Crystal Structures of $[NBu^n_4]_2[M(C_3S_5)(C_3Se_5)]$ (M = Ni or Pd) and Properties of the Nickel(II) Complex†

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The complexes $[NBu^n_4]_2[M(C_3S_5)(C_3Se_5)]$ (M = Ni **1** or Pd **2**) were isolated. Oxidation reactions of **1** with $[Fe(C_5H_5)_2][PF_6]$, $[Fe(C_5Me_5)_2][BF_4]$ and $[ttf]_3[BF_4]_2$ ($ttf^{\bullet +}$ = the radical cation of tetrathiafulvalene) and the current-controlled electrolysis of **1** afforded partially oxidized complexes $[NBu^n_4]_{0.7}[Ni(C_3S_5)(C_3Se_5)]$, $[Fe(C_5Me_5)_2]_{0.7}[Ni(C_3S_5)(C_3Se_5)]$, $[ttf]_{0.7}[Ni(C_3S_5)(C_3Se_5)]$ and $[NBu^n_4]_{0.3}[Ni(C_3S_5)(C_3Se_5)]$, respectively. These partially oxidized complexes have electrical conductivities of 4.2×10^{-1}–5.5×10^{-5} S cm^{-1} at 25 °C for compacted pellets. Cyclic voltammetry and electronic absorption spectra of **1**, together with IR, ESR and powder reflectance spectra of the partially oxidized species, are discussed. Single-crystal X-ray structure analyses of **1** and **2** reveal that the anions are separately arranged in the crystal phase and that the metal atoms are located at centres of symmetry, the positions of the S and Se atoms being disordered. The monoclinic crystals, space group $P2_1/c$, have cell dimensions $a = 8.498(5)$, $b = 14.981(6)$, $c = 19.620(7)$ Å, $\beta = 96.13(4)$ ° and $Z = 2$ for **1** and $a = 8.5837(5)$, $b = 15.012(1)$, $c = 19.717(3)$ Å, $\beta = 96.31(1)$ ° and $Z = 2$ for **2**. Block-diagonal least-squares refinements, based on 1825 and 2723 reflections $[|F_o| > 3\sigma(F)]$, converged at $R = 0.076$ and 0.062 for **1** and **2**, respectively.

Metal complexes with the 4,5-dimercapto-1,3-dithiole-2-thionate(2–) ($C_3S_5{}^{2-}$) and the 4,5-di(hydroseleno)-1,3-diselenole-2-selonate(2–) ligands ($C_3Se_5{}^{2-}$) are well known to exhibit high electrical conductivities,[1–3] and some become superconductors.[4–8] Molecular interactions through sulfur–sulfur and selenium–selenium contacts form effective electrical conduction pathways in these crystal phases. Unsymmetrical planar metal complexes with both these ligands are of much interest, since some radical cation salts of unsymmetrical organic sulfur-and/or selenium-rich donors were also reported to behave as superconductors.[9,10] Although a few metal complexes containing both the $C_3S_5{}^{2-}$ and N,N chelate[11–13] or P,P ligands[14] and both the $C_3Se_5{}^{2-}$ and N,N chelate ligands[15] were reported, no metal complex having both the $C_3S_5{}^{2-}$ and $C_3Se_5{}^{2-}$ ligands is known.

This paper reports the isolation, spectroscopic and electrical properties of $[Ni(C_3S_5)(C_3Se_5)]^{2-}$ and some of its oxidized species, together with the crystal structures of $[NBu^n_4]_2[M(C_3S_5)(C_3Se_5)]$ (M = Ni or Pd).

Experimental

Materials.—4,5-Bis(benzoylthio)-1,3-dithiole-2-thione,[16] 4,5-bis(benzoylseleno)-1,3-diselenole-2-selone,[17] $[ttf]_3[BF_4]_2$ [$ttf^{\bullet +}$ = the radical cation of tetrathiafulvalene, 2-(1,3-dithiol-2-ylidene)-1,3-dithiole],[18] $[Fe(C_5H_5)_2][PF_6]$[19] and $[Fe(C_5Me_5)_2][BF_4]$[20] were prepared as described previously.

