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Complexes of Ni(II) with sterically-hindered thiolate ligands. Crystal structures of complexes with the $[NiS_2N_2]$, $[NiS_2P_2]$ and $[NiS_2O_2]$ cores

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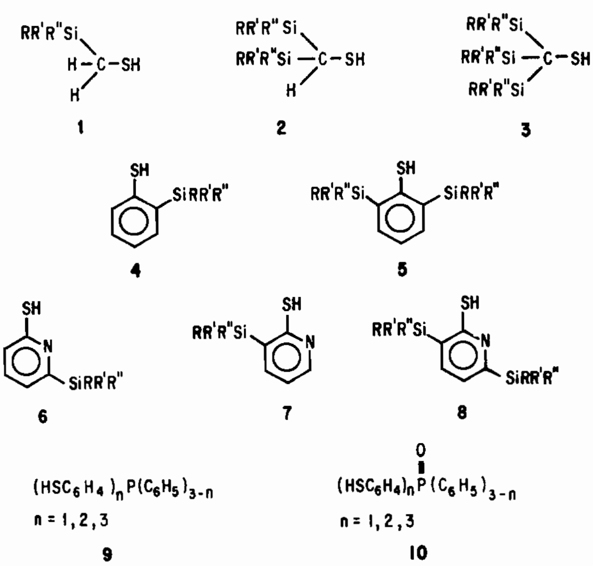
Abstract

The reactions of $NiCl_2 \cdot 6H_2O$ with the thiolate ligands HSC_5H_3N-3-$SiMe_3$, HSC_6H_4-2-PPh_2 and HSC_6H_3-6-$SiMe_3$-2-$OPPh_2$ yield the planar mononuclear species $[Ni(SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$, $[Ni(SC_6H_4\text{-}2\text{-}PPh_2)_2]$ and $[Ni(SC_6H_3\text{-}6\text{-}SiMe_3\text{-}2\text{-}OPPh_2)_2]$, respectively. The complexes are electrochemically active, displaying Ni(II)/Ni(III) oxidation processes in the high potential range common to most synthetic Ni(II) complexes. Crystal data: $C_{16}H_{24}N_2Si_2S_2Ni$: monoclinic $P2_1/n$, $a=6.697(1)$, $b=10.932(2)$, $c=14.108(3)$ Å, $\beta=95.31(1)°$, $V=1028.9(8)$ Å^3, $Z=2$, $D=1.366$ g cm^{-3}. $C_{36}H_{28}P_2S_2Ni$: triclinic $P\bar{1}$, $a=9.349(3)$, $b=10.673(3)$, $c=9.259(2)$ Å, $\alpha=105.35(1)$, $\beta=118.52(1)$, $\gamma=91.86(1)°$, $V=799.0(9)$ Å^3, $Z=1$, $D=1.393$ g cm^{-3}. $C_{42}H_{44}O_2Si_2P_2S_2Ni$: monoclinic $P2_1n$, $a=12.015(2)$, $b=27.458(5)$, $c=12.959(3)$ Å, $\beta=96.37(1)°$, $V=4248.9(12)$ Å^3, $Z=4$, $D=1.285$ g cm^{-3}.

Introduction

The contemporary interest in nickel-thiolate chemistry has been stimulated by the discovery of low-potential sulfur-ligated nickel centers at the active sites of several hydrogenase [1–3]. With the exception of distorted arenethiolate complexes, $[Ni(SAr)_4]^{2-}$ [4], homoleptic nickel thiolates are generally planar, four coordinate species which oligomerize through thiolate bridging to give species characterized by edge-sharing planar NiS_4 units [5–10]. Complexes with mixed N, O and S ligation [11, 12] exhibit similar properties. By suitable modification of ligand geometries or reaction conditions, mononuclear complexes with planar $[NiS_4]$ cores [13, 14], with planar cores with variable thiolate coordination $[NiS_{4-x}L_x]$ ($L=N$ or O) [15] and with five or six coordinate mixed donor cores $[NiS_xL_y]$ ($x+y=5$ or 6, $L=N$ or O) [16] have been prepared.

