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Nickel(II) complexes bearing a pincer ligand containing thioamide units: Comparison between SNS- and SCS-pincer ligands

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1. Introduction

In recent years, nickel complexes bearing pincer ligands [1–6] have been widely investigated because of their interesting chemical properties. Many reports have been published on the electrochemical behavior of Ni–pincer complexes [2]. The strong electron-donating ability of the pincer ligand leads to a negative shift of the Ni(III)/Ni(II) redox potential [3]. However, most of the reported Ni–pincer complexes have a benzene unit as a central aromatic ring of the pincer ligand. Recently, we have synthesized (κ^3 SNS)-pincer complexes constructed of a pyrrole unit as a central aromatic ring and thioamide units as side arms as shown in Scheme 1 [4].

These complexes are stable in air, and the results of X-ray studies suggest that delocalization of the electrons occur through the central pyrrole ring and the thioamide group. Such a replacement of the central benzene unit by other aromatic or non-aromatic units modulates the chemical and electronic properties of the pincer complexes, and revealing the effect of modulation will be intriguing [3b,d,5]. From the chemical and electrochemical viewpoints, the electronic properties of pincer complexes having a pyr-

ABSTRACT

Nickel(II) complexes bearing a κ^3 SNS pincer ligand, 2,5-bis(benzylaminothiocarbonyl)pyrrolyl (**L1**) and a κ^3 SCS-pincer ligand, 2,6-bis(benzylaminothiocarbonyl)phenyl (**L2**), were synthesized, and their structures and electrochemical properties were elucidated. The crystal structures of [Ni(SNS)Br] (**2**) and [Ni(SCS)Br] (**5**) were determined by X-ray crystallography. The electrochemical and crystallographic data obtained from the complexes revealed that the κ^3 SCS ligand has a stronger electron-donating ability than the κ^3 SNS ligand.

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role unit as a central aromatic ring are considered to be different from those of benzene-centered pincer complexes. However, there have been no reports on the electrochemical properties of pyrrolecentered pincer complexes to the best of our knowledge. In this paper, we compared the SNS- and SCS-pincer ligand frameworks and elucidated the structure and electronic properties of their pincer nickel complexes.

2. Experimental

2.1. General, measurement, and materials

¹H NMR spectra were recorded on a JEOL Lambda-300 NMR spectrometer. ¹³C{¹H} NMR spectra were recorded on a JEOL JNM EX-400 NMR and Bruker Avance III 400 MHz NMR spectrometer. IR spectra were recorded on a JASCO IR-810 spectrophotometer. UV–Vis spectra were measured with a Shimadzu UV-2550 UV–Vis spectrophotometer. Elemental analysis was carried out by the Center for Advanced Materials Analysis (Suzukakedai) in Tokyo Institute of Technology. Thermal analysis was performed with a Yanagimoto Seisakusho Micro Melting Point Apparatus. Electrochemical measurements were performed with a Hokuto Denko HSV-100 automatic polarization system. A conventional three-electrode configuration was used, with glassy carbon working (BAS electrode) and platinum wire auxiliary electrodes (Tokuriki, special order) and an Ag/0.1 M AgNO₃ reference (BAS RE-5). Cyclic



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Scheme 1. Molecular structure of the M-(κ^3 SNS) complex.

voltammograms were recorded at a scan rate of 50 mV s⁻¹. Fc⁺/ Fc = +115 mV versus 0.10 M AgNO₃/Ag, and +425 mV versus SCE. *N*,*N*'-dibenzyl-1*H*-pyrrole-2,5-dicarbothioamide (**L1H**), *N*,*N*'-dibenzyl-benzene-1,3-dicarbothioamide (**L2H**), and [2,5-bis(benzylaminothiocarbonyl)pyrrolyl- κ^3 N¹,S,S']chloronickel (**1**) were prepared according to the literature methods [4].