Preparation of $[M(C_3S_5)(C_3Se_5)]^{2-}$ *Complexes* (M = Ni *or* Pd).—4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (63 mg, 150 μmol) was dissolved in a methanol solution (10 cm^3) containing sodium metal (10 mg, 430 μmol) and stirred for 30 min at room temperature. To the resulting solution of $Na_2[C_3S_5]$ was added a methanol solution (10 cm^3) of $NiCl_2{\cdot}6H_2O$ (37 mg, 150 μmol) and the mixture stirred. A methanol solution (10 cm^3) of $Na_2[C_3Se_5]$ prepared by the reaction of 4,5-bis(benzoylseleno)-1,3-diselenole-2-selone (100 mg, 160 μmol) with sodium metal, as described for $Na_2[C_3S_5]$, was added, followed by a methanol solution (3 cm^3) of $[NBu^n_4]Br$ (100 mg, 0.31 mmol). The solution was allowed to stand in a refrigerator for 24 h to afford dark green crystals of $[NBu^n_4]_2[Ni(C_3S_5)(C_3Se_5)]$ **1** (72% yield) (Found: C, 39.1; H, 6.2; N, 2.45. Calc. for $C_{38}H_{72}N_2NiS_5Se_5$: C, 39.0; H, 6.2; N, 2.4%). Using $[NMe_4]Br$ or $[AsPh_4]Br$ instead of $[NBu^n_4]Br$ in the reaction described above, $[NMe_4]_2[Ni(C_3S_5)(C_3Se_5)]$ **3** (Found: C, 19.5; H, 3.0; N, 3.3. Calc. for $C_{14}H_{24}N_2NiS_5Se_5$: C, 20.15; H, 2.9; N, 3.35%) or $[AsPh_4]_2[Ni(C_3S_5)(C_3Se_5)]$ **4** (Found: C, 42.6; H, 2.75. Calc. for $C_{54}H_{40}As_2NiS_5Se_5$: C, 42.65; H, 2.75%) was obtained.

The complex $[NBu^n_4]_2[Pd(C_3S_5)(C_3Se_5)]$ **2** was also prepared as described above, using $Na_2[PdCl_4]$ instead of $NiCl_2{\cdot}6H_2O$ (60% yield) (Found: C, 36.95; H, 5.8; N, 2.8. Calc. for $C_{38}H_{72}N_2PdS_5Se_5$: C, 37.45; H, 5.95; N, 2.3%).

Preparation of Partially Oxidized $[Ni(C_3S_5)(C_3Se_5)]^{0.7-}$ *Complexes.*—To an acetonitrile solution (10 cm^3) containing complex **1** (20 mg, 17 μmol) was added an acetonitrile solution (10 cm^3) of $[ttf]_3[BF_4]_2$ (13 mg, 17 μmol) and the mixture stirred for 30 min at room temperature. Black microcrystals of $[ttf]_{0.7}[Ni(C_3S_5)(C_3Se_5)]$ **5** precipitated, which were filtered off, washed with acetonitrile and diethyl ether, and dried *in vacuo* (35% yield) (Found: C, 14.3; H, 0.3. Calc. for $C_{10.2}H_{2.8}NiS_{7.8}Se_5$: C, 14.75; H, 0.35%).

To an acetonitrile solution (3 cm^3) of $[Fe(C_5H_5)_2][PF_6]$ (17 mg, 51 μmol) was added an acetonitrile solution (10 cm^3) of complex **1** and the mixture stirred for 1 h. Dark brown solid $[NBu^n_4]_{0.7}[Ni(C_3S_5)(C_3Se_5)]$ **6** was obtained, collected by centrifugation, washed with acetonitrile and diethyl ether, and dried *in vacuo* (70% yield) (Found: C, 23.6; H, 3.05; N, 1.2. Calc. for $C_{17.2}H_{25.2}N_{0.7}NiS_5Se_5$: C, 24.15; H, 3.0; N, 1.15%).

