

**Dinuclear Nickel Complexes Modeling the Ni_d(II)-Ni_p(I) State
for the Active Site of Acetyl CoA Synthase****

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Supporting Information

General Procedures. All reactions and manipulation were conducted using standard Schlenk and vacuum line techniques or in a glove box under nitrogen atmosphere. THF, acetonitrile and toluene were purified according to the method described by Grubbs, in which the solvents were passed over columns of activated alumina and copper catalyst supplied by Hansen & Co. Ltd. IR spectra were recorded on a Perkin-Elmer 2000 FT/IR spectrometer. UV–Vis spectra were measured on a JASCO V560 spectrometer. Cyclic voltammogram was recorded on a BSA-660B electrochemical analyzer using a glassy carbon working electrode and 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte; potentials are referred to Ag/AgNO₃ electrode. EPR spectra were collected on a Bruker EMX-plus spectrometer at X-band frequencies with liquid helium cryostat. Magnetic susceptibility measurements for polycrystalline samples were carried out using a Quantum Design MPMSXL superconducting quantum interference device (SQUID) magnetometer under 1.0 T. Elemental analyses were recorded on a LECO-CHNS-932 elemental analyzer where the crystalline samples were sealed in silver capsules under nitrogen. Ni(SDmp)(PPh₃) (Dmp = 2,6-dimesitylphenyl),^[1] Ni(dadt^{Et}),^[2] and Co(dmgBF₂)₂(Me)(Py)^[3] were prepared according to the literature.

Synthesis of Ni(dadt^{Et})Ni(SDmp)(PPh₃) (3). To a toluene solution (30 mL) of Ni(SDmp)(PPh₃) (2, 500 mg, 0.751 mmol) was added Ni(dadt^{Et}) (230 mg, 0.751 mmol) in acetonitrile (20 mL) at room temperature. The resulting dark green solution was stirred for 3 h. The solution was evaporated to dryness and the solid was extracted with toluene (50 mL). After concentration to 5 mL, the toluene solution was kept at -30 °C to give **3** as brownish green crystals (526 mg, 72% yield). Anal. Calcd for C₅₃H₆₄N₂PS₃Ni₂: C, 65.38; H, 6.625; N, 2.877. Found: C, 64.95; H, 6.851; N, 2.642. UV- vis (THF): λ_{max} (ε, x 10³ M⁻¹cm⁻¹) 698 (1.2), 429 (3.6), 396 nm (4.8).

Reaction of 3 with Co(dmgBF₂)₂(Me)(Py). To a solution of **3** (407 mg, 0.445 mmol) in THF (50 mL) was added a solution of Co(dmgBF₂)₂(Me)(Py) (105 mg, 0.220 mmol) in acetonitrile (10 mL) at -40 °C to afford a dark green solution. After stirring for 24 h

at -40 °C, the solution was evaporated to dryness and the crude product was washed with Et₂O and extracted with THF. Crystallization from THF/hexane gave Ni(dadt^{Et})Ni(Me)(SDmp) (**3**)^[4] (51 mg, 34% yield) as red crystals.

Reaction of 3 with Co(dm_gBF₂)₂(Me)(Py) and CO. To a solution of **3** (300 mg, 0.328 mmol) in THF (30 mL) was added a solution of Co(dm_gBF₂)₂(Me)(Py) (77 mg, 0.16 mmol) in acetonitrile (8 mL) at -40 °C to afford a dark green solution. After stirring for 24 h at -40 °C, the solution was degassed with two freeze–pump–thaw cycles, and filled with 1 atm CO. After stirring for 4 h at -40 °C, the solution was warmed to room temperature and evaporated to dryness. The residue was separated by silica gel column chromatography eluted by ether to afford CH₃C(O)SDmp^[4] (56 mg, 90% yield) as a white powder.

