Transesterification vs Hydrolysis: the Reactivity of Metal-Bound Hydroxo Moiety in $[\mathrm{TPANi(II)(\mu\text{-}OH)_2Ni(II)TPA](ClO_4)_2}$ (TPA = tris(2-pyridylmethyl)amine)

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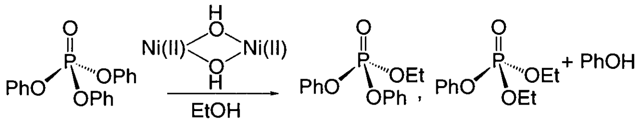
In the reaction of triphenyl phosphate with ethanol in the presence of complex **1**, the transesterification to give diethyl phenyl phosphate was observed, in which system direct nucleophilic attack of ligated hydroxo moiety in **1** toward triphenyl phosphate also proceeded to give μ-phosphate complex, **2**.



Hydrolytic enzymes such as phosphatases or nucleases are known to catalyze the hydrolysis of phosphate ester.[1] Many of these enzymes contain metals such as zinc at the active sites. The catalytic role of zinc is ascribed to the binding and activation of substrates, whereas deprotonation of coordinated water to produce a nucleophilic zinc hydroxide is also proposed as an essential catalytic hydrolysis function. On the other hand, one of these zinc containing enzymes such as alkaline phosphatase can perform transesterification in the presence of exogenous alcohol.[2-4] The reaction mechanism of transesterification catalyzed by this enzyme was not elucidated well at the present stage. While some model studies of intra-molecular transesterification by metal complexes have been reported,[5-7] the model study by use of exogenous alcohol is scarcely known.[8,9]

Recently, we reported the transesterification of carboxylic acid ester by (hydroxo)dinickel(II) complex, $[\mathrm{TPANi(II)(\mu\text{-}OH)_2Ni(II)TPA](ClO_4)_2}$ (TPA = Tris(2-pyridylmethyl)amine) (**1**)[10] in the presence of exogenous alcohol.[9] In this system, hydrogen-bonded alcohol to the metal-bound hydroxo moiety was the most plausible nucleophile for the transesterification toward carboxylic acid ester.

Here we will present the reaction of complex **1** with phosphate ester such as triphenyl phosphate under the presence of external alcohol to investigate how the transesterification of phosphate ester proceeds in this system.

Triphenyl phosphate (1 mmol) was treated with excess ethanol (5 mmol) in the presence of **1** (0.05 mmol) in MeCN (5 ml) at room temperature. After stirring for 12 h, the color change from blue to purple was noted, indicating the shift of d-d transition band of nickel(II) center, hence conformational change of complex **1**. The GC and GC-MS analysis of this reaction mixture turned out the formation of diphenyl ethyl phosphate (yield 150% comparison to the complex **1**). When two equiv of triphenyl phosphate (0.1 mol) was added to the reaction system, the formation of diphenyl ethyl phosphate (yield 75%) and further reacted product, diethyl phenyl phosphate (yield 30%) were observed under the same reaction condition.[11] These results indicate that this system can perform not only the transesterification of triphenyl phosphate but also the transesterification of diphenyl ethyl phosphate. While reaction mechanism of this system is not completely clear at the present stage, we supposed that hydrogen-bonded alcohol to the metal-ligated hydroxo moiety can be the good candidate for nucleophilic attack to transesterificate phosphate ester as previously proposed in the reaction of complex **1** with carboxylic acid ester under the presence of exogenous ethanol.[9,12] However the possibiliy of the presence of other reactive species such as (alkoxo)Ni(II) complex can not be excluded at the present stage.

To elucidate how the conformation of the nickel(II) complex was changed after the reaction, the formed complex was isolated and characterized from the reaction mixture. The solvent of the reaction mixture was removed in vacuo. The remained solid was washed by $\mathrm{Et_2O}$ to remove excess phosphate ester and dissolved in MeCN again. The blue purple single crystals suitable for the X-ray measurement could be obtained by $\mathrm{Et_2O}$ slow diffusion to this MeCN solution. The X-ray crystallography indicates the dinuclear nickel(II) bis(μ-phosphato) complex, $[\mathrm{TPANi(II)(OP(OPh)_2O)_2Ni(II)TPA](ClO_4)_2}$ (**2**) (isolated yield ca. 85%).[13,14] The structure shows center of imposed symmetry (Figure 1). Each nickel(II) ion adopts a slightly dis-

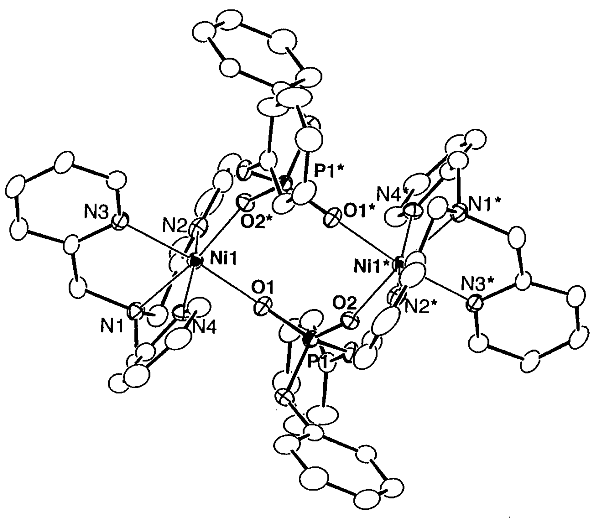


Figure 1. The ORTEP view of complex (**1**) The counter ions (perchlorate) are omitted for clarity. Selected distances (Å) and angles(deg):

