

Cyclopentadienylnickel thiolate complexes: synthesis, molecular structures and electrochemical detection of sulfur dioxide adducts

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Abstract

Simple reactions between $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)\text{Br}$ and the Schiff-base thiols, 4-HSC₆H₄NC(H)C₄H₂SBr-4' (**1**) and 4-HSC₆H₄NC(H)C₄H₃S (**2**), or organothiols, HSC₆H₄F-4 and HSC₆H₄NH₂-4, produced cyclopentadienylnickel thiolates of the formulae, $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_4\text{H}_2\text{SBr}-4)$ (**3**), $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_4\text{H}_3\text{S})$ (**4**) or $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{SC}_6\text{H}_4\text{X}-4)$ (R = Ph, X = F (**6**) or NH₂ (**7**) and R = Bu, X = F (**5**) or NH₂ (**8**)) which were characterized by a combination of analytical techniques. Complexes **3**, **6** and **7** were structurally characterized by X-ray crystallography, showing that they possess the familiar trigonal geometry around the nickel center. These complexes react with sulfur dioxide, with **5**, **6**, **7** and **8** exhibiting substantial differences between the redox potentials of the pre- and post-SO₂ compounds to suggest that these complexes can be developed as potentiometric SO₂ sensors.

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1. Introduction

Sulfur dioxide coordination to metal complexes continues to attract attention primarily because of environmental concerns about sulfur dioxide and the potential use of such reactions to develop sulfur dioxide scrubbers or sensors. Three main reaction types of sulfur dioxide with metal complexes are known. The best studied of these three reactions is the coordination of sulfur dioxide to a metal centre [1]. The second reaction type is insertion of sulfur dioxide into a bond formed by a central metal atom and another atom [1a–1e,2]. This can either be insertion into a metal–metal bond [1a] or insertion into a metal–ligand bond [1a–1e,2]. Recently Shaver and co-workers [3] reported the insertion of sulfur dioxide into S–S bonds in $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_2$ to form $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_3\text{O}_2$. This constitutes the first ex-

ample of sulfur dioxide insertion into the S–S bond. The third reaction type involves the binding of sulfur dioxide to a soft atom in a ligand, usually sulfur [4] but other atom-binding sites are known [5]. The soft atom in a ligand binds the sulfur dioxide by donating electrons into empty d-orbitals of the sulfur atom of the sulfur dioxide, in a reaction where the soft atom in the ligand behaves as a Lewis base. Such bonds are inherently weak and generally lead to unstable sulfur dioxide adducts compared to compounds formed *via* type 1 and type 2 reactions.

Ligand bound SO₂ is generally found for late-transition metal thiolato complexes. These are either SO₂ bound to the sulfur atom of a bidentate thiolato ligand complex [4b,4c] or SO₂ bound to the sulfur atom of a monodentate thiolato ligand complex [4a,6]. The latter are cyclopentadienylmetal complexes, which our group [6] and others [4a] have studied. Shaver was the first to report the reversible binding of SO₂ to the sulfur atom of cyclopentadienylmetal thiolato phosphine

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complex in 1992 [4a] and showed that the weak sulfur–sulfur interaction is responsible for the reversibility. The isoelectronic nickel analogues [6] show similar reversibility but are too labile to allow solids to be isolated and characterized. As such unequivocal characterization of the NiS(SO₂)R adducts is still lacking. It is however possible to use analytical techniques to establish the formation of labile SO₂ adducts. Previously we have used ¹H NMR spectroscopy as a tool for detecting SO₂-adduct formation [6]. This is based on electronic changes that occur upon adduct formation and hence changes in chemical shift. It is therefore possible that electronic changes that occur when SO₂ adducts are formed can give a different electrochemical response and allow SO₂ to be detected electrochemically. Literature reports show that SO₂ can be detected indirectly by amperometric methods, which involves reduction of the SO₂ and the measurement of the current necessary to maintain a constant concentration of titrant as SO₂ reduces the titrant [7]. Although this method is limited by the presence of other compounds that react with the titrant, it nevertheless demonstrates that electrochemistry can be used to establish the presence of SO₂. A more direct method in which an electrochemical response is produced by stable SO₂-adduct via a change in potential would be more desirable since it would not suffer from such interferences. We report here nickel thiolato compounds and their SO₂ adducts that demonstrate that these nickel thiolato compounds can be used as potentiometric SO₂ sensors.

2. Experimental

2.1. Materials and instrumentation

Analytical grade solvents were dried by standard procedures and stored over activated molecular sieves. However, dichloromethane used for electrochemical experiments was refluxed twice over P₂O₅ for 24 h, distilled under nitrogen and stored over activated molecular sieves. The commercially available chemicals 4-fluorothiophenol, 4-aminothiophenol, 4-bromo-2-thiophenecarboxyaldehyde and 2-thiophenecarboxyaldehyde were obtained from Aldrich and used as received. The nickel starting materials, Ni(η⁵-C₅H₅)(PBU₃)Br [8], Ni(η⁵-C₅H₅)(PPh₃)Br [9] and [Ni(η⁵-C₅H₅)(μ-SC₆H₄NH₂-4)₂] [10] were prepared by the literature procedures. All reactions were performed under a nitrogen atmosphere, but the air and moisture stable complexes that were formed were worked-up in air.

