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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 NEt<sub>3</sub> and DBU**

Takuya Teratani,<sup>a</sup> Take-aki Koizumi,<sup>\*a</sup> Takakazu Yamamoto,<sup>a</sup> and Takaki Kanbara<sup>\*b</sup>

<sup>a</sup>*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan*

<sup>b</sup>*Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan*

*Fax: +81-45-924-5976; Tel: +81-45-924-5222; E-mail: tkoizumi@res.titech.ac.jp*

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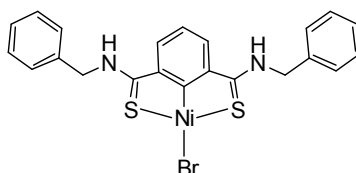
**ABSTRACT**

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*

*spectra; Acid-base equilibrium*

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].



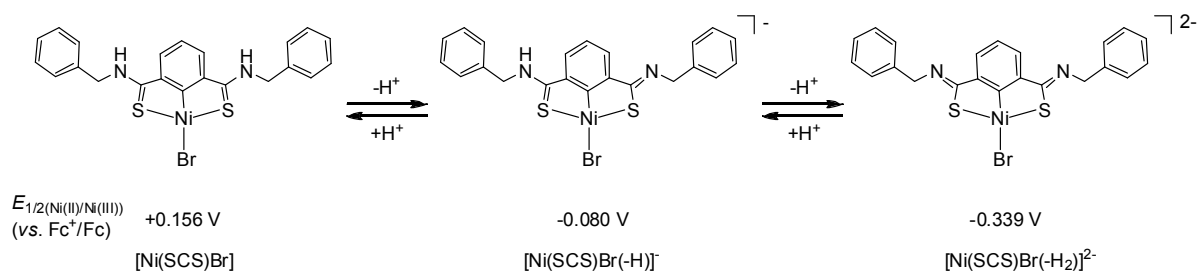
**Scheme 1.** Structure of [Ni(SCS)Br].

Deprotonation of the thioamide unit gives an anionic thioamidate unit,  $\text{-C(=S)-NH-} \longrightarrow \text{-C(=S)-N}^- + \text{H}^+$ , 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.  $\text{Fc}^+/\text{Fc}$ ), which is assigned to an Ni(II)/Ni(III) redox process. The  $E_{1/2(\text{Ni(II)/Ni(III)})}$  is comparable to that of a previously reported Ni-pincer complex,  $[\text{Ni}(\text{NCN})\text{Br}]$  ( $\text{NCN} = \text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}$ ;  $E_{1/2(\text{Ni(II)/Ni(III)})} = +0.15$  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,  $E_{1/2(\text{Ni(II)/Ni(III)})}$  of  $[\text{Ni}(\text{bpy})_3]^{2+}$  ( $\text{bpy} = 2,2'$ -bipyridyl) is observed at 1.66 V vs. SCE (or 1.13 V vs.  $\text{Fc}^+/\text{Fc}$ ) [6]. The second oxidation peak (shoulder) at  $E_{\text{pa}} = +0.854$  V may involve oxidation of the SCS ligand.

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



**Scheme 2.** Deprotonation-protonation reactions of  $[\text{Ni}(\text{SCS})\text{Br}]$ .

NEt<sub>3</sub> is a moderately strong base (pK<sub>a</sub> of NEt<sub>3</sub>·H<sup>+</sup> = 18.8 in MeCN [7]), and NEt<sub>3</sub> is thought to give only a one-proton lost complex [Ni(SCS)Br(-H<sup>+</sup>)]. When a strong organic base, DBU (pK<sub>a</sub> of DBU·H<sup>+</sup> = 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. Fc<sup>+</sup>/Fc. 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  $\text{NEt}_3\cdot\text{H}^+$  (18.8), and  $pK_a(2)$  for the second dissociation step is thought to be positioned between those of  $\text{NEt}_3\cdot\text{H}^+$  (18.8) and  $\text{DBU}\cdot\text{H}^+$  (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  $-\text{C}(=\text{S})-\text{NH}-$  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

