Valence Tautomerism

Chemical Control of Valence Tautomerism of Nickel(II) Semiquinone and Nickel(III) Catecholate States**

*Hideki Ohtsu and Koji Tanaka**

Transition-metal complexes with dioxolene ligands have been attracting much attention because of their characteristic ligand-localized redox reactions among the three redox states of quinone (Q), semiquinone (SQ), and catecholate (Cat) in addition to metal-centered redox reactions.[1] Interest has especially been paid to interconversion of valence tautomers in the metal–dioxolene framework.[1] Valence tautomers are characterized by displacement of electron density to one redox center or the other, for example, M^{II}-SQ

[*] Dr. H. Ohtsu, Prof. K. Tanaka
Institute for Molecular Science, CREST
Japan Science and Technology Agency (JST)
38 Nishigonaka, Myodaiji, Okazaki, Aichi, 444-8585 (Japan)
Fax: (+81) 564-55-5245
E-mail: ktanaka@ims.ac.jp

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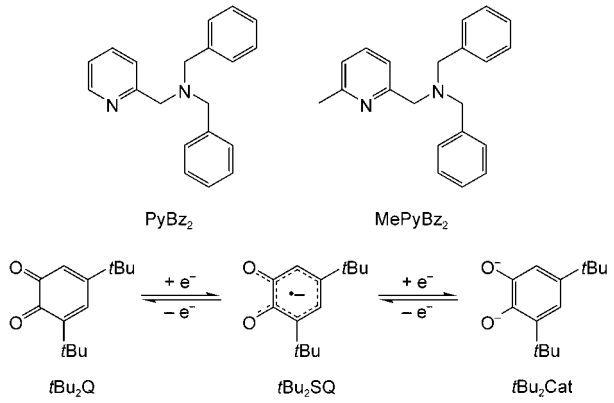
and M^{III}-Cat compounds, which interconvert by intramolecular electron transfer between the two redox centers. Knowledge gathered for a number of metal complexes with dioxolene[2] and other redox-active ligands[3–5] showing valence-tautomeric behavior greatly aids in exploiting this phenomenon for molecular switching devices.[6] However, neither nickel dioxolene complexes exhibiting interconversion of valence tautomers nor control of valence tautomerism by modification of electron-donor ability of ligands to central metal atoms has been reported so far.

We report herein the synthesis and characterization of nickel(II) semiquinonato and nickel(III) catecholato complexes containing bidentate ligands with modulated nitrogen-donor ability,[7] namely, $[Ni^{II}(PyBz_2)(tBu_2SQ)]PF_6$ (**1**) and $[Ni^{III}(MePyBz_2)(tBu_2Cat)]PF_6$ (**2**) as the first example for successful control of valence tautomerism between the Ni^{II}-SQ and Ni^{III}-Cat frameworks by fine-tuning of the donor ability of the bidentate ligands to the nickel ion (Scheme 1).

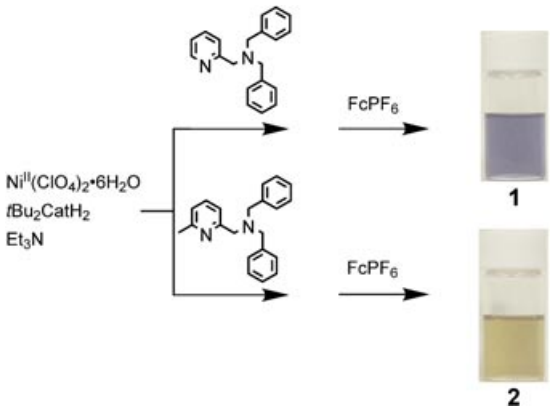


Scheme 1. Structures of bidentate ligands and dioxolene redox forms.

The Ni^{II} semiquinonato complex of $PyBz_2$, **1**, was obtained by mixing $PyBz_2$, tBu_2CatH_2, and $Ni^{II}(ClO_4)_2{\cdot}6H_2O$ in a 1:1:1 ratio in acetonitrile and subsequent addition of 2 equivalents of Et_3N and 1 equivalents of ferrocenium hexafluorophosphate ($FcPF_6$). The Ni^{III} catecholato complex, **2**, was prepared in a similar manner to **1** by using $MePyBz_2$ in place of $PyBz_2$. Solutions of **1** in CH_2Cl_2 are blue, whereas those of **2** are brown (see Scheme 2).

