

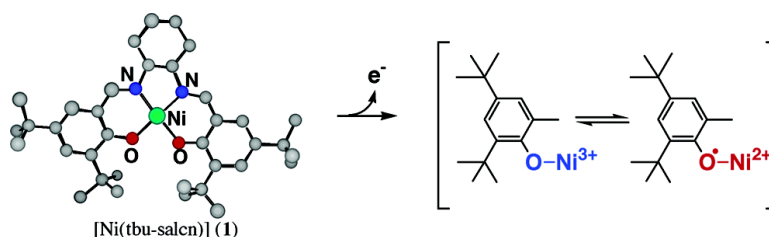
Communication

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 Ni(III)–Phenolate and Ni(II)–Phenoxy Radical States**

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## One-Electron Oxidized Nickel(II)–(Disalicylidene)diamine Complex: Temperature-Dependent Tautomerism between Ni(III)–Phenolate and Ni(II)–Phenoxy Radical States

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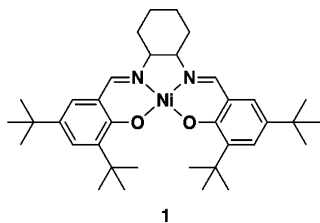
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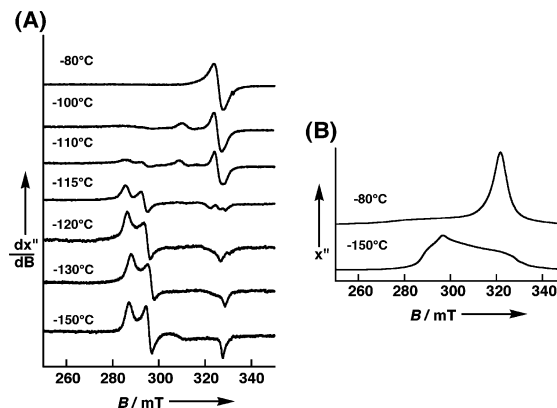
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Formation of the phenoxy radical in galactose oxidase<sup>1</sup> and metal complexes has attracted much attention, and a number of studies have been reported.<sup>2,3</sup> The electronic structures of one-electron oxidized forms of metal–phenolate complexes are known to depend mainly on the metal ions.<sup>2–4</sup> Although most oxidized metal–phenolate complexes have only one characteristic oxidation state, either a high-valent metal–phenolate or a metal–phenoxy radical state, complexes such as oxidized nickel–porphyrin complexes have been reported to be in a temperature-dependent tautomerism between the Ni(III)–porphyrin and Ni(II)–porphyrin  $\pi$ -cation radical states.<sup>5–9</sup> In the course of the studies on metal–phenoxy radical complexes,<sup>10</sup> we prepared a mononuclear nickel(II)–bis-(salicylidene)diamine complex and characterized its one-electron oxidized form, where the site of oxidation has been found to be temperature dependent.

A chelating N<sub>2</sub>O<sub>2</sub>-donor ligand, *N,N'*-bis(3',5'-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (H<sub>2</sub>tbu-salcn),<sup>11</sup> reacted with Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and triethylamine in 1:1 CH<sub>3</sub>OH–CH<sub>2</sub>Cl<sub>2</sub> to give a low-spin square-planar complex [Ni(tbu-salcn)] (**1**) as brownish yellow crystals.<sup>12,13</sup> The cyclic voltammogram (CV) of **1** exhibited



two quasi-reversible redox waves ( $E_{1/2} = 0.88$  and  $1.22$  V vs Ag/AgCl), and electrochemical oxidation at  $1.0$  V in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M tetrabutylammonium perchlorate) revealed a transfer of 0.9 electron per molecule with a concomitant color change from brown to greenish yellow at  $-40$  °C. The absorption spectrum of oxidized **1** exhibited characteristic new peaks at  $\lambda$  ( $\epsilon/M^{-1} \text{ cm}^{-1}$ ) = 311 (9100), 374 (7200), 430 (3500), 881 (1000), and 1103 (3000) nm in CH<sub>2</sub>Cl<sub>2</sub>. Both electrochemical oxidation and chemical oxidation by Ce(IV) gave the same oxidized species. These electrochemical and absorption spectral features of one-electron oxidized **1** at room temperature are different from those of the reported one-electron oxidized Ni(II)–Schiff base complexes.<sup>14a</sup> The ESR spectrum (Figure 1) of the oxidized complex in CH<sub>2</sub>Cl<sub>2</sub> at temperatures below  $-120$  °C indicated a rhombic symmetry and a large  $g$  tensor anisotropy ( $g_1 = 2.30$ ,  $g_2 = 2.23$ ,  $g_3 = 2.02$ , and  $g_{av} = 2.18$ ) typically associated with nickel-centered oxidized species.<sup>14</sup> The