To an acetonitrile solution (10 cm^3) of complex **1** (20 mg, 17 μmol) was added an acetonitrile solution (5 cm^3) of $[Fe(C_5Me_5)_2][BF_4]$ (14 mg, 34 μmol) and the mixture stirred for 1 h to afford a brown precipitate of $[Fe(C_5Me_5)_2]_{0.7}$-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

Table 1 Experimental data and structure refinement details[a] for complexes **1** and **2**

Complex	**1**	**2**
Formula	$C_{38}H_{72}N_2NiS_5Se_5$	$C_{38}H_{72}N_2PdS_5Se_5$
M	1170.8	1218.5
Crystal size/mm	0.8 × 0.13 × 0.50	0.06 × 0.13 × 0.28
a/Å	8.498(5)	8.5837(5)
b/Å	14.981(6)	15.012(1)
c/Å	19.620(7)	19.717(3)
β/°	96.13(4)	96.31(1)
U/Å^3	2484(2)	2525.2(5)
D_c/g cm^{-3}	1.565(1)	1.603(1)
F(000)	1184.0	1220.0
Radiation (λ/Å)	Mo-Kα (0.710 69)	Cu-Kα (1.5418)
μ/cm^{-1}	45.6	98.2
Scan interval/° min^{-1}	8	4
Collected octants	$-h, +k, \pm l$	$\pm h, +k, -l$
No of data collected at room temperature	6299	4207
No of independent data with $\lvert F_o \rvert > 3\sigma(F)$	1825	2723
Absorption correction range[b]	1.01–1.17	1.02–1.72
R	0.076	0.062
R'[c]	0.072	0.070

[a] Rigaku-AFC diffractometer; scan ranges $3 < 2\theta < 50°$ for complex **1** and $4 < 2\theta < 125°$ for **2**; monoclinic, space group $P2_1/c$, $Z = 2$. [b] Ref. 21. [c] $[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$, where $w^{-1} = \sigma^2(F_o) + 0.0005F_o^2$.

Table 2 Atomic coordinates (× 10^4) of $[NBu^n{}_4]_2[Ni(C_3S_5)(C_3Se_5)]$ **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Ni	0	0	0
S/Se(1)	−361(3)	1036(2)	795(1)
S/Se(2)	987(3)	1103(2)	2397(1)
S/Se(3)	3194(3)	431(2)	3699(1)
S/Se(4)	3005(3)	−523(2)	2264(1)
S/Se(5)	1804(3)	−761(1)	675(1)
N	4628(12)	2527(7)	608(5)
C(1)	912(16)	557(9)	1532(7)
C(2)	2428(16)	332(9)	7814(7)
C(3)	1786(16)	−165(9)	1487(7)
C(4)	3005(16)	2858(9)	788(7)
C(5)	3183(18)	3575(11)	1356(8)
C(6)	1579(19)	4051(10)	1355(8)
C(7)	216(19)	3450(11)	1549(8)
C(8)	4351(16)	1693(9)	151(7)
C(9)	3333(18)	1919(9)	−537(7)
C(10)	3320(19)	1031(10)	−965(7)
C(11)	2284(21)	1200(12)	−1653(8)
C(12)	5748(16)	2270(10)	1249(7)
C(13)	5068(20)	1487(12)	1665(8)
C(14)	6287(21)	1292(12)	2320(8)
C(15)	6303(34)	2036(13)	2819(10)
C(16)	5432(16)	3296(8)	253(7)
C(17)	6943(17)	2980(9)	−54(8)
C(18)	7691(17)	3837(9)	−314(7)
C(19)	9305(18)	3570(11)	−589(8)

$[Ni(C_3S_5)(C_3Se_5)]$ **7** (81% yield) (Found: C, 26.35; H, 2.6. Calc. for $C_{20}H_{21}Fe_{0.7}NiS_5Se_5$: C, 26.25; H, 2.3%).