2.2. Synthesis and characterization

2.2.1. [2,5-Bis(benzylaminothiocarbonyl)pyrrolyl- $\kappa^3 N^1$, S,S' |bromonickel (**2**)

NiBr₂ (43.7 mg, 0.20 mmol) and **L1H** (75.2 mg, 0.20 mmol) were dissolved in EtOH (5 mL) and stirred at room temperature for 24 h. The generated red precipitate was collected by filtration, washed with hexane, EtOH, and water, and dried in vacuo. (77.5 mg, 77% yield). M.p.: 148–150 °C (dec.). *Anal.* Calc. for C₂₀H₁₈BrN₃NiS₂: C, 47.75; H, 3.61; N, 8.35. Found: C, 47.45; H, 3.82; N, 8.13%. ¹H NMR (300 MHz, acetone-*d*₆): δ 10.14 (2H, s), 7.37 (10H, m), 6.57 (2H, s), 4.93 (4H, d, *J* = 6.7 Hz). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 187.732, 144.997, 135.761, 128.747, 128.353, 128.050, 112.359, 50.391. FT-IR (KBr, cm⁻¹): 3280, 3086, 2957, 1558, 1496, 1390, 1344, 1261, 1180, 752, 418.

2.2.2. [2,5-Bis(benzylaminothiocarbonyl)pyrrolyl- $\kappa^3 N^1$,S,S']iodonickel (3)

The procedure for **2** was adopted using NiI₂ (31.3 mg, 0.1 mmol) to afford a red precipitate of **3** (42.0 mg, 77% yield). M.p.: 128–130 °C (dec.). *Anal.* Calc. for $C_{20}H_{18}IN_3NiS_2$: C, 43.67; H, 3.3; N, 7.64. Found: C, 42.81; H, 3.67; N, 7.03%. ¹H NMR (300 MHz, acetone- d_6): δ 10.15 (2H, s), 7.36 (10H, m), 6.67 (2H, d, *J* = 8.1 Hz), 4.93 (4H, d, *J* = 6.7 Hz). ¹³C{¹H} NMR (100 MHz, acetone- d_6): δ 188.529, 144.616, 135.690, 128.764, 128.312, 128.076, 112.252, 50.513. FT-IR (KBr, cm⁻¹): 3289, 3248, 1653, 1387, 1348, 1263, 1240, 1055, 1028, 887, 744, 696.

2.2.3. [2,6-Bis(benzylaminothiocarbonyl)- κ^2 S,S'-phenyl- κC^1]chloronickel (**4**)

NiCl₂·6H₂O (120 mg, 0.5 mmol) and **L2H** (188 mg, 0.5 mmol) were dissolved in toluene (5 mL) and stirred at 110 °C for 72 h. The precipitation were collected by filtration, washed with hexane and small amount of EtOH, and dried in vacuo to afford **4** as a red powder. (163 mg, 70% yield). M.p.: 120–125 °C (dec.). *Anal.* Calc. for C₂₂H₁₉ClN₂NiS₂: C, 56.26; H, 4.08; N, 5.96. Found: C, 55.90; H, 3.94; N, 5.71%. ¹H NMR (300 MHz, acetone-*d*₆): δ 10.13 (2H, s), 7.59 (2H, d, *J* = 7.7 Hz), 7.45 (4H, d, *J* = 7.1 Hz), 7.34 (6H, m), 7.03 (1H, t, *J* = 7.7 Hz), 5.04 (4H, d, *J* = 6.2 Hz). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 197.9, 171.56, 146.71, 135.56, 128.34, 127.58, 127.42, 125.06, 121.42, 49.43 FT-IR (KBr, cm⁻¹): 3360, 3231, 1558, 1454, 1419, 1344, 1288, 1228, 1180, 1022, 924, 754, 733, 700.