**Figure 1.** ESR spectra of one-electron oxidized **1** in CH<sub>2</sub>Cl<sub>2</sub> ( $5.0 \times 10^{-4}$  M). (A) Temperature dependence of the derivative spectra; (B) integrated spectra at  $-80$  and  $-150$  °C. Microwave power, 1 mW; modulation amplitude, 0.63 mT.

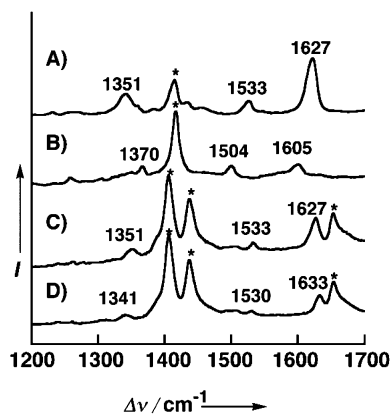
oxidized complex at  $< -120$  °C can thus be formulated as a Ni(III)–phenolate complex with the metal center in a low-spin  $^2A_1$  ( $d_{z^2}$ ) ground state.<sup>15</sup> In contrast to this, an isotropic signal appeared at  $g_{iso} = 2.04$  with the decrease of the rhombic ESR signals in the temperature range from  $-115$  to  $-100$  °C (some portions remained unfrozen) (Figure 1A). The integrated spectra showed that the spin number remained essentially the same in this temperature range, the amount of unpaired electron being more than 0.85 (Figure 1B). The isotropic  $g_{iso} = 2.04$  signal is assigned to a species of predominantly phenoxy character. This  $g$  value is, however, substantially larger than typical values for phenoxy radicals (2.009–2.002) and indicates a nonnegligible contribution from the Ni(III) character, the extent of which may be estimated as 22% from the  $\Delta g$  values ( $=g - 2.00$ ) of this signal and the Ni(III) signal ( $g_{av} = 2.18$ ). The ESR spectral change with temperature was reversible for the first few cycles, showing that the oxidation state of the nickel center is temperature dependent.

The spectral properties of oxidized **1** were found to be dependent on the solvent. In *N,N*-dimethylformamide (DMF), the ESR spectrum of one-electron oxidized **1** at  $< -80$  °C exhibited characteristic signals of an axially symmetrical  $S = 1/2$  Ni(III)–Schiff base complex ( $g_1 = 2.27$ ,  $g_2 = 2.22$ ,  $g_3 = 2.02$ , and  $g_{av} = 2.17$ ), while the spectrum at room temperature showed an isotropic signal at  $g_{iso} = 2.18$ , which is in good agreement with the present value obtained at  $-120$  °C in CH<sub>2</sub>Cl<sub>2</sub> and reported  $g_{av}$  values.<sup>9,14</sup> The results show that in DMF a Ni(III)–phenolate complex is formed irrespective of the temperature. The absorption spectrum of oxidized **1** in DMF at room temperature exhibited peaks at  $\lambda$  ( $\epsilon/M^{-1} \text{ cm}^{-1}$ ) = 332 (11 800), 414 (5900), 464 (5600), 630 (420), and 1134 (390) nm, which correspond well with those of the

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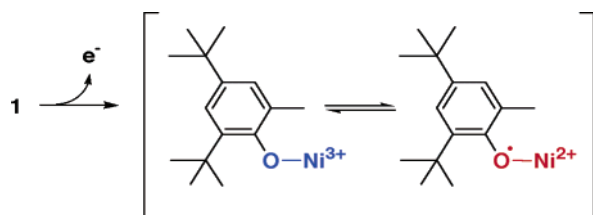
**Figure 2.** Resonance Raman spectra of **1** and one-electron oxidized **1** (2.0 mM) at  $-45\text{ }^{\circ}\text{C}$  ( $\lambda_{\text{ex}} = 413.1\text{ nm}$ , 20 mW). (A) **1** in  $\text{CH}_2\text{Cl}_2$ ; (B) one-electron oxidized **1** in  $\text{CH}_2\text{Cl}_2$ ; (C) **1** in DMF; (D) one-electron oxidized **1** in DMF. The asterisks denote the solvent peaks.

reported Ni(III)–Schiff base complexes.<sup>14a</sup> Interestingly, these absorption peaks are different from those observed for oxidized **1** in  $\text{CH}_2\text{Cl}_2$ , whose intense band at 1103 nm ( $\epsilon = 3000$ ) is absent in DMF. Because this band was not observed for Ni(III)–Schiff base complexes,<sup>14a</sup> we may assign it to the intervalence transition (IT) between the Ni(II)–phenoxyl radical and Ni(III)–phenolate states.