An acetonitrile solution (50 cm^3) containing complex **1** (20 mg, 17 μmol) and $[NBu^n{}_4][ClO_4]$ (1.03 g, 3 mmol) was subjected to a controlled-current (1 μA) electrolysis under a nitrogen atmosphere in a cell with platinum-wire electrodes for 20 d. Black microcrystals of $[NBu^n{}_4]_{0.3}[Ni(C_3S_5)(C_3Se_5)]$ **8** produced on the anode were collected and dried *in vacuo* (4 mg) (Found: C, 17.75; H, 1.55; N, 0.5. Calc. for $C_{10.8}H_{10.8}N_{0.3}NiS_5Se_5$: C, 17.1; H, 1.45; N, 0.55%).

Table 3 Atomic coordinates (× 10^4) of $[NBu^n{}_4]_2[Pd(C_3S_5)(C_3Se_5)]$ **2** with e.s.d.s in parentheses

Atom	x	y	z
Pd	0	0	0
S/Se(1)	−339(2)	1081.2(9)	856.3(7)
S/Se(2)	1022(2)	1137.8(9)	2447.1(8)
S/Se(3)	3201(2)	461(1)	3753.5(9)
S/Se(4)	3018(2)	−508.8(9)	2329.7(8)
S/Se(5)	1854(2)	797(1)	752.0(8)
N	4657(8)	2504(5)	620(4)
C(1)	931(10)	591(6)	1588(5)
C(2)	2430(12)	358(7)	2869(6)
C(3)	1808(11)	−160(6)	1539(5)
C(4)	3033(11)	2857(7)	805(5)
C(5)	3263(12)	3604(7)	1360(5)
C(6)	1614(15)	4097(8)	1351(7)
C(7)	329(15)	3520(9)	1551(7)
C(8)	4373(12)	1687(6)	170(5)
C(9)	3394(13)	1875(7)	−501(5)
C(10)	3358(15)	1015(7)	−942(6)
C(11)	2361(16)	1177(10)	−1651(6)
C(12)	5754(11)	2228(7)	1274(5)
C(13)	5044(14)	1507(8)	1688(6)
C(14)	6266(16)	1302(9)	2360(6)
C(15)	6342(27)	2013(10)	2822(8)
C(16)	5476(10)	3259(6)	267(5)
C(17)	6985(11)	2946(7)	−13(5)
C(18)	7712(12)	3786(7)	−316(5)
C(19)	9280(13)	3508(8)	−572(6)

Crystal Structure Determinations of $[NBu^n{}_4]_2[Ni(C_3S_5)(C_3Se_5)]$ **1** *and* $[NBu^n{}_4]_2[Pd(C_3S_5)(C_3Se_5)]$ **2**.—Crystal data and details of the measurements are listed in Table 1. The unit-cell parameters were determined from 25 independent reflections having $20 < 2\theta < 30°$ (Mo-Kα radiation) for complex **1** and $37 < 2\theta < 50°$ (Cu-Kα radiation) for **2**. For both the complexes, systematic absences ($h0l$, with l odd; $0k0$, with k odd; and $00l$, with l odd) enabled assignment of space group $P2_1/c$.

The structures of both complexes were solved according to the direct (MULTAN) method.[22] Subsequent Fourier maps revealed all the coordinates of the non-hydrogen atoms, and that the position of sulfur and selenium atoms were disordered. They were refined anisotropically by the block-diagonal least-squares procedure. Atomic scattering factors used in the refinements were taken from ref. 23. For the disordered sulfur and selenium atoms the averaged values were used. Atomic coordinates for complexes **1** and **2** are listed in Tables 2 and 3, respectively.