IR spectra were recorded on a Perkin–Elmer Paragon 1000 PC FTIR spectrometer as nujol mulls. ¹H and ³¹P NMR spectra were recorded on a Varian Gemini 2000 spectrometer at 200.00 and 80.96 MHz, respectively, and

referenced to residual CHCl₃ (δ 7.26) internally for ¹H spectra and externally to PPh₃ (δ –5.00) for ³¹P spectra. Electrochemistry experiments were performed on a BAS CV-50W electrochemical analyzer using a three-electrode system that consist of platinum working electrode (1.5 mm diameter), a silver/silver chloride (Ag/AgCl) reference electrode and a platinum wire as a counter electrode. All experiments were carried out under a dry nitrogen atmosphere. Cyclic voltammetry experiments were performed in dichloromethane solutions (10^{–3} M) with [*n*-Bu₄N][BF₄] as supporting electrolyte (0.10 M). Redox potentials were referenced internally to the potential of the oxidation of ferrocene at 0.44 V [11].

2.2. Synthesis of Schiff-base ligands

Schiff-base ligands that were used in synthesising cyclopentadienylnickel complexes were prepared following the procedure described recently [12]. In a typical reaction 4-aminothiophenol was reacted with the aldehyde in ethanol in a 1:1 mole ratio to give compounds **1** and **2** as analytically pure yellow solids.

2.2.1. 4-HSC₆H₄N=C(H)C₄H₂SBr-4' (**1**)

Yield 68%. Anal. Calc. for C₁₁H₈BrNS₂: C, 44.30; H, 2.70; N, 4.70. Found: C, 44.55; H, 2.60; N 4.80%. ¹H NMR(CDCl₃): δ 8.48 (s, 1H, N=CH); 7.52 (d, 2H, J_{HH} = 8.6 Hz, SC₆H₄N=C(H)C₄H₂SBr-4'); 7.39 (m, 2H, SC₆H₄N=C(H)C₄H₂SBr-4'); 7.16 (d, 2H, J_{HH} = 8.6 Hz, SC₆H₄N=C(H)C₄H₂SBr-4'). IR (nujol mull cm^{–1}) ν(C=N): 1604.

2.2.2. 4-HSC₆H₄N=C(H)C₄H₃S (**2**)

Yield 85%. Anal. Calc. for C₁₁H₉NS₂: C, 60.24; H, 4.14; N, 6.39. Found: C, 59.65; H, 4.30; N, 6.50%. ¹H NMR(CDCl₃): δ 8.53 (s, 1H, N=CH); 7.47 (m, 4H, SC₆H₄N=C(H)C₄H₃S); 7.16 (m, 3H, SC₆H₄N=C(H)C₄H₃S). IR (nujol mull cm^{–1}) ν(C=N): 1609.

2.3. Synthesis of nickel thiolato complexes

2.3.1. Ni(η⁵-C₅H₅)(PBU₃)(SC₆H₄N=C(H)C₄H₂SBr-4') (**3**)

To a mixture of 4-HSC₆H₄N=C(H)C₄H₂SBr-4' (0.10 g; 0.34 mmol) and Ni(η⁵-C₅H₅)(PBU₃)Br (0.18 g, 0.34 mmol) was added degassed CH₂Cl₂ (50 mL) followed by excess Et₃N (1.0 mL). The maroon solution gradually turned brownish-green after stirring the mixture for 2 h. The reaction mixture was stirred for 24 h at room temperature to ensure that the reaction was complete. The solvent was removed in vacuo and the residue extracted with toluene (50 mL). The toluene extract was evaporated to dryness and the residue recrystallised from CH₂Cl₂/hexane (1:1) to give dark green X-ray quality crystalline solid. Yield 0.14 g (67%). Anal. Calc. for C₂₈H₃₉BrNSP₃Ni: C, 53.95; H, 6.31; N, 2.26. Found:

C, 53.62; H, 5.83; N, 2.13%. $^1\text{H NMR}(\text{CDCl}_3)$: δ 8.51 (s, 1H, N=CH); 7.62 (d, 2H, $J_{\text{HH}} = 8.8$ Hz, $\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_4\text{H}_3\text{SBr}-4'$); 7.33 (s, 1H, $\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_4\text{H}_3\text{SBr}-4'$); 7.31 (s, 1H, $\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_4\text{H}_3\text{SBr}-4'$); 6.95 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, $\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_3\text{SBr}$); 5.27 (s, 5H, C_5H_5); 1.42 (m, 18H, PBu_3); 0.92 (t, 9H, $J_{\text{HH}} = 7.5$ Hz, PBu_3). IR (nujol mull cm^{-1}) $\nu(\text{C}=\text{N})$: 1595.