As part of our investigations of the properties of sterically-hindered thiolate ligands [17–30] we have exploited the triorganosilyl group to introduce a substituent capable of providing a tunable degree of steric constraint. Ligands **1–10** are characteristic of the classes prepared to date. While ligand



types **1–5** react with Ni(II) to give cyclic 'tiara' structures $[Ni(SR)_2]_n$ [5, 30], ligands **6–8** and HSC_6H_4-2-PPh_2 and HSC_6H_3-6-$SiMe_3$-2-$OPPh_2$ of classes **9** and **10** yield mononuclear complexes with the $[NiS_2L_2]$ core ($L=N$, O, and P). In this paper we discuss the

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TABLE 1. Summary of crystal data and experimental conditions for the X-ray studies

	$[Ni(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$	$[Ni(SC_6H_4PPh_2)_2]$	$[Ni(SC_6H_3\text{-}6\text{-}SiMe_3\text{-}2\text{-}OPPh_2)_2]$
Crystal data			
Empirical formula	$C_{16}H_{24}N_2Si_2S_2Ni$	$C_{36}H_{28}P_2S_2Ni$	$C_{42}H_{44}O_2Si_2P_2S_2Ni$
Color, habit	red needle	brown prism	red prism
Crystal size (mm)	$0.25 \times 0.36 \times 0.24$	$0.30 \times 0.35 \times 0.32$	$0.31 \times 0.29 \times 0.28$
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions			
a (Å)	6.697(1)	9.349(2)	12.015(2)
b (Å)	10.937(2)	10.673(3)	27.458(5)
c (Å)	14.108(3)	9.259(2)	12.959(3)
α (°)	90.00	105.35(1)	90.00
β (°)	95.31(1)	118.52(1)	96.37(1)
δ (°)	90.00	91.86(1)	90.00
Volume (Å^3)	1028.9(8)	799.0(9)	4248.9(12)
Z	2	1	4
Formula weight	423.38	645.38	821.74
Density (calc.) (g cm^{-3})	1.366	1.393	1.285
Density (exp.) (g cm^{-3})	1.34(1)	1.38(1)	1.26(1)
Absorption coefficient (cm$^{)1}$)	12.56	8.89	7.11
$F(000)$	444.0	334.0	430.0
Data collection			
Diffractometer	RIGAKU AFC5S		
Radiation	Mo Kα ($\lambda = 0.71073$ Å)		
Temperature (K)	296		
Monochromator	Highly oriented graphite crystal		
2θ range (°)	2.5–45.0		
Scan speed (°/min)	6		
Scan range	1.20° plus Kα-separation		
Background measurement	stationary crystal and stationary counter beginning and end of each scan		
Standard reflections	3 measured every 200 reflections		
Index ranges	$0 \leqslant h \leqslant 6$	$0 \leqslant h \leqslant 12$	$-12 \leqslant h \leqslant 12$
	$0 \leqslant k \leqslant 11$	$-13 \leqslant k \leqslant 13$	$0 \leqslant k \leqslant 29$
	$-15 \leqslant l \leqslant 14$	$-11 \leqslant l \leqslant 11$	$0 \leqslant l \leqslant 13$
Reflections collected	2103	3362	3421
Observed reflections	1079	2224	2334
Absorption correction	based on Ψ-scan on 5 reflections with χ near 90° and 270°		
Solution and refinement			
System used	MSC TEXAN solution package		
Solution	Patterson method		
Refinement method	full-matrix least-squares		
Quantity minimized	$\Sigma w(F_o - F_c)^2$		
Hydrogen atoms	riding model		
Weighting scheme	$w^{-1} = \sigma(F) + 0.0011F^2$		
Final R indices (obs. data)			
R	0.029	0.049	0.054
R_w	0.036	0.053	0.062
Goodness of fit	1.70	1.58	1.29
Largest and mean Δ/σ	0.009, 0.006	0.008, 0.005	0.006, 0.002
Data to parameter ratio	10.2:1	22.7:1	9.3:1
Largest difference peak (e Å^{-3})	0.34	0.33	0.25
Largest difference hole (e Å^{-3})	0.22	0.25	0.27

