O(3) 63.9(2); O(1)NI(2)N(5) 108.4(3);
O(1)NI(2)N(6) 91.9(3); O(1)NI(2)N(7) 167.6(3); O(1)NI(2)N(8) 88.0(3);
O(3)NI(2)N(5) 172.3(3); O(3)NI(2)N(6) 98.3(3); O(3)NI(2)N(7) 103.7(3);
NI(1)N(1)C(7) 108.9(6); O(3)NI(2)N(8) 98.0(3); N(5)NI(2)N(6) 81.7(3);
N(5)NI(2)N(7) 84.0(3)

solution of complex **3** with 0.1 N NaOH aqueous solution afforded the complex **2**, bis(hydroxy) Ni(II) complex quantitatively and instantaneously.[10] Half of the complex **3** was converted to complex **2** within a minute by the additon of 0.01 N NaOH aqueous solution to acetonitrile 5 mM solution of complex **3**.[10] It is striking that such a weak base is effective to dissociate carbonate from the complex **3**. The development of catalytic CO_2 hydration system by use of complex **2** is now in progress.

In summary, the new bis(hydroxo) dinuclear Ni(II) complex was synthesized. This complex has high reactivity toward atmospheric CO_2, and the formed carbonato complex shows high accessibility to hydration.

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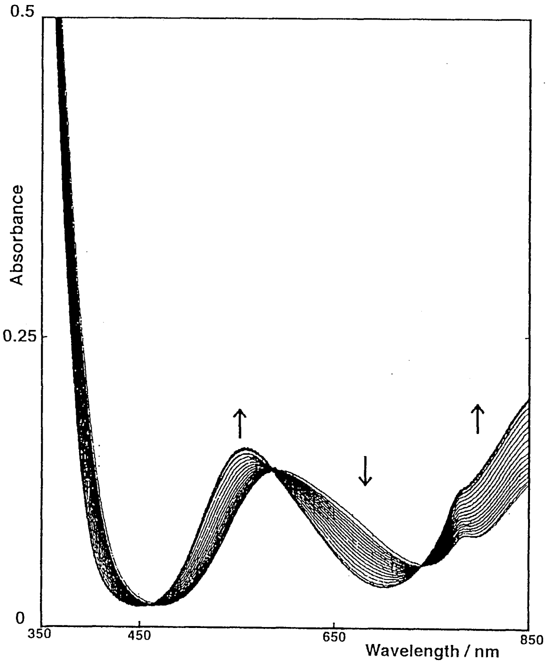

Figure 3. The time dependency changes of UV-vis spectrum. Complex: [TPANi(OH)$_2$NiTPA]$^{2+}$ 1.5mM, 1 scan per 10min, under air, solvent: MeOH.

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4 Anal. Found C, 46.44; H, 4.03; N, 11.81%. Calcd for **2** $Ni_2C_{36}N_8H_{38}O_{10}Cl_2$: C. 46.44; H. 4.11; N. 11.81 %. IR(KBr, cm^{-1}), ν(C=C), 1601, ν(ClO_4), 1150. UV-vis(nm; ε/$M^{-1}cm^{-1}$) 585(70), 770(31), 890(43).

5 The complex **1** can be synthesized by the reaction of TPA($3HClO_4$)$_3$ with $NiCl_2$ under the presence of 3 equiv. of triethylamine. The single crystals were obtained by recrystalization in methanol. The detail of crystal structure will be reported elsewhere.

6 The structure was solved by direct methods (MITHRIL) and refined by the full matrix least squares techniques with TEXSAN. All non-hydrogen atoms were refined anisotropically, and they were refined isotropically. Hydrogen atoms were calculated and fixed in final refinement cycles. X-ray data for **2**, monoclinic space system with *P21/a*, a = 16.0166(25) Å, b = 13.2909(15) Å, c = 9.5625(39) Å, α = 90.00°, β = 98.92(24)°, γ = 90.00°, V = 2011.0(1.5) Å^3. Z = 2, The *R(Rw)* value is 7.8(6.8)% for 2833 reflections($3° < \theta < 50°$, $Fo > 6\sigma(Fo)$).

7 Analytically pure solid of **3** was obtained by the recrystallization in MeOH (yield ca. 75%). Anal. Found C, 46.50; H, 4.06; N; 1.34%. Calcd for **3** $Ni_2C_{37}N_8H_{36}O_{11}Cl_2$: C. 46.47; H. 3.77; N. 11.72%. IR(KBr, cm^{-1}), ν(C=C), 1603, ν(C=O) 1573, ν(ClO_4), 1130. UV-vis(nm; ε/$M^{-1}cm^{-1}$)542(80), 772(45), 890(95).

8 The structure was solved by direct methods (MITHRIL) and refined by the full matrix least squares techniques with TEXSAN. All non-hydrogen atoms were refined anisotropically, and they were refined isotropically. Hydrogen atoms were calculated and fixed in final refinement cycles. X-ray data for **3**, monoclinic space system with *P21/a*, a = 15.0345(37) Å, b = 14.9787(72) Å, c = 18.9072(73) Å, α = 90.00°, β = 98.40(2)°, γ = 90.00°, V = 4212(2) Å^3. Z = 4, The *R(Rw)* value is 6.6(5.4)% for 4386 reflections ($5° < \theta < 50°$, $Fo > 4\sigma(Fo)$).

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10 These observations are based on UV-vis spectra.