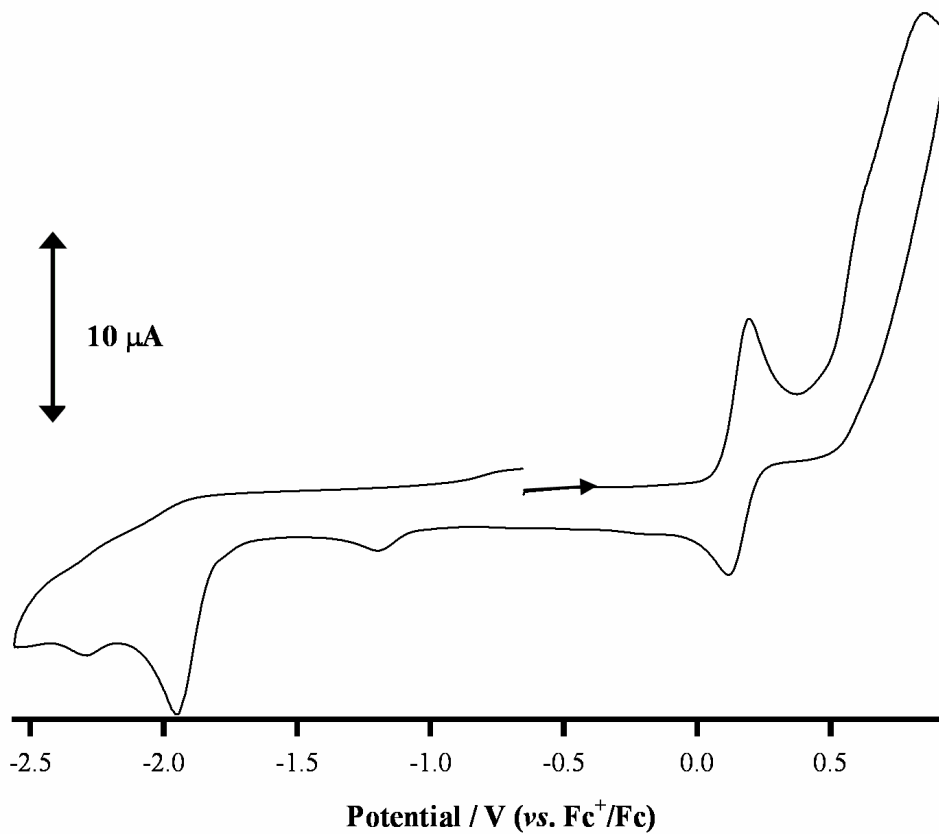
**Figure 1.** Cyclic voltammogram of [Ni(SCS)Br] (1.0 mM) in DMF containing 0.1 M [(*n*-Bu)<sub>4</sub>N][PF<sub>6</sub>] under N<sub>2</sub> at sweep rate of 100 mV s<sup>-1</sup>. The irreversible reduction peaks at  $E_{pc} = -1.20$  and  $-1.97$  V are assigned to SCS-ligand<sup>+ / 0</sup> and SCS-ligand<sup>0 / -</sup> reductions, respectively.

**Figure 2.** Effects of NEt<sub>3</sub> on cyclic voltammogram of [Ni(SCS)Br] (1 mM) in DMF containing [(*n*-Bu)<sub>4</sub>N][PF<sub>6</sub>] (0.1 M) under N<sub>2</sub> at sweep rate of 100 mV s<sup>-1</sup>. The amount of NEt<sub>3</sub>, (a) 0, (b) 2.5, (c) 5.0, (d) 7.5, and (e) 10.0 mol per 1 mol of [Ni(SCS)Br].