structures and electrochemical properties of the complexes $[Ni(SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$, $[Ni(SC_6H_4\text{-}2\text{-}PPh_2)_2]$ and $[Ni(SC_6H_3\text{-}6\text{-}SiMe_3\text{-}2\text{-}OPPh_2)_2]$, referred to as $[NiS_2N_2]$, $[NiS_2P_2]$ and $[NiS_2O_2]$, respectively.

Experimental

The ligands **6–10** were prepared as previously described [25, 29]. Dichloromethane was technical grade and was distilled from $CoCl_2$ and P_4O_{10}. The following instruments were used in the study: IR, Perkin-Elmer 283B IR spectrophotometer, X-ray crystallography, Rigaku AFC5S four circle diffractometer, electrochemistry, BAS electroanalytical analyzer.

Synthesis of $[Ni(SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$

A mixture of $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), $HSC_5H_3N\text{-}3\text{-}SiMe_3$ (0.384 g, 2.1 mmol) and triethylamine (0.212 g, 2.1 mmol) in ethanol (50 ml) was refluxed for 1 h to give a dark green–brown solution. This solution was concentrated to 20 ml and treated with 25 ml of diethyl ether. The crude dark green product was dissolved in dichloromethane, which was carefully layered with diethyl ether. After standing for 4 days at 4 °C brown crystals of $[NiS_2N_2]$ deposited in 35% yield. *Anal.* Calc. for $C_{16}H_{24}N_2Si_2S_2Ni$: C, 45.3; H, 5.67; N, 6.61. Found: C, 45.2; H, 5.53; N, 6.47%.

The complexes $[Ni(SC_5H_3N\text{-}3\text{-}SiEt_3)_2]$ and $[Ni(SC_5H_2N\text{-}3,6\text{-}SiMe_2Bu^t)_2]$ were prepared in an analogous fashion from the appropriate ligand precursors.

Synthesis of $[Ni(SC_6H_4\text{-}2\text{-}PPh_2)_2]$

An ethanolic solution (25 ml) of $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol) was added to a solution of $HSC_6H_4\text{-}2\text{-}PPh_2$ (0.617 g, 2.1 mmol) and triethylamine (0.212 g, 2.1 mmol) in ethanol (20 ml). After stirring overnight and collecting a small amount of white precipitate by filtration, the dark brown filtrate was concentrated to 20 ml and layered with diethyl ether. After standing for 3 days at 4 °C, brown prismatic crystals of $[NiS_2P_2]$ were collected in 20% yield. *Anal.* Calc. for $C_{36}H_{28}P_2S_2Ni$: C, 66.9; H, 4.43. Found: C, 66.6; H, 4.52%.

Synthesis of $[Ni(SC_6H_3\text{-}6\text{-}SiMe_3\text{-}2\text{-}OPPh_2)_2]$

A solution of $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), $HSC_6H_3\text{-}6\text{-}SiMe_3\text{-}2\text{-}OPPh_2$ (0.802 g, 2.1 mmol) and triethylamine (0.212 g, 2.1 mmol) in ethanol (35 ml) was refluxed overnight to give a dark brown solution. Addition of diethyl ether to this solution produced a copious brown precipitate, which was dissolved in dichloromethane. Sufficient diethyl ether was added to the dichloromethane solution to produce turbidity, and the solution was allowed to stand at room temperature for 7 days. The red–brown prisms which deposited were collected and dried in air (yield 45%). *Anal.* Calc. for $C_{42}H_{44}O_2Si_2P_2S_2Ni$: C, 61.3; H, 5.35. Found: C, 60.9; H, 5.27%.