2.3.2. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBu}_3)(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_4\text{H}_3\text{S})$ (**4**)

A similar procedure as for **3** was followed using $\text{HSC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{C}_4\text{H}_3\text{S}$ (0.1 g, 0.46 mmol) and $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBu}_3)\text{Br}$ (0.18 g, 0.34 mmol). A green oily product was obtained from which green crystals were isolated after allowing a solution of the product in a 1:1 mixture of CH_2Cl_2 /hexane to stand at -15°C for several days. Yield 0.15 g (60%). Anal. Calc. for $\text{C}_{18}\text{H}_{40}\text{NSPNi}$: C, 61.77; H, 7.41; N, 2.57. Found: C, 61.27; H, 7.56; N, 2.73%. $^1\text{H NMR}(\text{CDCl}_3)$: δ 8.58 (s, 1H, N=C(H)); 7.61 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, $\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_4\text{H}_3\text{S}$); 7.43 (t, 2H, $\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_4\text{H}_3\text{S}$); 7.12 (t, 1H, $\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_4\text{H}_3\text{S}$); 6.95 (d, 2H, $J_{\text{HH}} = 8.6$ Hz, $\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_4\text{H}_3\text{S}$); 5.26 (s, 5H, C_5H_5); 1.44 (m, 18H, PBu_3), 0.91 (t, 9H, $J_{\text{HH}} = 7.5$ Hz PBu_3). IR (nujol mull, cm^{-1}) $\nu(\text{C}=\text{N})$: 1590.

2.3.3. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBu}_3)(\text{SC}_6\text{H}_4\text{F}-4)$ (**5**)

A similar procedure as for **3** was followed using $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBu}_3)\text{Br}$ (0.37 g, 0.79 mmol) and $\text{HSC}_6\text{H}_4\text{F}-4$ (0.12 g, 0.90 mmol). The product isolated was as dark green crystals. Yield 0.17 g, (52%). Anal. Calc. for $\text{C}_{23}\text{H}_{36}\text{FPSNi} \cdot 1/2\text{CH}_2\text{Cl}_2$: C, 56.94; H, 7.59. Found: C, 56.99; H, 8.00%. $^1\text{H NMR}(\text{CDCl}_3)$: δ 7.69 (t, 2H, $J_{\text{HF}} = 8.6$ Hz, $\text{SC}_6\text{H}_4\text{F}-4$), 7.04 (t, 2H, $J_{\text{HF}} = 8.6$ Hz, $\text{SC}_6\text{H}_4\text{F}-4$); 5.22 (s, 5H, C_5H_5), 1.57 (m, 18H), 0.94 (t, 9H, $J_{\text{HH}} = 8.0$ Hz, PBu_3). $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3): δ 22.2 (s, PBu_3).

2.3.4. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{SC}_6\text{H}_4\text{F}-4)$ (**6**)

The reaction of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Br}$ (0.36 g, 0.79 mmol) and $\text{HSC}_6\text{H}_4\text{F}-4$ (0.09 g, 0.08 mmol) was performed in a similar manner to that of **3**. Yield 0.25 g (77%). Anal. Calc. for $\text{C}_{29}\text{H}_{24}\text{FPSNi} \cdot 1/4\text{CH}_2\text{Cl}_2$: C, 65.73; H, 4.59. Found: C, 65.79; H, 4.87%. $^1\text{H NMR}(\text{CDCl}_3)$: δ 7.67 (m, 6H, PPh_3), 7.37 (m, 9H, PPh_3), 7.26 (t, 2H, $J_{\text{HF}} = 8.8$ Hz, $\text{SC}_6\text{H}_4\text{F}$), 6.59 (t, 2H, $J_{\text{HF}} = 8.8$ Hz, $\text{SC}_6\text{H}_4\text{F}$), 5.09 (s, 5H, C_5H_5). $^{31}\text{P}\{^1\text{H}\}$ NMR(CDCl_3): δ 35.4 (s, PPh_3).

2.3.5. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{SC}_6\text{H}_4\text{NH}_2-4)$ (**7**)

A mixture of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\mu_2\text{-SC}_6\text{H}_4\text{NH}_2-4)]_2$ (0.40 g, 0.81 mmol) and PPh_3 (0.42 g, 1.62 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature for 4 h. The resultant dark brown solution was concentrated to about 20 mL and hexane (20 mL) added. The solution was cooled at -15°C overnight to form green crystals of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{SC}_6\text{H}_4\text{NH}_2-4)$. Yield 0.35 g, (85%).