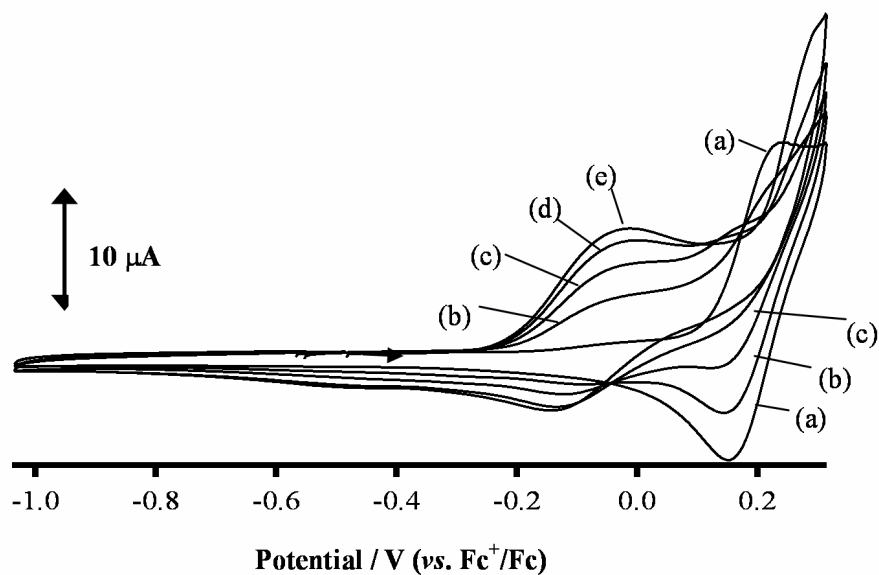
**Figure 3.** Effects of DBU on cyclic voltammogram of [Ni(SCS)Br] (1 mM) in DMF containing [(*n*-Bu)<sub>4</sub>N][PF<sub>6</sub>] (0.1 M) under N<sub>2</sub> at sweep rate of 100 mV s<sup>-1</sup>. The amount of DBU, (a) 0, (b) 2.5, (c) 5.0, (d) 7.5, and (e) 10.0 mol per 1 mol of [Ni(SCS)Br].

**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 N<sub>2</sub>. The inset shows expanded charts. [Ni(SCS)Br] = 2.0 x 10<sup>-4</sup> M.