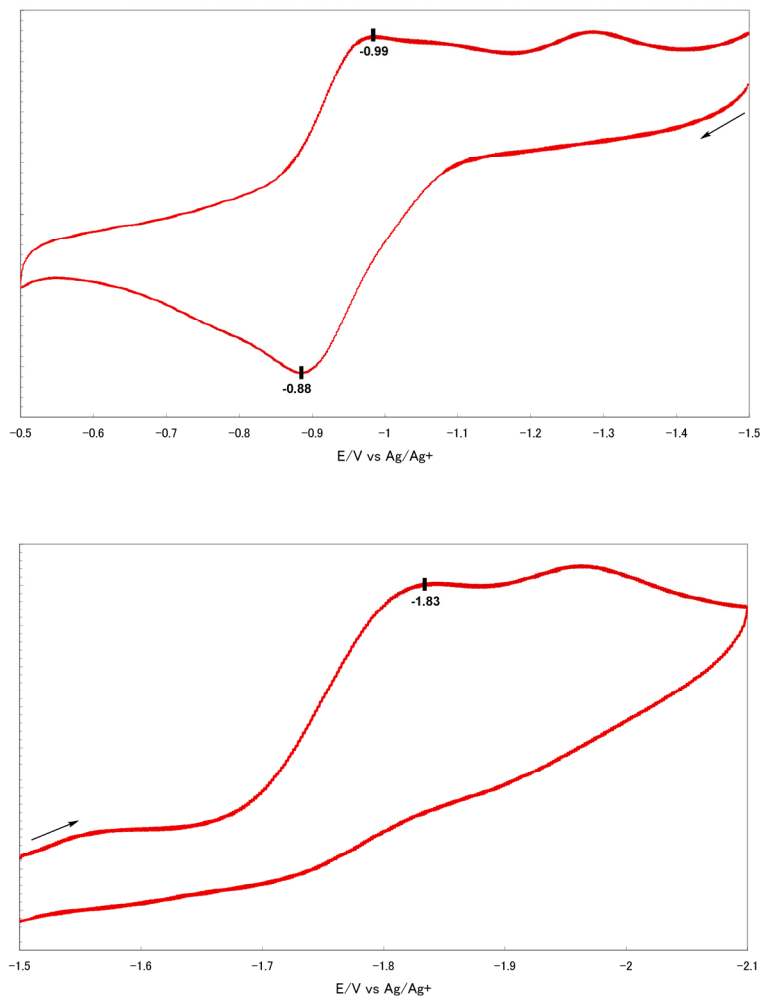
X-ray Structural Analysis of 3•toluene. The crystal contains **3** and a toluene molecule in the asymmetric unit. The single crystal was mounted on a loop using oil (CryoLoop, Immersion Oil type B: Code 1248, Hampton Laboratories, Inc.). Diffraction data was collected at -100 °C under a cold nitrogen stream on a Rigaku AFC8 equipped with a Saturn 70 CCD area detector, equipped with a graphite monochromatized MoK α source ($\lambda = 0.71070$ Å). Data was collected on 1200 oscillation images with oscillation range of 0.3°. The frame data were integrated and corrected for absorption using a Rigaku/MSO CrystalClear program package. The structure was solved by a direct method (SIR-97), and was refined by full-matrix least squares on F^2 using SHELXL-97⁵ in a Rigaku/MSO CrystalStructure program package. Anisotropic refinement was applied to all non-hydrogen atoms except for the disordered atoms, and all hydrogen atoms were put at the calculated positions. Crystal data: C₆₀H₇₂N₂PS₃Ni₂; orthorhombic; $P2_12_12_1$ (#19); $a = 13.5400(17)$, $b = 14.7402(19)$, $c = 27.322(4)$ Å; $V = 5452.9(12)$ Å³; $Z = 4$; $T = 173$ K; $\lambda = 0.71073$ Å; $F(000) = 2260$; $\mu =$

0.874 cm⁻¹; $\rho_{calc} = 1.298 \text{ g cm}^{-3}$; 44205 reflections ($2\theta < 55.0^\circ$), 12301 unique ($R_{int} = 0.040$); $RI = 0.0477$ ($I > 2\sigma(I)$), $wR2 = 0.1672$ (all data), GOF = 1.104, Flack parameter = $-0.043(13)$. CCDC-373907 contain the supplementary crystallographic data for **3**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Selected Bond Distances (Å) and Angles (deg) for **3**

	distance/angle
Ni(1)-N(1)	2.008(3)
Ni(1)-N(2)	2.019(3)
Ni(1)-S(1)	2.1925(12)
Ni(1)-S(2)	2.1848(12)
Ni(2)-S(1)	2.3529(12)
Ni(2)-S(2)	2.3995(13)
Ni(2)-S(3)	2.2273(12)
Ni(2)-P	2.2309(12)
Ni(1)-Ni(2)	2.6811(7)
N(1)-Ni(1)-N(2)	100.07(15)
N(1)-Ni(1)-S(1)	88.76(11)
N(2)-Ni(1)-S(2)	88.24(11)
S(1)-Ni(1)-S(2)	82.96(4)
S(1)-Ni(2)-S(2)	75.18(4)
S(1)-Ni(2)-P	108.07(4)
S(2)-Ni(2)-P	100.45(4)
S(1)-Ni(2)-S(3)	110.51(4)
S(2)-Ni(2)-S(3)	111.66(4)
S(3)-Ni(2)-P	134.62(4)

Figure S1. Cyclic Voltammogram of **3** in THF (2 mM solution) containing 0.2 M [n-Bu₄N][PF₆] at 298 K with 100 mV s⁻¹ scan rate.



References

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