Anal. Calc. for $\text{C}_{35}\text{H}_{26}\text{NPSNi} \cdot 1/2\text{CH}_2\text{Cl}_2$: C, 66.71; H, 5.31; N, 2.63. Found: C, 66.87; H, 5.46; N, 2.95%. $^1\text{H NMR}(\text{CDCl}_3)$: δ 7.71 (t, 6H, PPh_3), 7.37 (m, 9H, PPh_3), 7.12 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, $\text{SC}_6\text{H}_4\text{NH}_3-4$), 6.35 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, $\text{SC}_6\text{H}_4\text{NH}_2-4$), (s, 2H, NH_2), 5.03 (s, 5H, C_5H_5); 3.77 (s, br, 2H, NH_2).

2.3.6. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBu}_3)(\text{SC}_6\text{H}_4\text{NH}_2-4)$ (**8**)

Starting with (0.50 g, 3.99 mmol) 4-aminothiophenol and (1.86 g, 3.99 mmol) $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBu}_3)\text{Br}$ in toluene (60 mL), brown-green oil of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBu}_3)(\text{SC}_6\text{H}_4\text{NH}_2-4)$ was obtained in a yield of 1.37 g (76%). $^1\text{H NMR}(\text{CDCl}_3)$: δ 7.33 (d, 2H, $J_{\text{HH}} = 8.1$ Hz, $\text{SC}_6\text{H}_4\text{NH}_2-4$); 6.38 (d, 2H, $J_{\text{HH}} = 8.1$ Hz, $\text{SC}_6\text{H}_4\text{NH}_2-4$), 5.15 (s, 5H, C_5H_5); 2.95 (s, br, 2H, NH_2); 1.49 (m, 18H, PBu_3); 0.91 (t, 9H, $J_{\text{HH}} = 7.8$ Hz, PBu_3).

2.3.7. X-ray structural determination

Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation and the diffractometer to crystal distance of 4.9 cm. Crystal data, data collection, and refinement parameters are listed in Table 1. The initial cell constants were obtained from three series of ω scans at different starting angles. The reflections were successfully indexed by an automated indexing routine built in the SMART program. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [13]. The structures were solved by direct methods and refined by least-squares techniques using the SHELXTL program [14]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.

3. Results and discussion

3.1. Synthesis of ligands and metal complexes

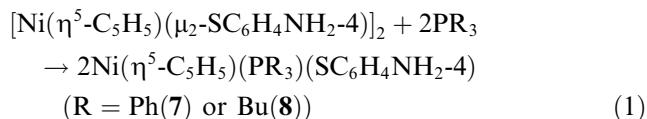
Two Schiff-base thiols (**1** and **2**) were synthesized *via* the condensation of 4-aminothiophenol and different thiophene carboxyaldehydes. Compounds **1** and **2** readily precipitated from ethanol as pure products; thus these sparingly soluble products in CH_2Cl_2 did not need further purification. Infrared spectroscopic analysis was a quick way to establish the formation of the Schiff-base ligands. This revealed the absence of the carbonyl functionality of the aldehyde used in preparing each compound and the presence of a $\nu(\text{C}=\text{N})$ peak characteristic of imines at 1604 cm^{-1} for **1** and 1609 cm^{-1} for **2**.

Table 1
Crystal and structural refinement data for **3**, **6** and **7**

	3	6	7
Empirical formula	C ₂₈ H ₃₉ BrNPS ₂ Ni	C ₂₉ H ₂₄ FPSNi	C ₂₉ H ₂₆ NPSNi
Formula weight	623.31	513.22	510.25
Temperature (K)	173(2)	173(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions			
<i>a</i> (Å)	12.4741(9)	9.6530(5)	9.3599(19)
<i>b</i> (Å)	15.8951(14)	9.6530(5)	11.535(2)
<i>c</i> (Å)	17.0772(13)	11.4173(6)	12.002(2)
α (°)	113.4480(10)	79.7450(10)	79.566(3)
β (°)	91.976(3)	83.4110(10)	69.056(3)
γ (°)	106.477(2)	74.2320(10)	81.047(3)
<i>V</i> (Å ³)	2936.8(4)	1184.08(11)	1184.4(4)
<i>Z</i>	4	2	2
<i>D</i> _{calc.} (mg m ⁻³)	1.410	1.439	1.431
Absorption coefficient (mm ⁻¹)	2.235	0.999	0.993
<i>F</i> (000)	1296	532	532
Crystal size (mm)	0.42 × 0.26 × 0.14	0.40 × 0.30 × 0.30	0.42 × 0.25 × 0.21
Reflections collected	19,272	10,520	19,610
Completeness to $\theta = 26.36\%$	96.1%	99.3%	99.1%
Data/Restraints/Parameters	11,524/0/612	4802/0/298	4840/0/298
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0965, <i>wR</i> ₂ = 0.1315	<i>R</i> ₁ = 0.0340, <i>wR</i> ₂ = 0.0780	<i>R</i> ₁ = 0.0320, <i>wR</i> ₂ = 0.0838
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0503, <i>wR</i> ₂ = 0.133	<i>R</i> ₁ = 0.0283, <i>wR</i> ₂ = 0.0753	<i>R</i> ₁ = 0.0305, <i>wR</i> ₂ = 0.0826
Largest difference peak and hole (e Å ⁻³)	0.28 and -0.692	0.330 and -0.233	0.597 and -0.558

NMR data and elemental analysis confirmed the formation of these compounds.