X-ray crystallographic studies

The methods used in the X-ray studies of the complexes were discussed in ref. 31. The crystal data and experimental conditions employed are summarized in Table 1.

Results and discussion

The syntheses of $[NiS_2N_2]$, $[NiS_2P_2]$ and $[NiS_2O_2]$ were effected by addition of an organic base to a methanol solution of the acid form of the ligand and reaction with $NiCl_2 \cdot 6H_2O$. The complexes are diamagnetic and exhibit absorption spectra with d–d bands in the 600–630 and 475–500 nm ranges.

The structure of $[NiS_2N_2]$ is shown in Fig. 1 and atomic positional parameters and selected bond lengths and angles are given in Tables 2 and 3, respectively. The complex $[NiS_2N_2]$ exists as discrete mononuclear units with the Ni atom located on a crystallographic inversion center, which confers strict

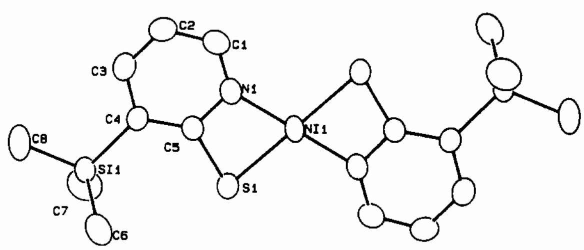

Fig. 1. ORTEP view of the structure of $[Ni(SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$.

TABLE 2. Atomic positional parameters for $[Ni(SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$

Atom	*x*	*y*	*z*
Ni(1)	0	0	0
S(1)	0.0361(1)	−0.06775(8)	−0.14637(6)
Si(1)	0.4111(1)	−0.00384(7)	−0.30448(6)
N(1)	0.2307(3)	0.0767(2)	−0.0367(2)
C(1)	0.3714(5)	0.1536(3)	0.0010(2)
C(2)	0.5269(5)	0.1871(3)	−0.0491(2)
C(3)	0.5382(5)	0.1404(3)	−0.1395(2)
C(4)	0.3947(4)	0.0601(3)	−0.1813(2)
C(5)	0.2419(4)	0.0310(3)	−0.1244(2)
C(6)	0.1694(5)	0.0160(4)	−0.3770(2)
C(7)	0.4793(5)	−0.1676(3)	−0.2945(3)
C(8)	0.6078(5)	0.0817(4)	−0.3607(2)

TABLE 3. Selected bond lengths (Å) and angles (°) for $[Ni(SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$

Ni–S1	2.2281(8)	S1–Ni–N1	74.30(8)
Ni–N1	1.873(2)	S1–Ni–N1a	105.70(8)
S1–C5	1.756(3)	Ni–Ni–C5	101.9(2)
		N1–C5–S1	106.3(2)
		C5–S1–Ni	77.46(9)

planarity on the $[NiS_2N_2]$ core. The *trans* thiolate configuration is somewhat unusual since the weakly π-donating thiolate donors generally assume the mutually *cis* orientation. Although several examples of $[NiS_2N_2]$ core complexes have been described [15, 16, 31–34], these have invariably exploited tetradentate S_2N_2 donor ligands with thiolate sulfur donors and amine nitrogen or amidate nitrogen groups. Table 4 compares structural parameters of $[NiS_2N_2]$ with those of other members of this class. A significant difference between $[NiS_2N_2]$ and the other members of the class is the C_n–S–Ni–N chelate ring size. Whereas for $[NiS_2N_2]$, n is 1, producing a four-membered ring, all other complexes of this class exhibit $n=2$ or 3 resulting in significantly less strained five- and six-membered chelate rings. A consequence of a four-membered ring geometry is apparent in the chelate 'bite' angle of 74.30(8)° assumed by $[NiS_2N_2]$ as compared to a range of 88–96° observed for other complexes of this class. The unusually long Ni–S bond length of 2.2281(8) Å associated with $[NiS_2N_2]$, as compared to the 2.149–2.179 Å range cited for other examples, may be related to the strained chelate geometry and concomitant less effective metal–ligand overlap and to the *trans* thiolate geometry which should also result in Ni–S bond lengthening.