The resonance Raman spectrum of oxidized **1** in the  $1400\text{--}1700\text{ cm}^{-1}$  range obtained in  $\text{CH}_2\text{Cl}_2$  at  $-45\text{ }^{\circ}\text{C}$  exhibited two intense bands at  $1504$  and  $1605\text{ cm}^{-1}$  (Figure 2B), which are assigned to the characteristic  $\nu_{7a}$  and  $\nu_{8a}$  vibrational modes of phenoxyl radicals predominantly including the C–O stretching and the  $\text{C}_{\text{ortho}}\text{--C}_{\text{meta}}$  stretching vibrations, respectively.<sup>3,16–20</sup> The positions of the bands as well as their Raman intensity ratio can be used for distinguishing between coordinated and uncoordinated phenoxyl radicals.<sup>3,17</sup> The frequency difference,  $\nu_{8a} - \nu_{7a}$ , and the Raman intensity ratio,  $I(\nu_{8a})/I(\nu_{7a})$ , have been reported to be  $>90\text{ cm}^{-1}$  and  $>1$ , respectively, for metal-coordinated phenoxyl radicals and  $<90\text{ cm}^{-1}$  and  $<0.1$ , respectively, for uncoordinated radicals.<sup>3,16–20</sup> Oxidized **1** at  $-45\text{ }^{\circ}\text{C}$  exhibited  $\nu_{8a} - \nu_{7a} = 101\text{ cm}^{-1}$  and  $I(\nu_{8a})/I(\nu_{7a}) \approx 1$  (Figure 2B), which are close to the values for a coordinated phenoxyl radical species, substantiating that it is in the Ni(II)–phenoxyl radical state at this temperature. The Ni(II)–phenoxyl radical complex using a 1,4,7-triazacyclononane derivative with a pendant phenol moiety was recently reported to show the  $\nu_{8a} - \nu_{7a}$  value of  $110\text{ cm}^{-1}$ .<sup>16</sup> On the other hand, the Raman spectrum of oxidized **1** in DMF did not exhibit the bands due to the phenoxyl radical (Figure 2D), which is in agreement with the ESR spectral finding that no phenoxyl radical was formed in DMF.

Taken together, the present observations show that one-electron oxidation of **1** in  $\text{CH}_2\text{Cl}_2$  yielded the corresponding Ni(III)–phenolate complex at  $< -120\text{ }^{\circ}\text{C}$  and the Ni(II)–phenoxyl radical species at  $> -100\text{ }^{\circ}\text{C}$ , which is regarded as a tautomerism of the oxidation states governed by temperature (Scheme 1).

#### Scheme 1. Tautomeric Oxidation States of Oxidized **1**



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**Supporting Information Available:** The ORTEP view of **1** drawn with the thermal ellipsoids at the 50% probability level and the atomic labeling scheme and the absorption and ESR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Synthesis of **1**: To a solution of  $\text{H}_2\text{tbu-salcn}^{\text{II}}$  (0.55 g, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.37 g, 1.0 mmol) in  $\text{CH}_3\text{OH}$  (10 mL). A few drops of triethylamine were added to the resulting solution, which gave brown crystals upon standing at room temperature for 2–3 h. Elemental analysis (%) calcd for  $\text{1} \cdot \text{CH}_3\text{OH}$  ( $\text{C}_{37}\text{H}_{56}\text{N}_2\text{O}_3\text{Ni}$ ): C, 69.92; H, 8.88; N, 4.41. Found: C, 70.15; H, 8.60; N, 4.39.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.37$  (s, 2H), 7.27 (d, 2H), 6.86 (d, 2H), 2.93 (m, 2H), 2.42 (m, 2H), 1.90 (m, 2H), 1.38 (s, 18H), 1.31 (m, 4H), 1.23 (s, 18H) ppm.
- The crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 199966. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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