2.2.4. [2,6-Bis(benzylaminothiocarbonyl)- κ^2 S,S'-phenyl- κC^1]bromonickel (**5**)

The procedure for **4** was modified using NiBr₂ (43.7 mg, 0.2 mmol) to afford a red precipitate of **5** (54.5 mg, 53% yield).

M.p.: 146–148 °C (dec.). *Anal.* Calc. for $C_{22}H_{19}BrN_2NiS_2$: C, 51.39; H, 3.72; N, 5.45. Found: C, 50.98; H, 4.18; N, 6.07%. ¹H NMR (300 MHz, acetone- d_6): δ 10.18 (2H, s), 7.67 (2H, d, J = 7.9 Hz), 7.50 (4H, d, J = 6.6 Hz), 7.36 (7H, m), 5.08 (4H, d, J = 6.1 Hz). ¹³C{¹H} NMR (100 MHz, acetone- d_6): δ 198.816, 147.506, 136.290, 129.114, 128.325, 128.203, 125.763, 122.188, 50.083. FT-IR (KBr, cm⁻¹): 3362, 3225, 1651, 1553, 1495, 1454, 1290, 1184, 1024, 928, 797, 754, 700.

2.2.5. [2,6-Bis(benzylaminothiocarbonyl)- κ^2 S,S'-phenyl- κ C¹]iodonickel (**6**)

The procedure for **4** was modified using NiI₂ (31.25 mg, 0.1 mmol) to afford a red precipitate of **6** (42 mg, 77% yield). M.p.: 178–185 °C (dec.). *Anal.* Calc. for C₂₂H₁₉IN₂NiS₂: C, 47.09; H, 3.41; N, 4.99. Found: C, 46.61; H, 3.44; N, 4.91%. ¹H NMR (300 MHz, acetone-*d*₆): δ 10.23 (2H, s), 7.74 (2H, d, *J* = 8.0 Hz), 7.49 (2H, d, *J* = 7.9 Hz), 7.36 (8H, m), 7.11 (1H, t, *J* = 8.0 Hz), 5.08 (4H, d, *J* = 6.1 Hz). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 202.061, 147.244, 135.659, 128.704, 128.281, 127.963, 124.231, 121.929, 50.227. FT-IR (KBr, cm⁻¹): 3362, 3264, 1553, 1495, 1455, 1420, 1343, 1291, 1181, 1022, 922, 795, 739, 718, 698.

2.3. Crystal structure determination

Crystals of 2 and 5 for X-ray analysis were obtained as described in the preparations. The crystal of 2 suitable for X-ray diffraction study was obtained by recrystallization from MeCN/EtOH and that of 5 was obtained from DMF. The suitable crystal was mounted on a glass fiber. Data collection for **2** and **5** was performed at $-160 \degree C$ on a Rigaku/MSC Saturn CCD diffractometer with graphite monochromated Mo K α radiation (λ = 0.7107 Å). The data were collected to a maximum 2θ value of 55°. A total of 720 oscillation images were collected. A sweep of data was done using ω scans from -110° to 70° in 0.5° steps, at $\gamma = 45.0^{\circ}$ and $\varphi = 0.0^{\circ}$. The structures were solved by using the CRYSTALSTRUCTURE software package [7]. Atom scattering factors were obtained from the literature. Refinements were performed anisotropically for all non-hydrogen atoms by the full-matrix least-square method. Hydrogen atoms except for H1 and H2 were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. H1 and H2 of 2 and 5 were determined by difference Fourier map and refined isotropically. The residual electron densities were of no chemical significance. Crystal data and processing parameters are summarized in Table 6.

2.4. Computational details

All the TD-DFT calculations and natural population analysis (NPA) reported in this study were carried out using the GAUSSIAN 03 suite of programs [8]. We employed the B3PW91 functional with LANL2DZ basis set implemented in GAUSSIAN 03 programs suits. The molecular and crystal structures of all Ni–pincer complexes derivative have been determined by X-ray diffraction were used for the NPA calculations. Geometry optimization for TD-DFT calculation was carried out under the constraint of C_s symmetry.

