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Changes in redox potential of a nickel-pincer complex bearing reactive secondary thioamide units: Changes caused by deprotonation/protonation reactions on addition of NEt₃ and DBU

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ABSTRACT
Shifts of Ni(II)/Ni(III) redox potentials of a nickel-pincer complex, [Ni(SCS)Br] (SCS = 2,6-bis(benzylaminothiocarbonyl)phenyl), on addition of bases have been investigated. The complex showed two-step shifts of the Ni(II)/Ni(III) redox potential, and the shifts are associated to two-step deprotonation of the SCS ligand on addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). DBU led to a negative shift of the Ni(II)/Ni(III) redox potential by approximately 500 mV.

Keywords: Nickel; Pincer complex; Secondary thioamide; Electrochemistry; UV-vis
In recent years, there have been significant interests in metal-thioamide complexes [1]. In particular, transition metal complexes bearing secondary thioamides have been the subject of recent interest [2]. Several transition metal pincer complexes having reactive secondary thioamide unit(s) (-C(=S)-NH-) in the pincer ligand have been reported as exemplified by the complex shown in Scheme 1 [3].

![Scheme 1. Structure of [Ni(SCS)Br].](image)

Deprotonation of the thioamide unit gives an anionic thioamidate unit, \(-\text{C(=S)-NH-} \rightarrow \text{C(=S)-N^- + H}^+\), which results in an increase in the electron-donating ability of the pincer ligand to the metal center; the oxidation potential of the complex is thought to be shifted to a lower potential by the deprotonation. Actually such an interesting shift in the oxidation potential by addition of base to pincer complexes have been reported for several transition metal complexes [4], however, there has not been such a report for Ni complexes to our knowledge. In this paper, we report the control of the oxidation potential of the secondary thioamide-containing nickel pincer complex, [Ni(SCS)Br] (cf. Scheme 1), by addition of bases.

[Ni(SCS)Br] was prepared as reported previously [3a]. Fig. 1 displays the cyclic voltammogram (CV) of [Ni(SCS)Br] in DMF. As shown in Fig. 1, [Ni(SCS)Br] shows
reversible redox wave at $E_{1/2} = +0.156$ V (vs. Fe$^+/Fe$), which is assigned to an Ni(II)/Ni(III) redox process. The $E_{1/2(Ni(II)/Ni(III))}$ is comparable to that of a previously reported Ni-pincer complex, [Ni(NCN)Br] (NCN = C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-$o,o'$; $E_{1/2(Ni(II)/Ni(III))} = +0.15$ V (vs. SCE)) [5]. The strong electron-donating ability of the pincer ligand seems to give such a lower Ni(II)/Ni(III) potential than that of usual Ni(II) complexes; for instance, $E_{1/2(Ni(II)/Ni(III))}$ of [Ni(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridyl) is observed at 1.66 V vs. SCE (or 1.13 V vs. Fe$^+/Fe$) [6]. The second oxidation peak (shoulder) at $E_{pa} = +0.854$ V may involve oxidation of the SCS ligand.

Effects of the added base on the electrochemical processes were investigated using NEt$_3$ and DBU as a base. Fig. 2 shows changes in the CV curve of [Ni(SCS)Br] on addition of NEt$_3$ in DMF. As shown in Fig. 2, the most part of the original Ni(II)/Ni(III) redox wave of [Ni(SCS)Br] disappears on addition of NEt$_3$, and a new redox wave appears at $E_{1/2} = -0.08$ V vs. Fe$^+/Fe$. When methanesulfonic acid (MSA) is added to the [Ni(SCS)Br]-NEt$_3$ solution, the redox wave of original [Ni(SCS)Br] is recovered completely. These results suggest that the redox potential of [Ni(SCS)Br] can be controlled by deprotonation/protonation reactions of the thioamide unit.

![Scheme 2. Deprotonation-protonation reactions of [Ni(SCS)Br].](image)
NEt₃ is a moderately strong base (pKₐ of NEt₃·H⁺ = 18.8 in MeCN [7]), and NEt₃ is thought to give only a one-proton lost complex [Ni(SCS)Br(-H⁺)]. When a strong organic base, DBU (pKₐ of DBU·H⁺ = 24.3 in MeCN [7]), was added to [Ni(SCS)Br], \( E_{1/2(\text{Ni(II)/Ni(III)})} \) showed second-step shifts to a negative potential. Fig. 3 exhibits CV curves of [Ni(SCS)Br] on addition of DBU. Addition of DBU apparently leads to decrease in the original redox wave at \( E_{1/2} = +0.156 \) V with appearance of new redox couples at \( E_{1/2} = -0.08 \) V and -0.34 V vs. Fe⁺/Fe. After the addition of 10 mol/[Ni(SCS)Br] of DBU, only one redox couple at \( E_{1/2} = -0.34 \) V is observed. When MSA was added to the DBU-treated solution, the redox potential of Ni(II)/Ni(III) was recovered completely. As shown in Scheme 2, the shift of \( E_{1/2(\text{Ni(II)/Ni(III)})} \) of [Ni(SCS)Br] by addition of DBU is thought to be brought by the two-step deprotonation on the SCS pincer ligand.