The X-ray molecular structure of **1**[8] is shown in Figure 1. The nickel ion in **1** has a tetracoordinate square-planar environment formed by the pyridine N atom, tertiary amine N atom, and the two O atoms of the dioxolene ligand. The C(1)–O(1) and C(2)–O(2) bond lengths of the dioxolene ligand in **1** are 1.305(5) and 1.294(5) Å, respectively. These C–O bond lengths are consistent with those of nickel(II) semiquinonato complexes reported so far.[9] Although many attempts to prepare single crystals of **2** suitable for X-ray structure determination failed, its coordination geometry is safely concluded to be distorted square-planar on the basis of EPR measurements.

The EPR spectrum of **1** in CH_2Cl_2 at 77 K (Figure 2a) exhibits a sharp isotropic signal with a g value of 2.0066,[10] close to the free-spin value ($g = 2.0023$), which can safely be



Scheme 2. Synthesis of **1** and **2**.

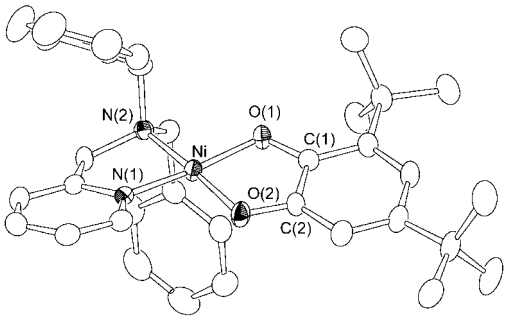


Figure 1. ORTEP view of **1**. Hydrogen atoms and counteranion are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ni–N(1) 1.858(3), Ni–N(2) 1.918(3), Ni–O(1) 1.860(3), Ni–O(2) 1.843(3), C(1)–O(1) 1.305(5), C(2)–O(2) 1.294(5); N(1)-Ni-N(2) 86.7(1), N(1)-Ni-O(1) 172.8(1), N(1)-Ni-O(2) 93.6(1), N(2)-Ni-O(1) 93.9(1), N(2)-Ni-O(2) 175.1(1), O(1)-Ni-O(2) 86.5(1).

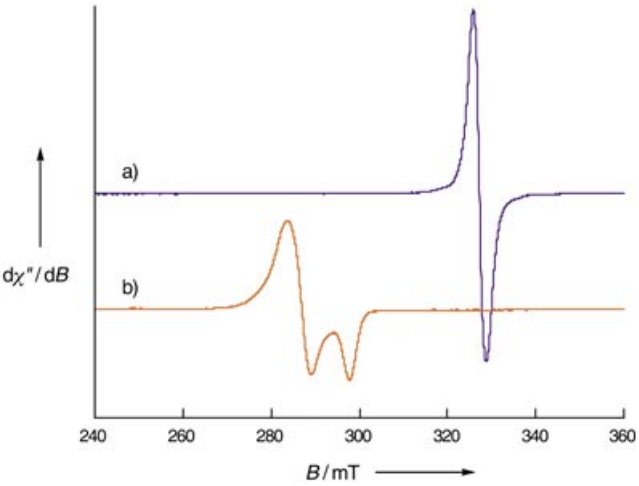


Figure 2. EPR spectra of a) **1** (10^{-3} M) and b) **2** (10^{-3} M) in CH_2Cl_2 at 77 K.