The reactions of these Schiff-base thiols, **1** and **2**, as well as the commercially available thiols, 4-fluorothiophenol and 4-aminothiophenol, with Ni(η^5 -C₅H₅)(PBU₃)Br and Ni(η^5 -C₅H₅)(PPh₃)Br are described in Scheme 1. The scheme represents a facile route to the synthesis of cyclopentadienylnickel thiolato compounds. Complexes **7** and **8** on the other hand were also prepared by reacting [Ni(η^5 -C₅H₅)(μ_2 -SC₆H₄NH₂-4)]₂ with PR₃ [Eq. (1)], a reaction we have used previously to prepare Ni(η^5 -C₅H₅)(PR₃)(C₆H₄X-4)(X = Cl, Br; R = Ph, Bu) [6].



The nickel thiolate complexes were characterized by a combination of infrared and NMR spectroscopy and showed characteristic signals of the various functional groups in the complexes. Single crystal X-ray crystallography of **3**, **6** and **7** were used to confirm the formation of the nickel thiolate complexes deduced from the spectroscopic data.

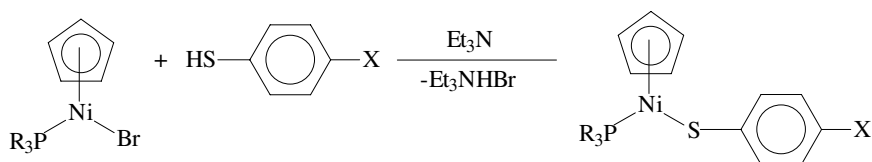
3.2. Molecular structures of **3**, **6** and **7**

The solid-state structures of **3**, **6** and **7** are shown in Figs. 1–3. The crystallographic data are tabulated in

Table 1, while most relevant bond angles and distances provided in Tables 2 and 3.

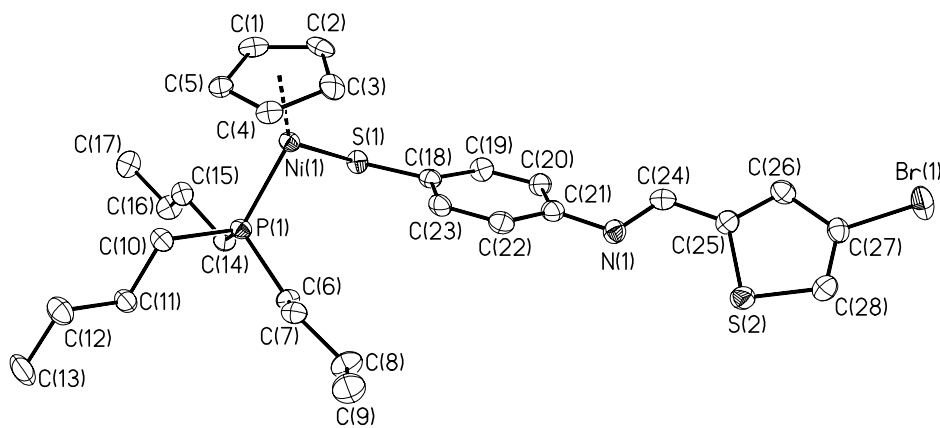
In each of the three complexes the Ni atom exhibits a pseudo-trigonal geometry, if the cyclopentadienyl ligand is considered a point ligand. The Ni–ligand bond distances (Table 2) are rather typical and compare well to the structural data reported to the Cambridge Crystallographic Database (CSD) [15]. For 12 compounds similar to **3**, **6**, and **7** in which the central Ni is bound to phosphorus, sulfur, and a cyclopentadienyl ligand only, the following bond length ranges have been determined: Ni–C(η^5 -C₅H₅ ring) 2.054–2.177 Å, Ni–Centroid(η^5 -C₅H₅ ring) 1.717–1.780 Å, Ni–P 2.135–2.183 Å, and Ni–S 2.144–2.203 Å. In general, distances of these types vary in wider ranges: Ni–C(η^5 -C₅R₅ ring) 1.721–2.705 Å (2570 bonds, av. 2.12(5) Å), Ni–Centroid(η^5 -C₅R₅ ring) 1.628–2.031 Å (514 bonds, av. 1.76(3) Å), Ni–P 2.145–2.522 Å (73 bonds, av. 2.20(6) Å), and Ni–S 2.144–2.52 Å (110 complexes, av. 2.30(12) Å).