The triorganosilyl group is sterically significant and may dictate the composition of the Ni(II) complexes of this ligand. Whereas the underivatized parent 2-mercaptopyridine and the analogous 2-mercaptopyrimidine ligand give octahedral Ni(II) species, $[Ni(SC_5H_4N)_3]^-$ and polymeric $[Ni(SC_4H_3N_2)_2]_n$, respectively [35, 36], reactions of the ligands **6–8** with a variety of Ni(II) precursors under different reaction conditions yield exclusively square planar $[NiS_2N_2]$ complexes.

The structure of $[NiS_2P_2]$ is depicted in Fig. 2 and atomic positional parameters and selected metrical parameters are listed in Tables 5 and 6, respectively. The structure consists of discrete mononuclear units with the Ni(II) center once again located at a crystallographic inversion center to give strictly planar $[NiS_2P_2]$ unit with the thiolate donors in the *trans* configuration. The Ni–S distance of 2.180(1) Å may be compared to Ni–thiolate distances for other planar complexes with the $[NiS_2X_2]$ cores. As noted above, in the absence of other constraints, a range of 2.149 to 2.179 Å is observed for Ni–thiolate distances, placing the Ni–S distance of $[NiS_2P_2]$ in the upper limit of this common range. However, the Ni–S distance of $[NiS_2P_2]$ is significantly shorter than that observed for $[NiS_2N_2]$. A relevant feature of the structure of $[NiS_2P_2]$ compared to that of $[NiS_2N_2]$ is the presence of a five-membered chelate ring C–C–P–Ni–S rather than a four-membered ring, which should improve Ni–S overlap and shorten the Ni–S distance. On the other hand, the *trans* thiolate configuration should serve to lengthen the bond with

TABLE 4. Selected bond parameters for $[NiS_2N_2]$ and related complexes [a]

Complex[b]	Ni–S	Ni–N	C–N	C–S	S–Ni–N(bite)	Reference
$[NiS_2N_2]$	2.2281(8)	1.873(2)	1.336(4)	1.756(3)	74.30(8)	this work
$[Ni(ebtsa)]^{2-}$	2.161(7)	1.90(2)	1.32(3)	1.74(2)	92.8(6)	31
	2.149(7)	1.89(2)	1.31(3)	1.74(2)	96.0(6)	
[Ni(tsalen)]	2.174	1.85	1.29	1.70		32
	2.139	1.86	1.30	1.73		
[Ni(ebmba)]	2.164	1.949	1.482	1.765		33
	2.170	1.941	1.487	1.750		
$[Ni(ema)]^{2-}$	2.179(1)	1.857(3)	1.458(6)	1.811(5)	88.4(1)	15
[Ni(dmmepd)]	2.176(1)	1.999(3)	1.495(5)	1.807(4)	89.31(9)	16
	2.174(1)	2.006(3)	1.496(5)	1.810(4)	88.26(8)	
[Ni(BME-DACO)]	2.159(2)	1.985(6)	1.506(10)	1.824(9)		34

[a]Bond lengths in Å, bond angles in °. [b]Abbreviations: ebtsa = *N,N'*-ethylene bis(o-mercaptobenzamide); tsalen = *N,N'*-ethylene bis(thiosalicylideneaminate): ebmba = *N,N'*-ethylene bis(thiosalicylideneamine); ema = *N,N'*-ethylene bis(2-mercaptoacetamide); dmmepd = *N,N'*-dimethyl-*N-N'*-bis(2-mercaptoethyl)-1,3-propanediamine; BME-DACO = 1,5 bis(mercaptoethyl)-1,5-diazacyclooctane.

