ニッケル・ピンケーキ複合体に含まれる反応性セカンドリーサイドアミド単位の酸化還元電位の変化: ニトロール/ポルタイン酸を加えた際の脱離/酸化反応に伴う変化

著者

Teratani Takuya, Koizumi Takeaki, Takakazu Yamamoto, Kanbara Takaki

抄録

変化は、ニトロール/ポルタイン酸の添加により引き起こされるニッケル・ピンケーキ複合体の酸化還元電位の変化に伴う。この変化は、セカンドリーサイドアミド単位の脱離/酸化反応によると考えられる。

著作権

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doi: 10.1016/j.inoche.2011.03.001
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

Takuya Teratani, a Take-aki Koizumi, *a Takakazu Yamamoto, a and Takaki Kanbara *b

aChemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan
bTsukuba 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

Received XX XXXXX 2010, Accepted XX XXXXX 2011

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].

Deprotonation of the thioamide unit gives an anionic thioamidate unit, \(-\text{C}(=\text{S})\text{-NH}^-\rightarrow \text{-C}(=\text{S})\text{-N}^- + \text{H}^+\), 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, $[\text{Ni(NCN)}\text{Br}]$ (NCN = C$_6$H$_3$(CH$_2$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 $[\text{Ni(bpy)}_3]^{2+}$ (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 $E_{pa} = +0.854$ 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 $[\text{Ni(SCS)}\text{Br}]$ 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 $[\text{Ni(SCS)}\text{Br}]$ disappears on addition of 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 $[\text{Ni(SCS)}\text{Br}]-\text{NEt}_3$ solution, the redox wave of original $[\text{Ni(SCS)}\text{Br}]$ is recovered completely. These results suggest that the redox potential of $[\text{Ni(SCS)}\text{Br}]$ can be controlled by deprotonation/protonation reactions of the thioamide unit.

![Scheme 2. Deprotonation-protonation reactions of $[\text{Ni(SCS)}\text{Br}]$.](image-url)
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], E₁/₂(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 E₁/₂ = +0.156 V with appearance of new redox couples at E₁/₂ = -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 E₁/₂ = -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 E₁/₂(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 E₁/₂(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 λ_max = 448 and 503 nm decrease with an increase in the amount of DBU, whereas the absorption bands at λ_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, pKa(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 pKa(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 pKa 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].

Acknowledgements

We gratefully acknowledge Dr. Ayako Takeoshi and Mr. Shota Aiki of University of
Tsukuba for measurement of CV.
References

   (d) R. W. Kluiber, Inorg. Chem. 4 (1965) 829;
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 $^+/0$ and SCS-ligand $^{0/-}$ 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)$_4$N][PF$_6$] under N$_2$ at sweep rate of 100 mV s$^{-1}$. The irreversible reduction peak at $E_{pc} = -1.20$ V is assigned to the SCS-ligand$^{+0}$ reduction.
Figure 2. Effects of NEt₃ on cyclic voltammogram of [Ni(SCS)Br] (1 mM) in DMF containing [(d-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 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.