3. Results and discussion

3.1. Synthesis of Ni complexes

The pincer ligand **L1H** [4] reacted with NiCl₂ in ethanol at room temperature to give the nickel- κ^3 SNS-pincer complex **1** with a 68% yield as shown in Eq. (1). Similarly, Br-complex **2** and I-complex **3** were obtained from the reaction of **L1H** with NiBr₂ and Nil₂, both with a 77% yield.

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SCS-pincer Ni complexes **4–6** were prepared by the reaction of NiX₂ (X = Cl, Br, I) with **L2H** in toluene as shown in Eq. (2).

1.859(4) Å) [2a,9], and shorter than those in benzene-centered PCP pincer complexes (1.879(2)-1.931(2) Å) [3b,3d,10]. The



All complexes, **1–6**, were characterized by IR and ¹H NMR spectroscopy. In the ¹H NMR spectra of **1**, **2**, and **3**, a broadened N–H resonance of the thioamide group appeared at δ 10.09, 10.14, and 10.15, respectively. The peak was shifted to a lower magnetic field from that of **L1H** (δ 8.98) by 1.11–1.17 ppm. The resonance of the pyrrole N–H proton in **L1H** (δ 10.62) reasonably disappeared for **1–3**. On the other hand, in the ¹H NMR spectra of **4–6**, the resonance based on the N–H in the thioamide group appeared at δ 10.13, 10.18, and 10.23, respectively. They were also shifted to a lower magnetic field from that of the N–H (thioamide) signal of **L2H**.

3.2. Molecular structures of Ni 2 and 5

Figs. 1 and 2 depict the molecular structures of **2** and **5**, respectively, determined by X-ray crystallography, and selected bond lengths and angles of the complexes are summarized in Tables 1 and 2, respectively. Complexes **2** and **5** have an almost planar structure; the sum of the bond angles around the Ni center of **2** and **5** are 359.98° and 360.00°, respectively. The Ni1–C1 bond length in **5** is 1.8630(11) Å, which is similar or longer than those in benzene-centered Ni(II)–NCN pincer complexes (1.814(2)–



Fig. 1. ORTEP drawing of **2**·MeCN with 50% ellipsoidal level. Hydrogen atoms except for H1 and H2 and a solvated MeCN molecule are omitted for clarity.



Fig. 2. ORTEP drawing of **5**·DMF with 50% ellipsoidal level. Hydrogen atoms except for H1 and H2 and a solvated DMF molecule are omitted for clarity.

 Table 1

 Selected bond lengths (Å) and angles (°) of 2·MeCN.

Complex 2			
Ni1-Br1	2.321(2)	Ni1-S1	2.229(3)
Ni1-S2	2.241(4)	Ni1-N1	1.817(12)
S1-C5	1.717(12)	S2-C13	1.703(15)
N2-C5	1.348(7)	N3-C13	1.311(6)
C1-C5	1.473(18)	C4-C13	1.43(2)
Br1-Ni1-N1	177.6(3)	Br1-Ni1-S1	94.38(11)
Br1-Ni1-S2	93.90(12)	S1-Ni1-S2	171.72(15)
S1-Ni1-N1	88.0(3)	S2-Ni1-N1	83.7(3)
Ni1-N1-C1	122.7(8)	Ni1-N1-C4	130.0(9)
N1-C1-C5	115.1(11)	N1-C4-C13	110.1(12)
S1-C5-C1	115.9(9)	S2-C13-C4	119.2(10)
Ni1-S1-C1	98.3(4)	Ni1-S2-C13	97.0(5)

Ni1–Br1 bond length in **2** is 2.321(2) Å, which is shorter than that in **5** (2.3686(2) Å); this is due to the *trans* influence of the benzene unit is more significant than that of the pyrrole unit.

