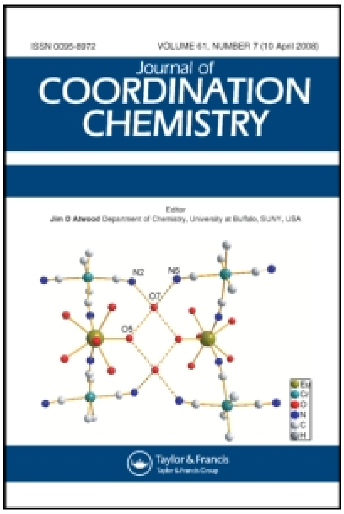

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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES OF NICKEL(II) SELENOLATES

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The synthesis and characterization of the complexes [NiCl(SeAr)(DPPE)] (1) and [Ni(SeAr)$_2$(DPPE)] (2) (where Ar = C_6H_5 (a), 4-MeOC_6H_4 (b) or 4-EtOC_6H_4 (c), and DPPE = 1,2-bis(diphenylphosphino)-ethane) is reported. Characterization of the compounds was based on elemental analysis, molecular weight and conductivity measurements, IR, electronic, ^{1}H and ^{31}P NMR spectra. Available evidence supports a square planar environment around Ni(II) in 1 and 2. Metathetical reaction between 1b and NaX (X = Br (d) or I (e)) in MeOH gives [NiX(SeAr)(DPPE)] (3). Electrochemical studies of 1 and 2 using cyclic voltammetry indicate an irreversible cathodic peak (*ca* −0.56 to −0.70 V) corresponding to reduction of nickel(II) to nickel (O).

KEYWORDS: arylselenolates, Ni(II), synthesis, electrochemical properties

INTRODUCTION

There is discernible growth in interest in the ligand chemistry of organochalcogens.[1-4] Sodium organochalcogenolate, NaER (E = S, Se or Te, R = alkyl or aryl) is an effective reagent for incorporating RE-ligands into the coordination sphere of a variety of metal ions and such coordination chemistry has been extensively explored.[5,6] Recently we reported the synthesis and electrochemical studies of Ni(II) tellurolates.[7] In continuation of our previous work on the coordination chemistry of palladium(II)[8-9] and platinium(II),[10-12] the present paper reports the synthesis, structures and electrochemical properties of nickel(II) selenolates.

EXPERIMENTAL

All operations were carried out under a dry nitrogen atmosphere using degassed solvents. All solvents were dried and distilled before use. Published methods[13-14] were used to prepare Ar_2Se_2 (Ar = Ph, C_6H_4OMe-4 or C_6H_4OEt-4). Sodium arylselenolates, NaSeAr were generated *in situ* by $NaBH_4$ reduction of the corresponding diaryldiselenide Ar_2Se_2, in EtOH. Ni(DPPE)Cl_2 was prepared by the literature method.[15] Elemental analyses were carried out on a Carlo Erba 1106 rapid analyser. Conductivity measurements were made on *ca* 1 mM solution in MeCN with a

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Metrohm 660 conductometer. Molecular weights were determined in $CHCl_3$ (*ca* 10 mM) solution using a Knauer vapour pressure osmometer. IR spectra (CsI pellets) in the range 200–700 cm^{-1} were recorded on a Nicolet 5DX-FTIR spectrometer. Electronic spectra in chloroform were recorded on a Shimadzu 160A spectrophotometer. ^1H and ^{31}P NMR were recorded on a Bruker AMX-400 NMR spectrometer at 400 and 162 MHz, respectively. Cyclic voltammetry experiments were performed using a BAS CV-27 potentiostat connected to an Omnigraph X-Y/t recorder. The working and reference electrodes were glassy carbon and Ag-AgCl in MeCN solution, respectively. Solutions containing 0.1 mM of the respective complex and 0.1 M $[NEt_4][ClO_4]$ were placed in a cell and pure nitrogen, pre-saturated with solvent, passed through the solution during the experiment. Scan speeds of 50–100 mV sec^{-1} were employed. Controlled-potential coulometry experiments were carried out in MeCN using the same equipment.