Crystallographic calculations were performed using the programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS 930S computer at the Research Centre for Protein Engineering, Institute for Protein Research, Osaka University. Fig. 1 was drawn by the local version of the ORTEP II program.[24]

Physical Measurements.—Electronic absorption spectra were recorded on a Shimadzu UV-2200 spectrophotometer and powder reflectance spectra with a 60Φ integrating sphere unit. Infrared,[25] ESR and X-ray photoelectron spectra (XPS)[26] were recorded as described elsewhere. Electrical resistivities of the complexes were measured for compacted pellets by the conventional two-probe method,[25] and cyclic voltammograms were recorded in acetonitrile as described previously.[27]

Results and Discussion

Crystal Structures of $[NBu^n{}_4]_2[M(C_3S_5)(C_3Se_5)]$ (M = Ni **1** *or* Pd **2**).—Both the complexes are in the monoclinic system, space group $P2_1/c$, which is the same as that of $[NBu^n{}_4]_2[Ni(C_3S_5)_2]$.[28] They contain planar $C_3S_5{}^{2-}$ and $C_3Se_5{}^{2-}$

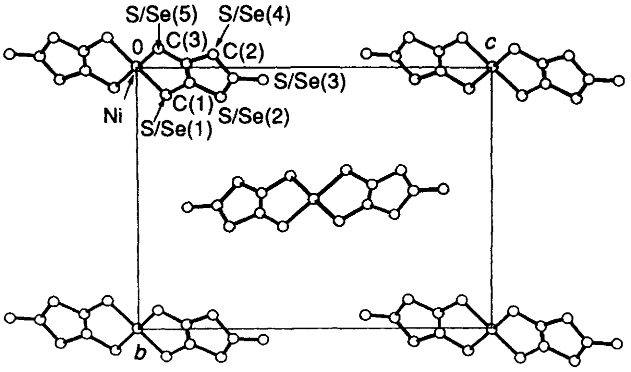

Fig. 1 Packing diagram of the anions of $[NBu^n_4]_2[Ni(C_3S_5)(C_3Se_5)]$ **1** projected along the *a* axis, together with the atom-labelling scheme; the anions of complex **2** are packed essentially in the same manner

Table 4 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for the anions of $[NBu^n_4]_2[M(C_3S_5)(C_3Se_5)]$ (M = Ni **1** or Pd **2**)

	M = Ni	M = Pd
M–SSe(1)	2.245(1)	2.383(1)
M–SSe(5)	2.229(3)	2.376(2)
S/Se(1)–C(1)	1.855(13)	1.862(9)
S/Se(2)–C(1)	1.878(14)	1.876(9)
S/Se(2)–C(2)	1.814(13)	1.817(10)
S/Se(3)–C(2)	1.793(14)	1.803(11)
S/Se(4)–C(2)	1.777(14)	1.788(11)
S/Se(4)–C(3)	1.829(13)	1.851(10)
S/Se(5)–C(3)	1.828(14)	1.827(10)
C(1)–C(3)	1.320(19)	1.364(13)
S/Se(1)–M–S/Se(5)	94.4(1)	91.5(1)
M–S/Se(1)–C(1)	99.3(4)	100.0(3)
C(1)–S/Se(2)–C(2)	95.0(6)	95.2(4)
C(2)–S/Se(4)–C(3)	97.3(6)	97.2(4)
M–S/Se(5)–C(3)	101.5(4)	101.0(3)
S/Se(1)–C(1)–C(3)	123.4(11)	123.5(7)
S/Se(2)–C(1)–C(3)	116.9(10)	117.2(7)
S/Se(2)–C(2)–S/Se(3)	122.9(8)	122.9(6)
S/Se(2)–C(2)–S/Se(4)	113.6(7)	114.4(6)
S/Se(4)–C(3)–C(1)	117.2(11)	115.9(7)
S/Se(5)–C(3)–C(1)	121.0(10)	123.8(7)