A Density Functional Theory (DFT) geometry optimization of a simplified analog of **3**, **6**, and **7**, mononuclear complex Ni(η^5 -C₅H₅)(PMe₃)(SMe) has been performed at the B3LYP/LANL2DZ level of theory [16]. By performing the DFT calculations we are able to compare the literature data that encompass a wide range of bond distances and angles and the theoretical values for the trigonal geometry found in our nickel complexes. The theoretically calculated bond angles (Table 3) are in good agreement with the experiment, however the



Complex	X	R
3		Bu
4		Bu
5	F	Bu
6	F	Ph
7	NH ₂	Ph
8	NH ₂	Bu

Scheme 1.

Fig. 1. Molecular structure of **3**, drawn with 40% probability ellipsoids. The H atoms are omitted for clarity.

theoretical bond distances (Table 2) are considerably longer (by ~4.8%) than those determined by X-ray single crystal analysis. Nonetheless the relative ratio of the calculated bond distances (Ni–P:Ni–S:Ni–Centroid) is very similar to the experimental value.

3.3. Sulfur dioxide adducts

3.3.1. Spectroscopic characterization of sulfur dioxide adducts

In order to investigate the use of electrochemistry as a detection technique for SO₂ complexes **3**, **5**, **6**, **7** and **8** were selected for reactions with SO₂. These complexes

readily reacted with SO₂, changing from greenish-brown to dark red solutions. We first established SO₂-adduct formation by monitoring reactions using ¹H NMR spectroscopy. Chemical shifts associated with the cyclopentadienyl ligand, except for **3**, which had no change in the cyclopentadienyl resonance, showed that SO₂ adducts were formed. Generally a chemical shift difference of at least 0.25 ppm was observed between the thiolato complex and its SO₂ adduct (Table 4). Sulfur dioxide reactions with **5**, **6**, **7** and **8** were found to be reversible. These were established by first running the ¹H NMR spectrum of the thiolato complex before reacting SO₂, and then the spectrum was re-run after the

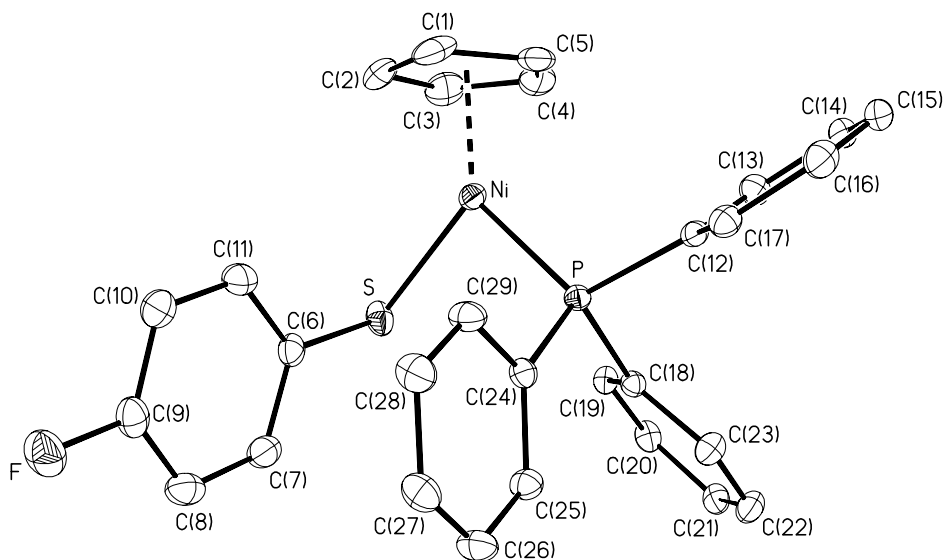


Fig. 2. Molecular structure of **6**, drawn with 30% probability ellipsoids. The H atoms are omitted for clarity.

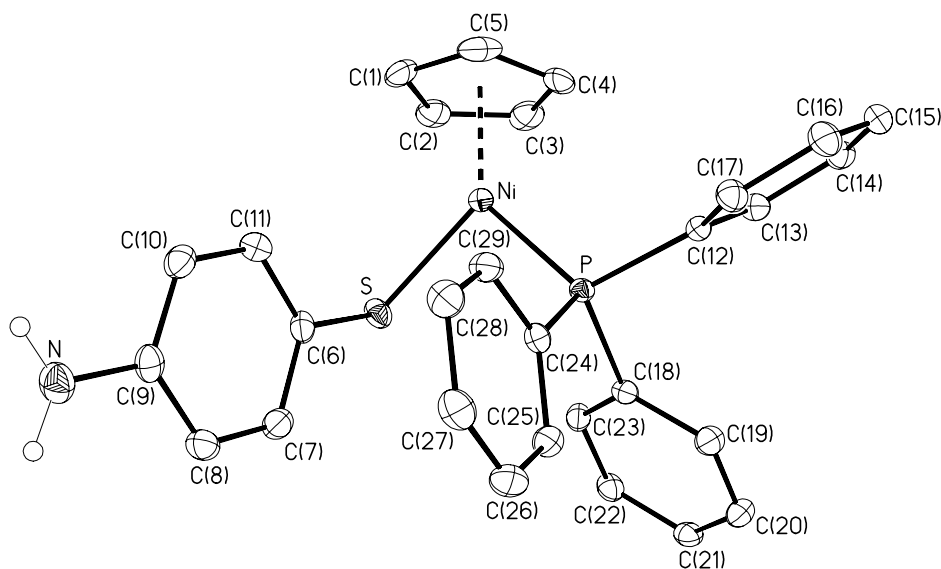


Fig. 3. A molecular drawing of **7**, shown with 50% probability ellipsoids. All H atoms except amino hydrogens have been omitted for clarity.