Synthesis of [NiCl(SeAr)(DPPE)] (1a–1c)

Diaryldiselenide, Ar_2Se_2 (0.50 mmol) was dissolved in EtOH (25 cm^3) and a solution of $NaBH_4$ in EtOH was slowly added until the solution became almost colourless. A suspension of $Ni(DPPE)Cl_2$ (1 mmol) in benzene (30 cm^3) was then added in one portion. Stirring was continued for 4 h during which $Ni(DPPE)Cl_2$ dissolved to give a clear brown solution. This was filtered (celite) to remove NaCl and anssy unreacted nickel complex. The clear filtrate was evaporated to dryness under reduced pressure to give a light brown solid which was dissolved in the minimum amount of $CHCl_3$ and poured into 200 cm^3 of a mixture of petroleum ether (40–60°) and ether (1:1 V/V) with rapid stirring. The product separated out in the form of microscopic crystals and was dried *in vacuo*. Elemental analyses, physical properties, IR, ^1H and ^{31}P NMR and CV data for 1a–1c are given below.

1a: Yield 70%; m.p. 134°C (dec.). Analysis: found: C, 58.87; H, 4.31; Cl, 5.13; Se, 11.67; Ni, 8.7%; $C_{34}H_{33}ClP_2SeNi$ calc.: C, 59.20; H, 4.47; Cl, 5.47; Se, 12.17; Ni, 9.05%. Λ_M (10^{-3}M, CH_3CN):30. Characteristic IR bands: (CsI, cm^{-1}): ν(Ni-P) 418(s), 398(s); ν(Ni-Cl) 331(s). NMR (^1H, $CDCl_3$, 25°C): δ, 1.73 (s, 4H, CH_2 of DPPE), 6.40–7.79 (m, 29H, phenyl protons); ($^{31}P\{^1H\}$, $CDCl_3$, 25°C): δ, 49.98 (*trans* Cl); 32.20 (*trans* Se). CV data (E_{pc}(V)): −0.65.

1b: Yield 75%; m.p. 214°C (dec.). Analysis: found: C, 58.39; H, 4.57; Cl, 5.23; Se, 11.64; Ni, 8.65%. Calc. for $C_{33}H_{31}P_2ClOSeNi$: C, 57.92; H, 4.60; Cl, 4.90; Se, 12.24; Ni, 8.24%. Mol. wt.: found: 660; calc.: 678.12. Λ_M(10^{-3}M, CH_3CN): 23. Characteristic IR bands: ν(Ni-P) 418(s), 397(s); ν(Ni-Cl) 332(s). NMR (^1H, $CDCl_3$, 25°C): δ, 3.65 (s, 3H, OCH_3), 1.81 (s, 4H, CH_2 of DPPE), 6.42–7.69 (m, 31H, phenyl protons); ($^{31}P\{^1H\}$, $CDCl_3$, 25°C): δ, 50.26 (*trans* Cl), 32.14 (*trans* Se). CV data (E_{pc}(V)): −0.56.

1c: Yield 78%; m.p. 140°C (dec.). Analysis: found: C, s58.87; H, 4.65; Cl, 4.85; Se, 10.80; Ni, 8.12%. Calc. for $C_{34}H_{33}P_2ClOSeNi$: C, 58.95; H, 4.76; Cl, 5.12; Se, 11.40; Ni, 8.48%. Mol. wt.: found: 679; calc.: 692.12; Λ_M(10^{-3}M, CH_3CN): 38. Characteristic IR bands: ν(Ni-P) 418(s), 398(s); ν(Ni-Cl) 331(s). NMR (^1H, $CDCl_3$ 25°C): δ, 3.94 (q, 2H, OCH_2, J = 7 Hz), 1.37 (t, 3H, CH_3 J = 7 Hz), 1.90 (s, 4H, CH_2 of DPPE), 6.77–7.68 (m, 33 H, phenyl protons); (^{31}P-$\{^1H\}$ $CDCl_3$, 25°C): δ, 49.93 (*trans* Cl); 32.06 (*trans* Se). CV data (E_{pc}(V)): −0.69.

Synthesis of [Ni(SeAr)$_2$(DPPE)](2a–2c)

These complexes were prepared by a similar procedure to that for **1** but using Ni(DPPE)Cl$_2$ and NaSeAr in 1:2 molar ratio, respectively. Elemental analyses, physical properties, IR, ^{1}H and ^{31}P NMR and CV data for 2a–2c are given below

2a: Yield 80%; m.p. 194°C (dec.). Analysis: found: C, 58.65; H, 4.46; Se, 21.13, Ni 7.12%. Calc. for $C_{38}H_{34}P_2Se_2Ni$: C, 59.32; H, 4.42; Se, 20.54; Ni, 7.64%. Mol. wt.: found: 750; calc.: 768.63. Λ_M (10^{-3}M, CH_3CN):25. Characteristic IR bands: ν(Ni-P) 415(s), 395(s). NMR (^{1}H, $CDCl_3$ 25°C): δ, 1.79 (s, 4H, CH_2 of DPPE) 6.53–7.48 (m, 34H, phenyl protons); (^{31}P-{^{1}H}, $CDCl_3$, 25°C): δ, 32.17 (*trans* Se). CV data (E_{pc}(V): −0.66.