ligands co-ordinated to Ni^{II} and Pd^{II}, and the metal ions are located on a centre of symmetry, resulting in disorder with respect to the positions of both the ligands. The C_3S_5/C_3Se_5 moieties are almost planar (±0.02 and ±0.04 Å for **1** and **2**, respectively). Fig. 1 shows the molecular packing diagram of the anion moieties of complex **1** projected along the *a* axis, together with the atom-labelling scheme. Selected bond distances and angles are in Table 4. The Ni–S/Se distances [2.229(3), 2.245(1) Å] are close to those of $[NBu^n_4]_2[Ni(C_3S_5)_2]$ [2.211(6), 2.221(6) Å],[28] $[NBu^n_4]_2[Ni(bds)_2]$ [bds = benzene-1,2-diselenolate(2−)] (average 2.259 Å)[29] and $[tmtsf]_2[Ni(tds)_2]$ [$tmtsf^{\cdot +}$ = the radical cation of tetramethyltetraselenafulvalene, 2-(4,5-dimethyl-1,3-diselenol-2-ylidene)-4,5-dimethyl-1,3-diselenole; tds = 2,2-bis(trifluoromethyl)ethylene-1,1-diselenolate(2−)] (average 2.255 Å).[30]

The anions are located separately from each other having no significant contact between the chalcogen atoms within the sum of their van der Waals radii. This is essentially as in $[NBu^n_4]_2[Ni(C_3S_5)_2]$.[28] For the palladium analogue **2** the geometry of the anion moiety and its packing in the crystal phase are essentially the same as those of **1**. The Pd–S/Se distances are somewhat longer than the Ni–S/Se distances, resulting in a smaller S/Se(1)–Pd–S/Se(5) angle.

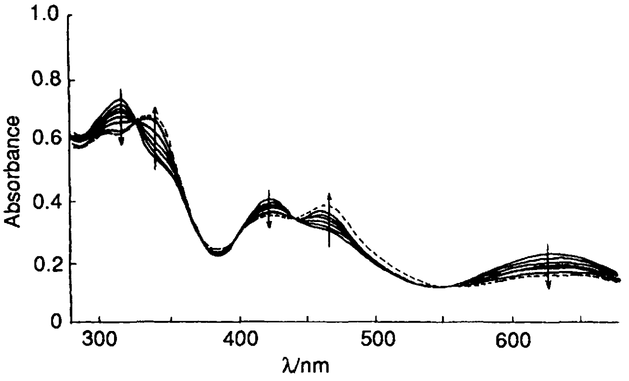

Fig. 2 Time-dependent spectral changes of a dimethylformamide solution containing equimolar (2.1×10^{-4} mol dm^{-3}) $[NBu^n_4]_2[Ni(C_3S_5)_2]$ and $[NBu^n_4]_2[Ni(C_3Se_5)_2]$ (recorded six times every 20 min) and the spectrum (– – –) of $[NBu^n_4]_2[Ni(C_3S_5)(C_3Se_5)]$ (2.1×10^4 mol dm^{-3})

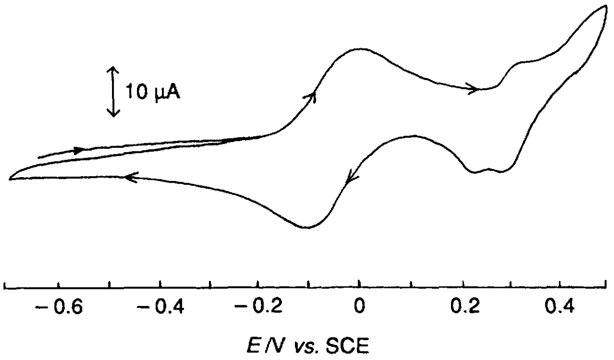

Fig. 3 Cyclic voltammogram of $[NBu^n_4]_2[Ni(C_3S_5)(C_3Se_5)]$ **1** (8.0×10^{-4} mol dm^{-3}) in dimethylformamide, 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$; scan rate 0.1 V s^{-1}