As described above, the deprotonation/protonation reactions take place reversibly, suggesting that the main framework of [Ni(SCS)Br] is stable. The obtained results indicate that \( E_{1/2(\text{Ni(II)/Ni(III)})} \) of the Ni complex can be changed by a such a large degree of approximately 500 mV by addition of a base and an acid. There have been no precedents for controlling the redox potential of secondary thioamide-coordinated Ni complexes the acid-base reaction to our knowledge.

The acid-base reaction of [Ni(SCS)Br] was also followed by UV-vis spectroscopy. Fig. 4 shows changes of UV-vis spectrum of [Ni(SCS)Br] on addition of DBU. The absorption bands at \( \lambda_{\text{max}} = 448 \) and 503 nm decrease with an increase in the amount of DBU, whereas the absorption bands at \( \lambda_{\text{max}} = 346 \) and 402 nm increase and an isosbestic point is observed at 415 nm. The UV-peaks at 448, 503, 346, and 402 nm are most probably assigned to a metal-to-ligand charge transfer (MLCT) band in view of there
moderately large $\varepsilon$ values. If the UV-vis peaks can be assigned to the MLCT band, the deprotonation by DBU will decrease the electron-accepting ability of the pincer ligand, in agreement with the UV-vis shift to a shorter wavelength. When 2 mol/[Ni(SCS)Br] of MSA was added to the solution, the spectrum is recovered completely. From the above shown CV and UV-vis results, $pK_a(1)$ for the first dissociation step of the N-H proton in the SCS ligand is thought to be comparable or somewhat smaller than that of NEt$_3$·H$^+$ (18.8), and $pK_a(2)$ for the second dissociation step is thought to be positioned between those of NEt$_3$·H$^+$ (18.8) and DBU·H$^+$ (24.3); however, more accurate $pK_a$ values have not been estimated.

In summary, electrochemical behavior of the Ni-pincer complex containing secondary thioamide units, [Ni(SCS)Br], has been elucidated. The two –C(=S)-NH- groups in [Ni(SCS)Br] are thought to undergo reversible deprotonation/protonation reactions on addition of a base and an acid. By the deprotonation of the N-H group, the Ni(II)/Ni(III) redox potential of the Ni center shifted to a lower potential by 240 – 500 mV from that of original [Ni(SCS)Br]. These interesting electrochemical properties of the Ni complex are expected to contribute to design of catalytic systems using Ni complexes [8].

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Figure Captions

**Figure 1.** Cyclic voltammogram of [Ni(SCS)Br] (1.0 mM) in DMF containing 0.1 M [(n-Bu)₄N][PF₆] under N₂ at sweep rate of 100 mV s⁻¹. The irreversible reduction peaks at $E_{pc} = -1.20$ and -1.97 V are assigned to SCS-ligand⁺/⁻ and SCS-ligand⁻/⁺ reductions, respectively.

**Figure 2.** Effects of NEt₃ on cyclic voltammogram of [Ni(SCS)Br] (1 mM) in DMF containing [(n-Bu)₄N][PF₆] (0.1 M) under N₂ at sweep rate of 100 mV s⁻¹. The amount of NEt₃, (a) 0, (b) 2.5, (c) 5.0, (d) 7.5, and (e) 10.0 mol per 1 mol of [Ni(SCS)Br].

**Figure 3.** Effects of DBU on cyclic voltammogram of [Ni(SCS)Br] (1 mM) in DMF containing [(n-Bu)₄N][PF₆] (0.1 M) under N₂ at sweep rate of 100 mV s⁻¹. The amount of DBU, (a) 0, (b) 2.5, (c) 5.0, (d) 7.5, and (e) 10.0 mol per 1 mol of [Ni(SCS)Br].

**Figure 4.** Changes in the absorption spectrum of [Ni(SCS)Br] (spectrum (a)) caused by addition of DBU ((b) 0.5, (c) 1.0, (d) 1.5, and (e) 2.0 mol/[Ni(SCS)Br]) in MeCN under N₂. The inset shows expanded charts. [Ni(SCS)Br] = 2.0 x 10⁻⁴ M.
Figure 1. Cyclic voltammogram of [Ni(SCS)Br] (1.0 mM) in DMF containing 0.1 M [(n-Bu)₄N][PF₆] under N₂ at sweep rate of 100 mV s⁻¹. The irreversible reduction peak at $E_{pc} = -1.20$ V is assigned to the SCS-ligand⁺/⁻ reduction.
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Figure 3. Effects of DBU on cyclic voltammogram of [Ni(SCS)Br] (1 mM) in DMF containing [(n-Bu)₄N][PF₆] (0.1 M) under N₂ at sweep rate of 100 mV s⁻¹. The amount of DBU, (a) 0, (b) 2.5, (c) 5.0, (d) 7.5, and (e) 10.0 mol per 1 mol of [Ni(SCS)Br].
**Figure 4.** Changes in the absorption spectrum of [Ni(SCS)Br] (spectrum (a)) caused by addition of DBU ((b) 0.5, (c) 1.0, (d) 1.5, and (e) 2.0 mol equiv) in MeCN under N₂. The inset shows expanded charts. [Ni(SCS)Br] = 2 x 10⁻⁴ M. In the concentration regions of [Ni(SCS)Br] of DBU in MeCN, only the first deprotonation reaction to give [Ni(SCS)Br(-H⁺)] (cf. Scheme 2) is considered to occur.