2b: Yield 70%; m.p. 152°C (dec.). Analysis: found: C, 57.23; H, 4.49; Se, 18.67; Ni, 7.31%. Calc. for $C_{40}H_{38}P_2O_2Se_2Ni$: C, 57.92; H, 4.58; Se, 19.05; Ni, 7.08%. Mol. wt.: found: 812. Calc.: 828.63. Λ_M(10^{-3}M, CH_3CN): 27. Characteristic IR bands: ν(Ni-P) 416(s), 396(s). NMR (^{1}H, $CDCl_3$, 25°C): δ, 3.79 (s, 3H, OCH_3), 1.61 (s, 4H, CH_2 of DPPE), 6.41–7.56 (m, 38H, phenyl protons); (^{31}P-{^{1}H}, $CDCl_3$, 25°C):δ, 32.18 (*trans* Se). CV data (E_{pc}(V): −0.70)).

2c: Yield 80%; m.p. 158°C (dec.). Analysis: found: C, 58.39; H, 4.84; Se, 18.10; Ni, 6.75%; Calc. for $C_{42}H_{42}P_2O_2Se_2Ni$: C, 58.83; H, 4.90; Se, 18.43; Ni, 6.85%. Mol. wt.: found: 840; calc.: 856.63. Λ_M (10^{-3}M, CH_3CN): 32. Characteristic IR bands: ν(Ni-P) 419(s), 399(s). NMR (^{1}H, $CDCl_3$, 25°C): δ, 4.01 (q, 2H, OCH_2; J = 7 Hz), 1.39 (t, 3H, CH_3; J = 7 Hz), 1.84 (s, 4H, CH_2 of DPPE), 6.37–7.96 (m, 42H, phenyl protons); (^{31}P-{^{1}H}, $CDCl_3$, 25°C). δ, 32.15 (*trans* Se). CV data (E_{pc}(V) : −0.66.

Preparation of [Ni(X)(SeAr)(DPPE) (3d–3e)

A suspension of 1b (0.2 g) in MeOH (100 cm^3) was treated with an excess of NaX (X = Br or I) (0.2 g) and the mixture stirred at room temperature for 24 h. The solid obtained after stripping of the solvent was treated with CH_2Cl_2 (30 cm^3) and a little charcoal, filtered (Celite) and the filtrate concentrated under low pressure. Addition of *n*-pentane precipitated the product which was removed by filtration, washed with Et_2O and dried *in vacuo*. Yield and results of elemental analyses are given below.

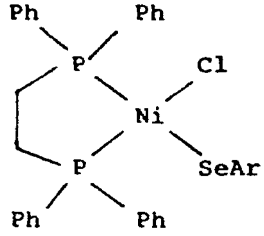
3d: Yield 70%; m.p. 190°C (dec.). Analysis: found: C, 55.83; H, 4.40; Br, 11.14; Se, 10.96; Ni, 8.16%. Calc. for $C_{33}H_{31}P_2BrSeNi$: C, 56.04; H, 4.38; Br, 11.3; Se, 11.17; Ni, 8.31%. Mol. wt.: found: 685; calc.: 706.58.

3e: Yield 75%; m.p. 188°C (dec.). Analysis: found: C, 52.26; H, 4.10; I, 16.50; Se, 10.24; Ni, 7.60%. Calc. for $C_{33}H_{31}P_2ISeNi$: C, 52.55; H, 4.11; I, 16.84; Se. 10.47; Ni, 7.79%. Mol. wt. found: 736; calc.: 753.57.