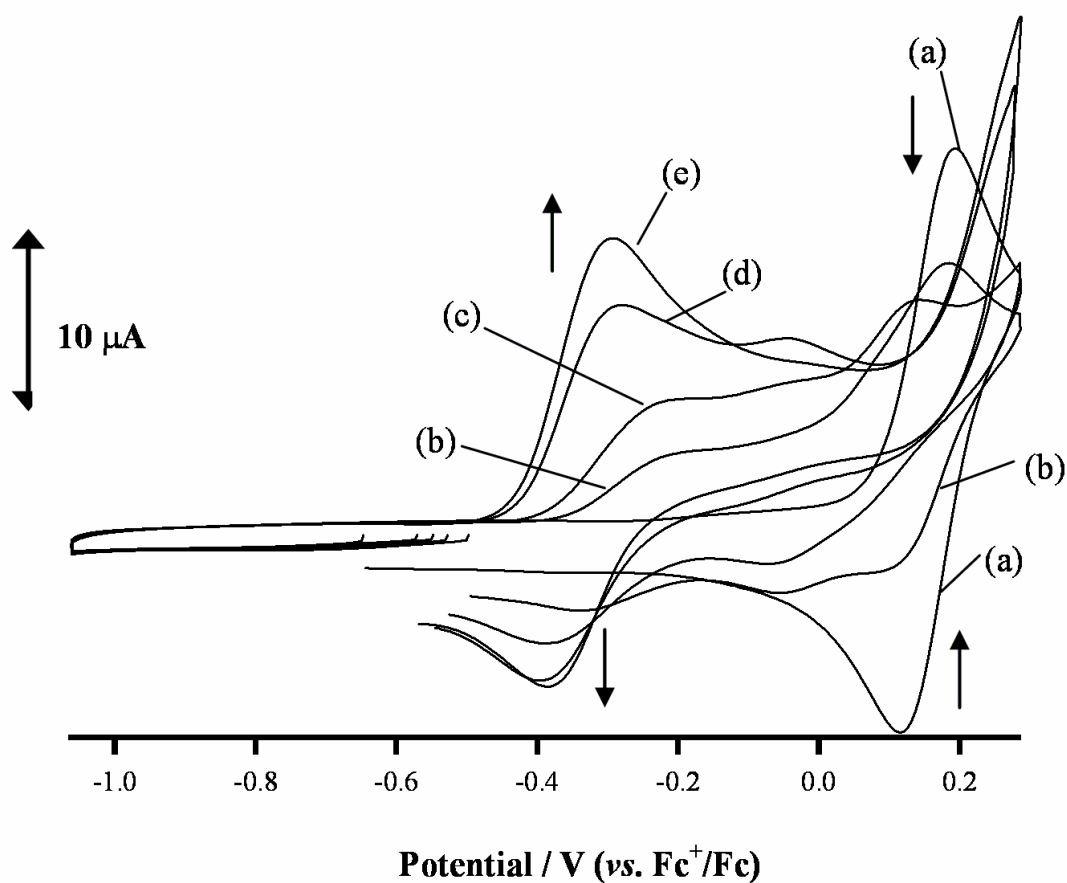




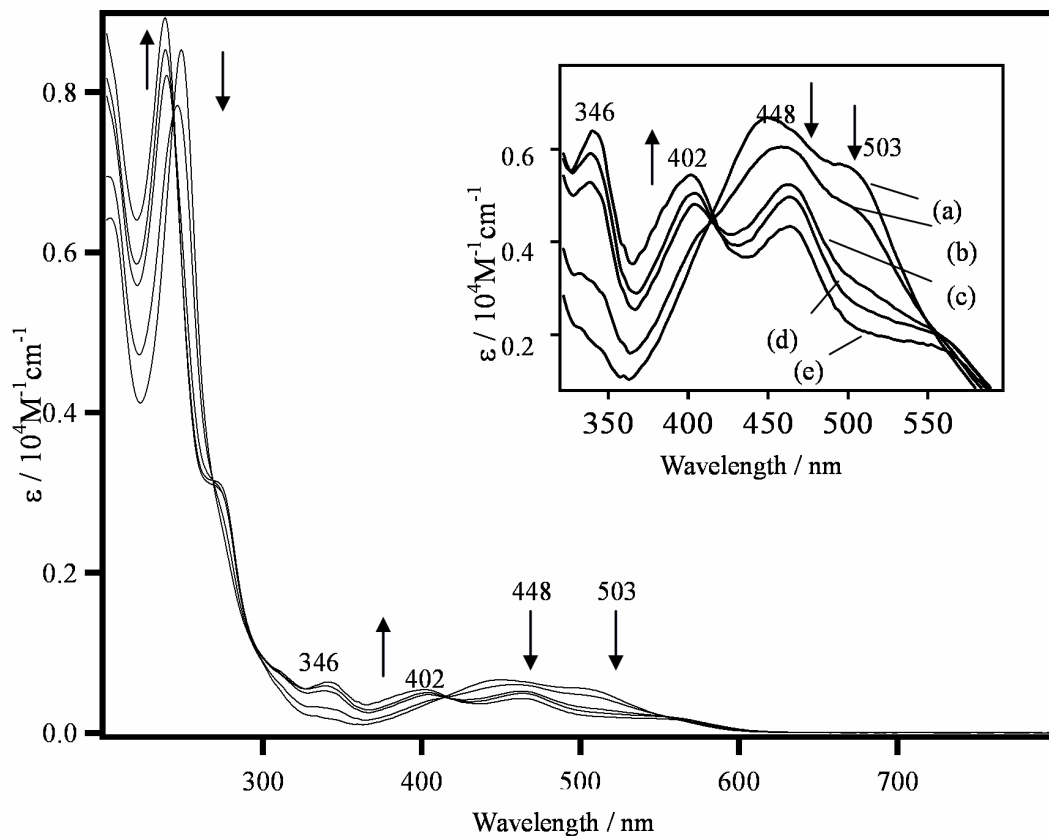
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**Figure 2.** Effects of  $\text{NEt}_3$  on cyclic voltammogram of  $[\text{Ni}(\text{SCS})\text{Br}]$  (1 mM) in DMF containing  $[(n\text{-Bu})_4\text{N}][\text{PF}_6]$  (0.1 M) under  $\text{N}_2$  at sweep rate of  $100 \text{ mV s}^{-1}$ . The amount of  $\text{NEt}_3$ , (a) 0, (b) 2.5, (c) 5.0, (d) 7.5, and (e) 10.0 mol per 1 mol of  $[\text{Ni}(\text{SCS})\text{Br}]$ .



**Figure 3.** Effects of DBU on cyclic voltammogram of [Ni(SCS)Br] (1 mM) in DMF containing [(*n*-Bu)<sub>4</sub>N][PF<sub>6</sub>] (0.1 M) under N<sub>2</sub> at sweep rate of 100 mV s<sup>-1</sup>. 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  $[\text{Ni}(\text{SCS})\text{Br}]$  (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  $\text{N}_2$ . The inset shows expanded charts.  $[\text{Ni}(\text{SCS})\text{Br}] = 2 \times 10^{-4} \text{ M}$ . In the concentration regions of  $[\text{Ni}(\text{SCS})\text{Br}]$  of DBU in MeCN, only the first deprotonation reaction to give  $[\text{Ni}(\text{SCS})\text{Br}(-\text{H}^+)]$  (cf. Scheme 2) is considered to occur.