 Table 2

 Selected bond lengths (Å) and angles (°) of 5.DMF.

Complex 5			
Ni1-Br1	2.3686(2)	Ni1-S1	2.1735(3)
Ni1-S2	2.1757(3)	Ni1-C1	1.8630(11)
S1-C7	1.7163(12)	S2-C15	1.7034(12)
N1-C7	1.3144(15)	N2-C15	1.3203(14)
C6-C7	1.4626(15)	C2-C15	1.4614(16)
Br1-Ni1-C1	175.82(3)	Br1-Ni1-S1	94.007(10)
Br1-Ni1-S2	90.797(10)	S1-Ni1-S2	175.195(14)
S1-Ni1-C1	87.73(3)	S2-Ni1-C1	87.47(3)
Ni1-C1-C2	121.46(8)	Ni1-C1-C6	121.56(8)
C1-C6-C7	114.35(10)	C1-C2-C15	114.58(10)
S1-C7-C6	115.83(8)	S2-C15-C2	115.80(8)
Ni1-S1-C7	100.52(3)	Ni1-S2-C15	100.41(4)

In the IR spectra, the v(N-H) band of **1–3** was observed as a shoulder peak at about 3300 cm⁻¹. On the other hand, the v(N-H) peaks of **4–6** were clearly observed at 3360–3362 cm⁻¹. As mentioned above, **L1** in **2** has an electron-delocalized resonance structure as shown in Scheme 2 [4]. The electronic structure appears to give a lower shift of the wavenumber of the v(N-H) band in complexes **1–3**.

The X-ray crystallographic data of 2 reveal that it contains solvated acetonitrile in the crystal state. The two N-H protons in 2 undergo on intermolecular interaction with other molecules. One N–H proton in **2** is positioned near the Br atom in the neighboring Ni complex (N–H···Br, 2.67(11) Å), and the other N–H proton interacts with the N atom in solvated acetonitrile (N-H···N, 2.09(15) Å). Fig. 3a shows the packing structure of 2 MeCN. As shown in Fig. 3a, 2 MeCN forms an alternating network by hydrogen bonding. The N-H hydrogens of 5 DMF also undergo intermolecular interactions. As depicted in Fig. 3b, one of the N-H hydrogen atoms interacts with the Br atom in the neighboring molecule with an Ni-Br···H-N distance of 2.750(15) Å. The other N-H hydrogen interacts with solvated DMF with a C=O···H–N distance of 1.909(13) Å. 2 MeCN and 5 DMF have different packing structures form each other. The packing structure of 2 MeCN is similar to that of the previously reported 1 MeCN [4], and 5 DMF has a packing structure similar to that of a DMF-solvated SCS-Ni-Cl complex [6b].

The electronic spectra of **2** and **5** are shown in Fig. 4, and the spectral data of **1–6** are summarized in Table 3. Complexes **1–3** exhibit intense absorption bands at $\lambda_{max} = 286-292$ and 369–372 nm, which are assigned to the $\pi - \pi^*$ transitions in the SNS pincer



Scheme 2. Delocalization of electrons in the Ni(SNS) complex.



Fig. 3. Packing diagrams of (a) 2-MeCN and (b) 5-DMF.



Fig. 4. Electronic spectra of (a) 2 and (b) 5 in MeCN.

Table 3

UV-Vis spectral data for the complexes in MeCN.

	λ_{max} (nm) ($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)
1	292 (43 100), 372 (16 700)
2	287 (42 700), 369 (9800)
3	246 (24 900), 286 (43 300), 369 (20 200)
4	248 (64 400), 452 (9000)
5	248 (57 400), 444 (8800)
6	246 (69 100), 440 (9250)

able 4	
elected calculated singlet excited-state transitions for complexes for 2 and 5 .	