Table 2
Selected bond distances in complexes **3**, **6** and **7**, and Ni(η^5 -C₅H₅)(PMe₃)(SMe)

Bond lengths (Å)	3 ^a	6	7	Ni(η^5 -C ₅ H ₅)(PMe ₃)(SMe) (DFT B3LYP/LANL2DZ data)
Ni–P	av. 2.1399(17)	2.1356(5)	2.1430(5)	2.25
Ni–S	av. 2.1884(11)	2.1995(2)	2.1881(6)	2.28
Ni–Centroid	av. 1.744(3)	1.752(2)	1.767(2)	1.857
Ni–C(av.)	av. 2.122(10)	2.122(16)	2.138(15)	2.24(6)

^a There are two symmetry independent molecules in the asymmetric unit in the lattice of **3**, thus the table contains values averaged between the two molecules.

SO₂ reaction. The solution of the SO₂ reaction product was then purged with dinitrogen for several minutes and the ¹H NMR spectrum was found to be exactly the same as the thiolato complex before reaction with SO₂. These spectral changes followed the same pattern as

observed for Ni(η^5 -C₅H₅)(PBu₃)(SC₆H₄X-4) (X = Cl or Br) [6].

Notwithstanding the same chemical shifts for **3** and its SO₂-adduct, sulfur dioxide reactions of complex **3** resulted in clear colour change from brownish-green to

Table 3
Selected bond angles in complexes **3**, **6** and **7**

Bond angles (°)	3 ^a	6	7	Ni(η^5 -C ₅ H ₅)(PMe ₃)(SMe) (DFT B3LYP/LANL2DZ data)
P–Ni–S	av. 92.03(8)	90.608(19)	92.2(5)	91.0
P–Ni–Centroid	av. 135.55(11)	136.2(1)	136.7(1)	136.4
S–Ni–Centroid	av. 132.45(4)	133.1(1)	132.4(1)	132.0

^a There are two symmetry independent molecules in the asymmetric unit in the lattice of **3**, thus the table contains values averaged between the two molecules.

Table 4
¹H NMR data of selected complexes and their SO₂ adducts

Complex	Without SO ₂		SO ₂ adducts	
	Cp	SC ₆ H ₄	Cp	SC ₆ H ₄
6	5.09	6.59(d)	5.41	6.73(d)
7	5.25	–	5.53	–
8	5.16	6.40(d)	5.53	6.57(d)

red. The major difference in the ¹H NMR spectrum of complex **3** before and after adding SO₂ is a peak at 9.99 ppm, characteristic of aldehydes. The appearance of this peak suggests some decomposition of **3** to an aldehyde, but it is not clear how SO₂ converts the Schiff-base ligand to an aldehyde.

In all other complexes ¹H NMR spectroscopic detection of SO₂-adduct formation was simple. All chemical shifts after SO₂-adduct formation were downfield from the starting nickel thiolate complex. This observation is diagnostic of the thiolato sulfur atom acting as a Lewis base in binding the SO₂ [6,17]. The involvement of thiolato sulfur atoms in SO₂-adduct formation is well documented with solid-state X-ray structures [4a,4b,4d]. There are also examples of labile SO₂ adducts that have only been identified in solution. Apart from our work on labile SO₂-adduct [6,17], Sadler et al. [4c] and recently Shaver and co-workers [18] have used NMR spectroscopy to document the formation of [*n*-Bu₄N][Au(SC₆H₃MeS(SO₂))] and Ru(η^5 -C₅H₅)(PPh₃)₂(S(SO₂)SiⁱPr₃). Both the Au and Ru SO₂ adducts readily desorb SO₂ when attempts were made to isolate them as solids. The lability of these Au and Ru SO₂ adducts, as well as those reported in this paper, is clearly linked to the strength of the SO₂-thiolate interaction, an interaction that involves electron density donation from the thiolate sulfur. This donor-acceptor relation between the thiolate sulfur and the SO₂ is expected to reflect in the redox behaviour of such complexes.

3.3.2. Electrochemical detection of sulfur dioxide adducts

The reaction of SO₂ with thiolate complexes in this paper was also monitored by cyclic voltammetry. This was accomplished by first running a cyclic voltammetry experiment on a solution of a thiolate nickel complex without sulfur dioxide, followed by bubbling sulfur dioxide through the same solution and repeating the cyclic voltammetry experiment. It was necessary to run a control experiment involving the electrolyte and sulfur

dioxide to ensure that any observed electrochemical activity is not from the interaction of the electrolyte and sulfur dioxide. In the control experiments we found no electrochemical response in the potential window that was used.