assigned to a ligand-centered radical species composed of low-spin d^8 Ni^{II} ($S = 0$) and the semiquinone ($S = 1/2$) framework. Indeed, the C–O bond lengths of **1** determined by X-ray analysis agree well with those of semiquinone radicals (see

above). In contrast to **1**, an anisotropic signal ($g_\perp = 2.29$, $g_\parallel = 2.20$, $g_{iso} = 2.26$) is observed in the EPR spectra of **2** (Figure 2b).[10] The significantly larger g value of **2** ($g_{iso} = 2.26$) compared with that of **1** ($g = 2.0066$) apparently results from an unpaired electron localized on the metal center. Thus, the electronic structure of **2** is explained by a combination of low-spin d^7 Ni^{III} ($S = 1/2$) and catecholate ($S = 0$). Furthermore, the EPR parameters ($g_\perp = 2.29$, $g_\parallel = 2.20$) provide valuable information about the coordination environment of the nickel(III) ion, which is a distorted square-planar structure with a d_{z^2} ground state.[11] The oxidation states of nickel in **1** and **2** were further confirmed by X-ray photoelectron spectra. The observed binding energy of the Ni $2p_{3/2}$ signals at 854.9 (**1**) and 856.1 eV (**2**) is consistent with oxidation states of Ni^{II} and Ni^{III}, respectively.[12]

Such a drastic difference in the electronic states of **1** and **2** can be ascribed to the steric effect induced by the *o*-methyl group[13–15] in the $MePyBz_2$ ligand. This group weakens the coordination of the pyridine moiety to the nickel ion compared with the unsubstituted $PyBz_2$ ligand. As a result, the dioxolene ligand of **2** binds to the nickel ion more strongly than that of **1**, and this results in the displacement of electron density to form the Ni^{II}-SQ and Ni^{III}-Cat frameworks in **1** and **2**, respectively.

Experimental Section

The complexes were synthesized under nitrogen atmosphere.

1: $Ni(ClO_4)_2 \cdot 6H_2O$ (0.366 g, 1.0 mmol) was added to a solution of $PyBz_2$ (0.288 g, 1.0 mmol) and tBu_2CatH_2 (0.222 g, 1.0 mmol) in acetonitrile (20 mL), and triethylamine (0.202 g, 2.0 mmol) was then added to the resulting solution. $FcPF_6$ (0.331 g, 1.0 mmol) was added to the mixture, and the solution was stirred for 2 h at room temperature. After removal of the solvent under reduced pressure, the resulting residue was dissolved in dichloromethane, and ammonium hexafluorophosphate (0.326 g, 2.0 mmol) was added to the solution. The mixture was stirred overnight at room temperature, and insoluble material was removed by filtration. Addition of pentane to the filtrate gradually gave a blue powder that was collected by filtration and recrystallized from dichloromethane/pentane. Yield: 0.380 g (53.4%). Elemental analysis (%) calcd for $C_{34}H_{40}F_6N_2O_2Ni_1P_1$: C 57.33, H 5.66, N 3.93; found: C 57.14, H 5.62, N 3.90. ESI-MS: m/z: 566 $[M-PF_6]^+$.

Complex **2** was prepared in the same manner as **1** by using $MePyBz_2$ instead of $PyBz_2$. Yield: 0.259 g (35.7%). Elemental analysis (%) calcd for $C_{35}H_{42}F_6N_2O_2Ni_1P_1 \cdot 0.5CH_3CN$: C 57.89, H 5.87, N 4.69; found: C 57.63, H 6.04, N 4.51. ESI-MS: m/z: 580 $[M-PF_6]^+$.

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[8] X-ray crystal structure determination was carried out on a Rigaku/MSC Mercury CCD diffractometer equipped with a Rigaku GNNP low-temperature device. Data were collected at 173 K under cold nitrogen gas with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). Crystallographic data for **1**: $C_{34}H_{40}F_6N_2O_2Ni_1P_1$, $M_r = 712.37$, blue crystals, monoclinic, $P2_1/c$, $a = 11.496(4)$, $b = 29.01(1)$, $c = 11.271(4)$ Å, $\beta = 114.390(4)°$, $V = 3423(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.382$ g cm^{-3}, $\mu = 6.79$ cm^{-1}, $R = 0.058$ ($I > 2.0\sigma(I)$), $R_w = 0.059$ ($I > 2.0\sigma(I)$), 7760 measured reflections, 7627 independent reflections, 415 parameters. CCDC-233975 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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