Spectroscopic and Electrochemical Properties of $[M(C_3S_5)(C_3Se_5)]^{2-}$ (M = Ni *or* Pd).—Fig. 2 illustrates the change with time of the electronic absorption spectrum of an equimolar mixture of $[NBu^n_4]_2[Ni(C_3S_5)_2]$ and $[NBu^n_4]_2[Ni(C_3Se_5)_2]$ in dimethylformamide. The final spectrum is essentially the same as that of complex **1** indicating the stable formation of the mixed-ligand complex in solution. The $[Ni(C_3S_5)_2]^{2-}$ anion shows the π–π^* bands at 316 and 600 nm and $[Ni(C_3Se_5)_2]^{2-}$ at 350 and 674 nm. The charge-transfer transitions occur at 407 (S) and 458 nm (Se), respectively, as deduced from the bands of other $[M(C_3S_5)_2]^{n-}$ and $[M(C_3Se_5)_2]^{n-}$ anions (M = Au^{III}, $n = 1$; Cu^{II}, $n = 2$).[3,27,31] The anion $[Ni(C_3S_5)(C_3Se_5)]^{2-}$ shows π–π^* bands at 335 and 615 nm ($\varepsilon = 2.2 \times 10^4$ and 5.1×10^3 dm^3 mol^{-1} cm^{-1}) and the sulfur- and selenium-to-metal charge-transfer bands at 410 and 454 nm ($\varepsilon = 1.0 \times 10^4$ and 1.2×10^4 dm^3 mol^{-1} cm^{-1}). Similar spectral changes were observed in a dimethylformamide solution of equimolar $[NBu^n_4]_2[Pd(C_3S_5)_2]$ and $[NBu^n_4]_2[Pd(C_3Se_5)_2]$, forming $[Pd(C_3S_5)(C_3Se_5)]^{2-}$. Such ligand exchanges were also reported for zinc(II) and nickel(II) complexes with $C_3S_5^{2-}$ and the dithiolate(−) and diselenolate(−) ligands.[32]

The ligand-exchange reactions described seem to follow formally a second-order rate law, as reported for other ligand-exchange reactions of copper(II) and nickel(II) complexes.[32,33] The rate constant for the exchange reaction $[Ni(C_3S_5)_2]^{2-} + [Ni(C_3Se_5)_2]^{2-} \longrightarrow 2[Ni(C_3S_5)(C_3Se_5)]^{2-}$ was estimated as $k_2 = 9.6 \pm 0.5$ dm^3 mol^{-1} s^{-1}.

A cyclic voltammogram of complex **1** measured in dimethylformamide is depicted in Fig. 3. A reversible redox wave is observed at $E_{\frac{1}{2}} = (E_{pc} + E_{pa})/2 = -0.050$ V *vs.* saturated calomel electrode (SCE) ($\Delta E = E_{pc} - E_{pa} = 60$ mV) which corresponds to the $[Ni(C_3S_5)(C_3Se_5)]^{2-}$–$[Ni(C_3S_5)(C_3Se_5)]^{-}$ redox couple. This $E_{\frac{1}{2}}$ value is intermediate between those of $[NBu^n_4]_2[Ni(C_3S_5)_2]$ (−0.032 V, $\Delta E = 65$ mV) and $[NBu^n_4]_2[Ni(C_3Se_5)_2]$ (−0.105 V *vs.* SCE, $\Delta E = 60$ mV). Further oxidation waves are observed at +0.30 and +0.43 V