Complex	Wavelength (nm)	Oscillator strength	Assignment (% of major transition contributing to the band)
2 5	506 437 401	0.0368 0.0724 0.0654	HOMO → LUMO (89%) HOMO-2 → LUMO (46%) HOMO-4 → LUMO (80%)

ligand. Weak absorption is observed in the region of 390–420 nm, which can be assigned to a metal-to-ligand charge transfer (MLCT) band [7,11]. In **4–6**, a significant MLCT band is observed at $\lambda_{max} = 440-452$ nm, whose intensities are stronger than those of **1–3**. The assignments of the π – π ^{*} transition and the MLCT absorption bands were examined by time-dependent density functional



Fig. 6. Cyclic voltammograms of (a) **1** and (b) **4** in MeCN; $0.10 \text{ M} [N(n-Bu)_4]PF_6$, scan rate 50 mV s⁻¹, glassy carbon working electrode.

Table 5Electrochemical data for complexes 1–6.

	<i>E</i> /V (<i>versus</i> Fc ⁺ /Fc)		
	[Ni] ⁺ /[Ni] ⁰	[Ni] ²⁺ /[Ni] ⁺	[Ni] ³⁺ /[Ni] ²⁺
1	$E_{\rm pa} = 0.397$ $E_{\rm pc} = 0.274$	$E_{\rm pa} = 0.768 \; ({\rm irr})$	
2	$E_{\rm pa} = 0.464$ $E_{\rm pc} = 0.223$	$E_{\rm pa} = 0.847 \ ({\rm irr})$	
3	$E_{\rm pa} = 0.457$ $E_{\rm pc} = 0.369$		
4	$E_{\rm pa} = 0.102$ $E_{\rm pc} = 0.008$	$E_{\rm pa} = 0.566 \; ({\rm irr})$	$E_{\rm pa} = 0.807 \; (\rm irr)$
5	$E_{\rm pa} = 0.092$ $E_{\rm pc} = -0.012$	$E_{\rm pa} = 0.362 \ ({\rm irr})$	$E_{\rm pa} = 0.787 \ ({\rm irr})$
6	$E_{\rm pa} = 0.139$ $E_{\rm pc} = -0.098$	$E_{\rm pa} = 0.362 \ ({\rm irr})$	

Condition: Sample: 1 mM/MeCN; electrolyte: $[N(n-Bu)_4]PF_6$ 0.1 M; working electrode: glassy carbon; counter electrode: Pt wire. Sweep rate: 50 mV s⁻¹.

theory (TD-DFT) calculations (Table 4) on isolated complexes. Three-dimensional plots of the HOMOs and LUMOs of **2** and **5**, and their molecular orbitals (MO) are depicted in Fig. 5 using GaussView 4.1 [12]. From the results of the TD-DFT calculation, **2**



Fig. 5. Molecular orbitals (MO) and their levels of (a) 2 and (b) 5 calculated at the B3PW91/LANL2-DZ level, respectively.

Table 6

Crystal data and details of the structure refinement of 2-MeCN and 5-DMF.

	2 ·MeCN	5·DMF
Formula Molecular weight Crystal system Space group a (Å) b (Å) c (Å) a (°)	C ₂₂ H ₂₁ BrN ₄ NiS ₂ 544.16 monoclinic P2 ₁ /c (no. 14) 9.084(10) 16.121(17) 15.850(16)	C ₂₅ H ₂₆ BrN ₃ NiS ₂ O 587.22 monoclinic P2 ₁ /c (no. 14) 9.1750(15) 18.545(3) 14.721(2)
β(°) γ(°)	103.260(5)	96.0577(9)
$V(A^3)$ Z	2259(4) 4	2490.8(7) 4
$\mu (cm^{-1})$ $F(0 0 0)$ $D_{calc} (g cm^{-3})$ No. of unique reflections No. of reflections used	28.265 1016.00 1.479 5083 5083	25.790 1200.00 1.566 5482 5482
No. of variables R1 ^a R Rw ^b	271 0.0808 0.1165 0.1878 ^c	402 0.0253 0.0315 0.0350 ^d

$$\begin{split} R_1 &= \sum ||F_0| - |F_c|| / \sum |F_0| \text{ for } I > 2.0\sigma(I) \text{ data.} \\ R_w &= \sum [w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}. \end{split}$$

b

Wei0067hting Scheme $1/[0.0159F_0^2 + 1.0000\sigma(F_0^2)]$.