Complexes **5** and **8** exhibited quasi-reversible redox behaviour, whilst complexes **6** and **7** had irreversible redox behaviour. This is reminiscent of the electrochemical properties of Ni(η^5 -C₅H₅)(PR₃)(SC₆H₄X-4) (X = Cl, Br; R = Ph, Bu) [6].

It was interesting to note distinct differences between the redox behaviour of thiolato complexes before and after introducing sulfur dioxide. The potentials where electrochemical activities were found for the complexes before addition of SO₂ shifted to more positive values on adding sulfur dioxide (Table 5). This indicates that the SO₂ adducts are more difficult to oxidize and corroborate the conclusion drawn from the ¹H NMR experiments that SO₂ adduct formation draws electron density from the nickel centre. The reversibility of the redox behaviour for the SO₂ adducts mirrors those of the original complexes. The more basic PBu₃ complexes showed quasi-reversibility (Fig. 4), whilst the PPh₃ analogues were irreversible. What is significant in these studies is the clear shift in redox potential in all cases between the complexes and their SO₂ adducts. It is therefore quite clear that cyclic voltammetry can be used as an analytical technique to detect the absorption of sulfur dioxide by complexes **5**, **6**, **7** and **8** hence these compounds can be used as potentiometric sensors for sulfur dioxide.

As observed in the ¹H NMR experiments, cyclic voltammetry experiments after reacting complex **3** with SO₂ were ill defined. There were no distinct voltammograms that would suggest SO₂ adduct formation as observed for the other complexes. Multiple scan experiments over a five minute period (Fig. 5) illustrates that any species formed by SO₂ on reacting with **3** is unstable and decomposes during this period. This combined with

Table 5
Oxidation potentials of selected complexes and their SO₂ adducts

Complex	<i>E</i> _{ox} (mV) without SO ₂	<i>E</i> _{ox} (mV) SO ₂ adducts
5	411	513
6	514	586
7	332	585
8	283	356

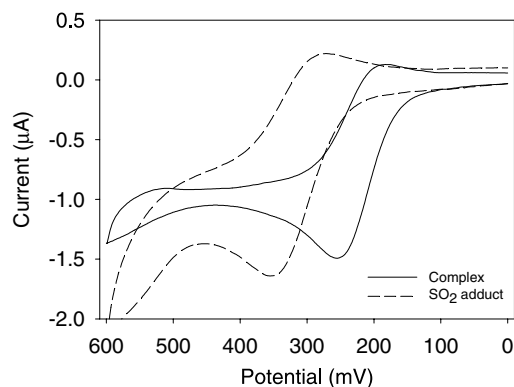


Fig. 4. Cyclic voltammogram of **8**, before and after bubbling SO_2 .

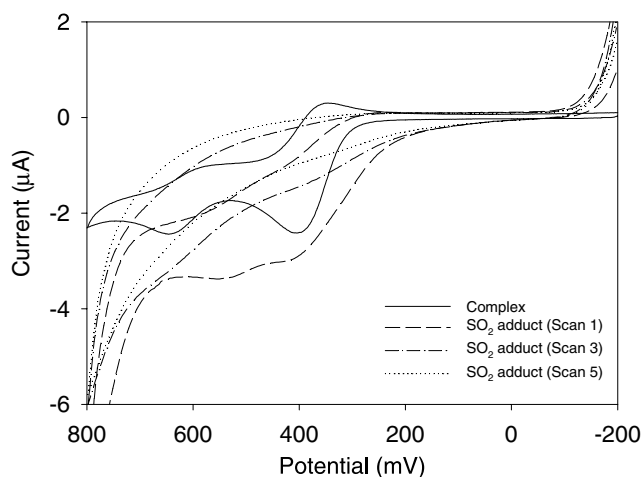


Fig. 5. Cyclic voltammogram of **3**, before and after bubbling SO_2 .

the NMR studies confirm that there is no well-defined SO_2 adduct of **3** formed when it reacts with SO_2 . Hence complex **3** cannot be used as an SO_2 sensor.

We have thus shown that simple cyclopentadienyl-nickel thiolato complexes, **5**, **6**, **7** and **8**, form SO_2 adducts that have sufficiently different redox potential from the unreacted complexes. Hence these compounds have the potential to be developed as amperometric sensors. They also allow direct electrochemical detection of SO_2 without having to oxidize the SO_2 to sulfate before detection.

4. Supplementary material

Crystallographic data for structures in this paper have been deposited with the Cambridge Crystallographic Data Centre with deposition numbers CCDC 221178 (**3**), CCDC 221179 (**6**) and CCDC 221180 (**7**). Copies of data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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