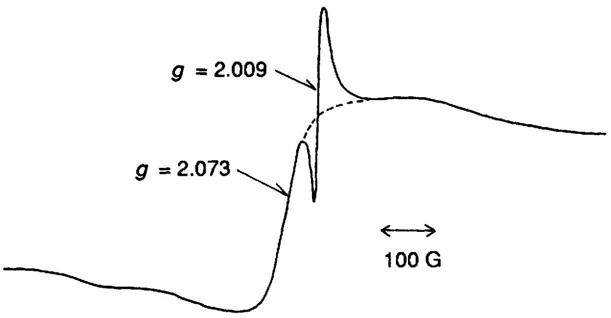

Fig. 4 The ESR spectrum of $[ttf]_{0.7}[Ni(C_3S_5)(C_3Se_5)]$ **5** in the solid state at room temperature; G = 10^{-4} T

which seem to be due to oxidation of the ligand. These oxidation waves are not observed for $[Ni(C_3S_5)_2]^{2-}$ and $[Ni(C_3Se_5)_2]^{2-}$. The findings support the presence of a complex having both $C_3S_5{}^{2-}$ and $C_3Se_5{}^{2-}$ ligands co-ordinated to the metal centre.

The energy of the nickel $2p_{\frac{3}{2}}$ electrons of complex **1** determined from XPS is 853.8 eV, which is an intermediate value between that of $[NBu^n{}_4]_2[Ni(C_3S_5)_2]$ (853.1 eV)[34] and that of $[NBu^n{}_4]_2[Ni(C_3Se_5)_2]$ (854.2 eV).[31] These observations are consistent with the presence of both ligands bound to the nickel(II) ion.

Partially Oxidized Complexes of $[Ni(C_3S_5)(C_3Se_5)]^{2-}$.—The complex $[NBu^n{}_4]_2[Ni(C_3S_5)(C_3Se_5)]$ is oxidized by $[Fe(C_5H_5)_2]^+$, $[Fe(C_5Me_5)_2]^+$ and the $ttf^{\bullet+}$ radical cation to afford $[Ni(C_3S_5)(C_3Se_5)]^{0.7-}$ complexes **5**–**7**. They exhibit broad C=C stretching IR bands at 1310, 1355 and 1350 cm^{-1}, respectively, which are at lower wavenumber than that of $[NBu^n{}_4]_2[Ni(C_3S_5)(C_3Se_5)]$ (1425 cm^{-1}). These findings suggest ligand-centred oxidation, as observed for other C_3S_5 and C_3Se_5 metal complexes.[3,34] In accordance with this, broad ESR signals [g = 2.073 (**5**), 2.080 (**6**) and 2.073 (**7**)] are observed which are close to the signals for other C_3S_5 and C_3Se_5 metal complexes obtained upon ligand-centred oxidation.[3,34] The ESR spectrum of complex **5** is illustrated in Fig. 4. The sharp signal at g = 2.009 due to the $ttf^{\bullet+}$ radical cation[35] overlaps with the broad signal (g = 2.073) of the partially oxidized anion.

The complexes in the present study behave as semiconductors: **1** exhibits a small conductivity of 7.3×10^{-8} S cm^{-1} (measured for a compacted pellet at 25 °C), while the partially oxidized species have higher conductivities, 4.2×10^{-1} (**5**), 5.5×10^{-5} (**6**), 3.0×10^{-5} (**7**) and 6.1×10^{-3} S cm^{-1} (**8**) (for compacted pellets). These electrical conductivities arise from electron conduction pathways involving molecular interactions through S ··· S, Se ··· Se and/or S ··· Se non-bonded contacts which are more effective among the partially oxidized ligands. Powder reflectance spectra of **5**–**7** exhibit broad bands at 850, 790 and 855 nm, respectively, which do not appear in the spectra of solid **1**, $[NBu^n{}_4]_2[Ni(C_3S_5)_2]$ and $[NBu^n{}_4]_2[Ni(C_3Se_5)_2]$. These bands seem to be due to interanionic interactions through sulfur and selenium atoms. The extremely high conductivity observed for **5** may arise from an effective molecular interaction through S ··· S and S ··· Se contacts including the $ttf^{\bullet+}$ radical cation.

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