Ni(1) O(1)	2.053(3);	Ni(1) O(2)	2.032(3);
Ni(1) N(1)	2.113(4);	Ni(1) N(2)	2.065(5);
Ni(1) N(3)	2.084(4);	P(1) O(1)	1.476(3);
P(1) O(2)	1.471(3);	Ni(1) N(4)	2.058(5);
O(1) Ni(1) O(2)	94.0(1);	O(1) Ni(1) N(1)	91.8(1);
O(1)Ni(1) N(2)	84.0(1);	O(1) Ni(1) N(3)	173.2(1);
O(1) Ni(1) N(4)	90.1(1);	O(2) Ni(1) N(1)	172.8(1);
O(2) Ni(1) N(2)	96.0(2);	O(2) Ni(1) N(3)	92.7(1);
O(2) Ni(1) N(4)	101.6(1);	N(1) Ni(1) N(2)	80.2(2);
N(1) Ni(1) N(3)	81.6(1);	N(1) Ni(1) N(4)	82.7(2);
N(2) Ni(1) N(3)	96.3(2);	N(2) Ni(1) N(4)	161.8(2);
N(3) Ni(1) N(4)	87.6(2);	O(1) P(1) O(2)	122.2(2).

torted octahedral coordination environment with diphosphate anions bridging in syn-anti mode. The intra-ring O(1')-P(1)-O(2) angle was expanded by ca. 10 ° from the ideal value to 122.2(2)°, whereas the other angles around the phosphorus atom only deviate slightly from tetrahedral (O(3)-P(1')-O(4'), 104.7(2)°). The distortion around the phosphoryl center appears to derive from the bridging bidentate coordination mode to the two nickel atoms. A similar expansion has been already found in other dimetallic complexes containing μ-η^2 phosphate ester ligands.[15,16] To our knowledge, **2** is the first nickel(II) complex which possesses two phosphate esters as $(\mu$-$\eta^2)_2$ binding mode with no additional ligand between the two metals,[15] while similar bridging mode of phosphate esters has been already reported in dinuclear zinc complex.[16] The phosphate diesters in **2** are quite stable, being ineffective for further hydrolytic reaction by **1** and transesterification by **1** in the presence of ethanol.[17]

The reaction pathway to afford **2** seems to limit the catalytic activity for the transesterification. To inhibit the direct nucleophilic attack toward the phosphate ester by the metal-ligated hydroxo moiety and improve the activity of this transesterification system, a synthesis of hydroxo complex with newly-designed sterically hindered ligand is now in progress.

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References and Notes

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11 The authentic samples of diphenyl ethyl phosphate and diethyl phenyl phosphate were readily prepared by the reaction of chlorophosphoric acid diphenyl ester and dichlorophosphoric acid phenyl ester with ethanol and purified by alumina column chromatography with methylene chloride elutant, respectively. The transesterificated products were identified by comparison of their GC retention times and MS spectra and quantified by GC-FID.

12 The dissociation of dinuclear complex **1** to afford monomeric (hydroxo)Ni(II) complex was suggested by the kinetic experiment of hydrolysis reaction of p-nitrophenyl acetate by complex **1** in acetonitrile, see ref. 9. However we have not had concrete evidence for that dissociation reaction yet.

13 Anal. Found C, 51.40; H, 4.06; N, 11.34%. Calcd for **2** $Ni_2C_{60}N_8H_{28}O_8P_2Cl_2$: C. 51.66; H. 4.01; N. 11.03%. IR (KBr, cm^{-1}), ν(C=C) 1603, ν(P-O) 1281, ν(ClO_4), 1130. UV-vis (nm; $\varepsilon/M^{-1}cm^{-1}$) 542 (80), 772 (45), 890 (95).

14 Crystal data for **2**, Mr = 697.7; **2** crystallized in the monoclinic space system with $P2_1/c$, a = 11.193(8), b = 13.070(3), c = 21.069(4) Å, β = 101.90(4)°, V = 3016(2) $Å^3$, Z = 2, Dc = 1.536 g cm^{-3}, μ(Mo-K) = 0.843 mm^{-1}. The $R(Rw)$ value is 5.9(5.6)% for 3894 reflections ($3° < \theta < 55°$, $Fo > 3\sigma(Fo)$). The X-ray data collection was carried out at room temperature. 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.

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17 It is supposed that the added alcohol itself doesn't have any effect to promote the formation of **2** by the treatment of **1** with triphenyl phosphate, since complex **2** can be obtained quantitatively by the reaction of **1** with triphenyl phosphate in MeCN even in the absence of alcohol.