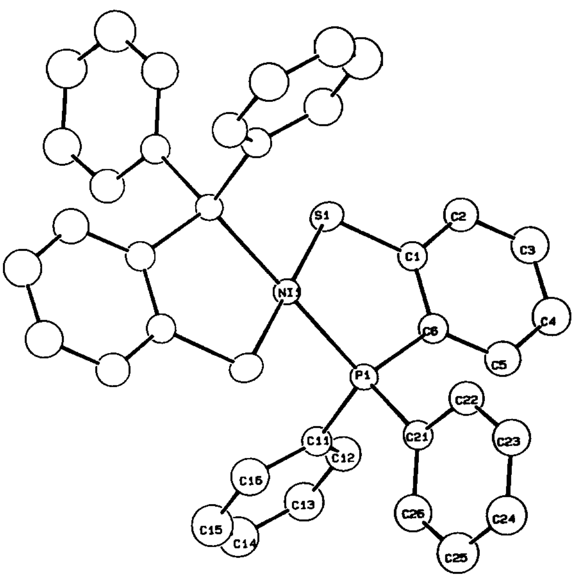

Fig. 2. A view of the structure of $[Ni(SC_6H_4\text{-}2\text{-}PPh_2)_2]$.

TABLE 5. Atomic positional parameters for $[Ni(SC_6H_4\text{-}2\text{-}PPh_2)_2]$

Atom	*x*	*y*	*z*
Ni(1)	0	0	0
S(1)	−0.1319(1)	0.1332(1)	−0.1383(1)
P(1)	0.1593(1)	0.1739(1)	0.2213(1)
C(1)	−0.0778(5)	0.2876(4)	0.0226(5)
C(2)	−0.1650(5)	0.3899(5)	−0.0160(6)
C(3)	−0.1257(6)	0.5276(5)	0.1135(6)
C(4)	−0.0006(6)	0.5281(5)	0.2819(7)
C(5)	0.0887(6)	0.4295(5)	0.3207(6)
C(6)	0.0503(5)	0.3093(4)	0.1911(5)
C(11)	0.3529(5)	0.2236(4)	0.2303(5)
C(12)	0.4032(6)	0.3496(5)	0.2394(6)
C(13)	0.5485(6)	0.3828(5)	0.2397(7)
C(14)	0.6435(6)	0.2896(6)	0.2306(7)
C(15)	0.5963(7)	0.1649(6)	0.2226(7)
C(16)	0.4501(6)	0.1303(5)	0.2200(6)
C(21)	0.2177(5)	0.1742(4)	0.4383(5)
C(22)	0.0892(5)	0.1557(5)	0.4705(6)
C(23)	0.1209(6)	0.1560(5)	0.6329(7)
C(24)	0.2833(6)	0.1742(5)	0.7636(7)
C(25)	0.4108(7)	0.1898(6)	0.7341(7)
C(26)	0.3798(6)	0.1897(5)	0.5711(6)

TABLE 6. Selected bond lengths (Å) and angles (°) for $[Ni(SC_6H_4\text{-}2\text{-}PPh_2)_2]$

Ni–S1	2.180(1)	S1–Ni–P1	88.08(5)
Ni–P1	2.181(2)	S1–Ni–P1a	91.92(5)
S1–C1	1.766(4)	Ni–S1–C1	105.6(1)
P1–C6	1.801(4)	Ni–P1–C6	106.8(1)

the result that $[NiS_2P_2]$ exhibits a relatively long Ni–S distance.