RESULTS AND DISCUSSION

The reaction of NaSeAr (generated *in situ*) with Ni(DPPE)Cl$_2$ in EtOH-benzene at 1:1 and 2:1 (or higher) molar ratios at room temperature resulted in the formation of complexes of the type [NiCl(SeAr)(DPPE)] **1a–1c** and [Ni(SeAr)$_2$(DPPE)] **2a–2c**, respectively. These reactions are analogous to the reaction of Ni(DPPE)Cl$_2$ with RENa (R = Ph or Et; E = S or Te), which yields the monomeric complex [Ni(ER)$_2$(DPPE).[16,7] Complexes 1 and 2 are soluble in common organic solvents except petroleum ether and diethyl ether. The molar conductance values for **1** and **2** in acetonitrile are fairly low (19–38 Ω^{-1} cm^2 mol^{-1}) compared to values reported[17] for 1:1 electrolytes (120–180Ω^{-1} cm^2 mol^{-1}), suggesting that they are non-electrolytes. Molecular weight determinations in chloroform established their monomeric nature in solution. Elemental analyses agree well with the proposed formulations. IR spectra of these diamagnetic complexes in the solid state exhibit one ν(Ni-Cl) band in **1** in the region 331–332 cm^{-1} and none in **2**. Free Ni(DPPE)Cl$_2$ shows ν(Ni-Cl) bands at 342 and 329 cm^{-1}. The observed ν(Ni-Cl) values are characteristic for terminal chloride ligands and are typical for Cl *trans* to P ligands.[18] The two ν(Ni-P) bands (395–418 cm^{-1}) are indicative of the presence of two *cis* P atoms. The ν(Ni-P) values are higher than ν(Ni-Cl) which has been attributed to the strong *trans* influence of phosphine ligands.[19] The ^{1}H NMR spectra of **1** and **2** show all the expected peaks in the proper intensity ratios. The data agree with earlier reports[10–11] and establish the equivalence of both aryl groups in the complex **2**. The ^{31}P-{^{1}H} NMR spectra show, in case of **1**, two (δ 49.98, 32.20; 50.26, 32.14; 49.93, 32.06 ppm) and for **2**, one (32.17; 32.18; 32.15 ppm) ^{31}P resonances. The two chemical shift values in **1** are indicative of the non-equivalence of the two phosphorous atoms, whereas a single chemical shift value in **2** suggests that the two phosphorous atoms in the complex are equivalent.[20] The observed values are in good agreement with phosphorous *trans* to chlorine and selenium ligands[21–22] (free Ni(DPPE)Cl$_2$ shows δP *trans* Cl at 56.90 ppm). Electronic spectra of **1** and **2** in CHCl$_3$ exhibit only one band in the 456–478 nm region before strong charge transfer bands take over at higher energies. This band seems to have major contribution from the $^1A_1 \rightarrow {}^1B_2$ transition[23–24] in C_2v symmetry characteristic of the square planar geometry of nickel. Since the DPPE ligand always occupies two adjacent positions in a metal complex, complexes **1** and **2** can be assigned a monomeric cis structure.

Metathetical reaction between **1b** and anionic ligands X$^-$ (X = Br(d) or I(e)) occurs in MeOH to give [NiX(SeAr)(DPPE)] (3d–3e). IR spectra of these complexes showed the absence of ν(Ni-Cl); elemental analyses were satisfactory for the proposed formulations.



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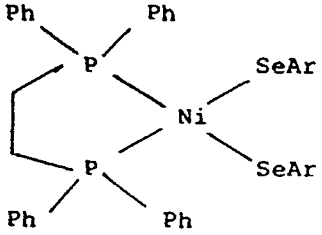

2

R

a = C_6H_5

b = 4-MeOC_6H_4

c = 4-EtOC_6H_4

Electrochemical Studies

A single reduction peak at *ca* −0.56 to −0.70 V with no corresponding oxidation peak is observed in acetonitrile for both complexes **1** and **2**. Unlike nickel(II) tellurolates, no oxidation peak corresponding to ligand oxidation is observed. This clearly indicates that oxidation of selenolate on the electrode surface is much faster than tellurolate. Controlled potential coulometry for **2b** in acetonitrile solution (1.0 mM) at −0.70 V indicated a two-electron reduction, *i.e.*, nickel(II) to nickel(0).

In the case of the diselenides, Ar_2Se_2, cyclic voltammograms show a single reduction ($Ar = C_6H_5$, −0.48 V; $Ar = C_6H_4OMe$-4, −0.81 V and $Ar = C_6H_4OEt$-4, −0.84 V) in acetonitrile with no corresponding oxidation peak. Controlled-potential coulometry for $(4\text{-}EtOC_6H_4)_2Se_2$ (1.0 mM) at −0.84 V indicated a one-electron reduction *i.e.*, $\frac{1}{2}Ar_2Se_2 + \bar{e} \rightarrow ArSe^-$.

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