d Weighting Scheme $1/[0.0005F_{0}^{2} + 1.0000\sigma(F_{0}^{2})]$.

has a relatively weak absorption at 506 nm that is dominated by a transition from HOMO to LUMO. On the other hand, 5 has two stronger transitions in the MLCT band originating from HOMO-2 to LUMO and HOMO-4 to LUMO. These occupied levels possess a certain amount of weight at the d orbitals of the nickel atom and the π orbitals of the ligand, respectively, and the LUMOs possess a strong ligand character.

3.3. Electrochemical and optical data of the Ni complexes

Cyclic voltammograms (CVs) of 1-6 were recorded in a DMF solution containing 0.10 M $[N(n-Bu)_4]PF_6$ as the supporting electrolyte using a glassy carbon working electrode. The CVs of **1** and 4 in the region of -0.3 to +0.5 V are displayed in Fig. 6, and the electrochemical data of complexes 1-6 are summarized in Table 5. In the region as shown in Fig. 6, 1 exhibits a quasi-reversible wave based on the Ni(III)/Ni(II) redox couple [13] at $E_{1/2}$ = +0.336 V (versus Fc⁺/Fc). The $E_{1/2}$ value of the Ni(III)/Ni(II) redox couple of **4** is observed at +0.055 V (versus Fc⁺/Fc). The occurrence of a more facile oxidation of 4 than that of 1 suggests a higher electron-donating ability of L2 to Ni than that of L1. A similar tendency is also observed for other couples of complexes (2 versus 5 and 3 versus 6, Table 5). These results are consistent with the X-ray crystallographic and electronic spectral data. In almost all cases, many of the Ni-pincer complexes exhibited an irreversible oxidative wave in a more positive region, suggesting the formation of higher oxidized Ni species or oxidation of the thioamide ligand, however, the formed species have not been identified.

The DFT calculation also suggests the higher electron-donating ability of L2 than that of L1. The contour plots of the HOMOs of 2



Fig. 7. Natural charge of (a) 2 and (b) 5 calculated by NPA.

and **5** are shown in Fig. 6. The HOMO level of **2** (-0.208 eV) is slightly deeper than that of **5** (-0.197 eV). We have also calculated the electron densities of **2** and **5** using a DFT method. The atomic charges were estimated by natural population analysis (NPA) [14], which is well known to be less dependent on the basis set than Mulliken population analysis. The NPA charges of **2** and **5** are shown in Fig. 7. These results indicate that the natural charge of the nickel atom of **2** is more positive than that of **5**, which is consistent with the results of the X-ray crystallographic study and cyclic voltammetry.

4. Conclusion

We have elucidated the synthesis, structures, and electrochemical properties of Ni–SNS and Ni–SCS-pincer complexes. The pincer ligands smoothly coordinate to Ni in a tridentate fashion *via* a cyclometalation process. The Ni(III)/Ni(II) redox potentials of complexes **1–6** are significantly influenced by the electronic effects of the N- and C- σ -bonded unit in the pincer ligand. The X-ray crystallography of **2** and **5** indicated that the *trans* influence of **L2** is larger than that of **L1**. These results reveal that the centered benzene unit of **L2** has a higher electron-donating capability to the metal center than centered pyrrole unit of **L1**. These findings are expected to contribute to the modulation of chemical properties of the pincer complexes.

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Appendix A. Supplementary material

CCDC 707890 and 707891 contain the supplementary crystallographic data for **2** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http:// www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.04.012.

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