The structure of $[NiS_2O_2]$ is presented in Fig. 3, the atomic positional parameters are given in Table 7, and the metrical parameters are listed in Table 8. This structure consists of a mononuclear complex with a planar $[NiS_2O_2]$ core. The sulfur donors adopt the *cis* configuration with Ni–S distances of 2.183(3) and 2.179(6) Å. These distances are somewhat longer than anticipated for *cis* thiolate donors to a planar Ni(II) site and may reflect a combination of ligand geometric factors. The puckered six-membered chelate rings are strained as a consequence of the presence of the bulky PPh_2 moiety and the short P–O distances (1.509(9) Å). The presence of a second sterically significant substituent, the ring $-SiMe_3$ group, may also serve to influence the ligand–metal geometry by preventing shortening of the Ni–distances, which would increase non-bonding contacts between the triorganosilyl groups.

The complexes are electrochemically active, displaying one electron oxidation, as listed in Table 9. The oxidation potentials for the Ni(II)/Ni(III) redox couples of $[NiS_2N_2]$, $[NiS_2P_2]$ and $[NiS_2O_2]$ fall in the high potential range commonly observed for synthetic complexes [38]. In order to achieve the lower redox potential associated with biological systems, certain factors have been noted in studies of the low potential Ni(II)/Ni(III) complexes [15]. Anionic polarizable ligands and overall negative charge of the complex favor low potentials. Likewise, replacements of phenylene bridges by ethylene bridges and aryl substituents by alkyl substituents serve to stabilize the Ni(III) state. The variation in redox potentials of the complexes of this study, spanning a +0.23 to +0.75 V range, are consequences of the donor sets and possibly chelate ring sizes. Thus, the

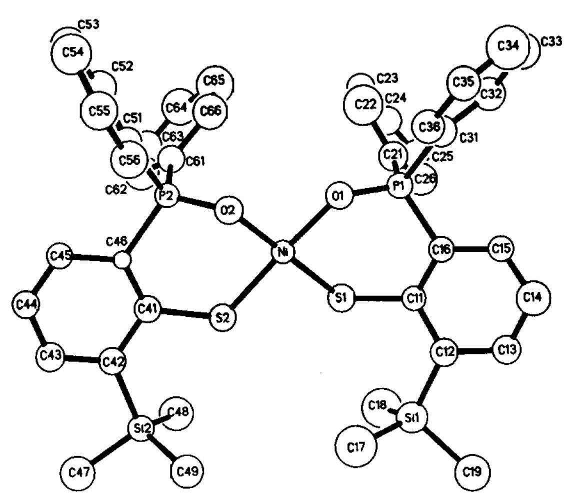

Fig. 3. The structure of $[Ni(SC_6H_3\text{-}6\text{-}SiMe_3\text{-}2\text{-}OPPh_2)_2]$.

TABLE 7. Atomic positional parameters for [$Ni(SC_6H_3$-6-$SiMe_3$-2-$OPPh_2)_2$]

Atom	x	y	z
Ni	−3946(1)	3532(1)	−1002(1)
S(1)	−2824(3)	3557(1)	442(3)
S(2)	−2725(3)	4032(1)	−1539(2)
P(1)	−5032(3)	2925(1)	607(3)
P(2)	−5267(3)	3991(1)	−2827(2)
Si(1)	−350(3)	3158(2)	1435(3)
Si(2)	−665(3)	4543(1)	−2567(3)
O(1)	−4988(7)	3098(3)	−492(6)
O(2)	−4933(6)	3523(3)	−2262(5)
C(11)	−2763(10)	2981(4)	1104(9)
C(12)	−1686(10)	2847(5)	1571(9)
C(13)	−1689(11)	2411(5)	2190(9)
C(14)	−2636(12)	2147(5)	2303(10)
C(15)	−3654(10)	2289(5)	1812(9)
C(16)	−3724(10)	2716(5)	1199(9)
C(17)	−86(17)	3167(7)	65(14)
C(18)	−342(15)	3784(6)	2005(13)
C(19)	809(12)	2811(6)	2184(11)
C(21)	−5501(11)	3386(5)	1455(10)
C(22)	−6474(15)	3637(6)	1138(14)
C(23)	−6819(17)	3997(7)	1813(15)
C(24)	−6255(17)	4095(7)	2681(16)
C(25)	−5328(16)	3850(7)	3020(15)
C(26)	−4944(13)	3496(6)	2388(12)
C(31)	−6015(10)	2430(5)	582(10)
C(32)	−6587(11)	2312(5)	1428(11)
C(33)	−7335(12)	1912(5)	1305(12)
C(34)	−7472(13)	1653(6)	441(12)
C(35)	−6908(15)	1757(7)	−376(14)
C(36)	−6166(13)	2156(6)	−307(12)
C(41)	−3048(10)	4287(4)	−2781(9)
C(42)	−2143(10)	4514(4)	−3223(9)
C(43)	−2376(10)	4714(4)	−4222(9)
C(44)	−3413(10)	4693(5)	−4777(10)
C(45)	−4310(10)	4479(4)	−4344(9)
C(46)	−4110(9)	4271(4)	−3351(8)
C(47)	177(11)	4935(5)	−3383(10)
C(48)	−577(12)	4842(6)	−1265(10)
C(49)	−28(12)	3928(5)	−2486(11)
C(51)	−6318(10)	3838(5)	−3885(9)
C(52)	−7298(11)	4088(5)	−4066(10)
C(53)	−8122(13)	3940(6)	−4855(11)
C(54)	−7906(13)	3531(6)	−5409(11)
C(55)	−6948(13)	3274(6)	−5241(12)
C(56)	−6124(12)	3428(5)	−4454(10)
C(61)	−5873(10)	4423(5)	−2042(10)
C(62)	−5558(13)	4895(6)	−1979(12)
C(63)	−6084(15)	5234(7)	−1346(13)
C(64)	−6886(14)	5067(6)	−772(12)
C(65)	−7203(14)	4593(6)	−804(12)
C(66)	−6684(13)	4272(6)	−1443(11)

more polarizable phosphorus donors of [NiS_2P_2] lower the potential 200 mV as compared to nitrogen donors in [NiS_2N_2] and 520 mV as compared to oxygen donors in [NiS_2O_2].

TABLE 8. Selected bond lengths (Å) and angles (°) for [$Ni(SC_6H_3$-6-$SiMe_3$-2-$OPPh_2)_2$]

Ni–S1	2.183(3)	S1–Ni–S2	83.1(1)
Ni–S2	2.179(4)	S1–Ni–O1	95.2(3)
Ni–O1	1.900(8)	S1–Ni–O2	179.0(3)
Ni–O2	1.909(7)	S1–Ni–O1	178.3(2)
S1–C11	1.79(4)	S2–Ni–O2	96.4(3)
S2–C41	1.76(1)	O1–Ni–O2	85.3(3)
P1–O1	1.508(9)	Ni–O1–P1	128.2(5)
P1–C16	1.76(1)	Ni–O2–P2	120.6(5)
P2–O2	1.510(8)	Ni–S1–C11	111.8(4)
P2–C46	1.79(1)	Ni–S2–C41	117.1(4)

TABLE 9. Comparative electrochemical properties of the complexes of this study and selected related Ni(II) species[a]

Complex	$E_{1/2}$ or E_p (V)[a]	E_p^f–E_p^r (mV)	(i_p^f/i_p^r)
[$Ni(ema)_2]^{2-}$ [b]	−0.34	70	1.0
[NiS_2N_2][c]	+0.42	85	1.2
[NiS_2P_2][c]	+0.23	80	1.1
[NiS_2O_2][c]	+0.75	[e]	[e]
[$Ni(hdt)_2]^{2-}$ [d]	−0.76	75	0.94

[a]vs. SCE at 25 °C. [b]In DMF solutions. [c]In acetonitrile, 0.1 M in n-Bu_4NPF_6. [d]In DMF, hdt = bicyclo[2.2.1] heptane-*exo-cis*-2,3-dithiolate, see ref. 37. [e]No reverse wave observed.

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