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Syntheses, X-ray crystal structures and properties of di- and tetra-ferrocenyl nickel-bis(1,4-dithiin-5,6-dithiolate) complexes

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Tetra-n-butylammonium salts of nickel-bis(2-ferrocenyl-1,4-dithiin-5,6-dithiolate) (**1**; TBA[Ni(fcvdt)$_2$]) and nickel-bis(2,3-diferrocenyl-1,4-dithiin-5,6-dithiolate) (**2**; TBA[Ni(dfcvdt)$_2$]) have been successfully synthesized. The crystal structures of complex **1** and **2** were determined by X-ray analysis. The [Ni(fcvdt)$_2$]$^-$ anion has a chair-like conformation with the two ferrocenyl groups folding up and down while the [Ni(dfcvdt)$_2$]$^-$ anion has a boat-like conformation with four ferrocenyl groups folding up. Cyclic voltammograms of these complexes show two reversible redox peaks at around −0.9 V and −0.2 V (Ag/Ag$^+$, THF) associated with the Ni(II) dithiolate complex and one quasi-reversible peak associated with the ferrocenyl moieties. The complexes exhibit a strong near-IR absorption at 1178 nm (log ε = 3.99) for complex **1** and at 1155 nm (log ε = 4.06) for complex **2**. This suggests the possibility of utilizing these complexes as near-IR dyes for absorbing lower energy.

Ferrocene and its derivatives[1] have received much attention because they are strong electron donors and show reversible redox properties and catalytic behavior. Utilizing these properties, they may be used as catalysts in organic synthesis and as building blocks in charge-transfer complexes, chemical sensors, liquid crystals and polymers. The combination of ferrocene with nickel-bis(1,2-ethylenedithiolate) (**I**; Ni(edt)$_2$) (Scheme 1), the simplest nickel-bis(dithiolate), opens up a new area of materials science. One example which combines ferrocenes and complex **I**, is complex **II** in which the Ni(edt)$_2$ moiety is directly connected to two ferrocenyl groups.[2] From cyclic voltammetry (CV) measurements of the tetra-n-butyl-ammonium (n-Bu$_4$N) salt of complex **II**, it was concluded that the Ni(edt)$_2$ and ferrocenyl moieties did not effectively communicate with each other. Another example is the tetraferrocenyl Ni(edt)$_2$ complex **III**,[3] which showed a strong near-IR absorption at 1310 nm in CH_2Cl_2 solution and opened up the possibility for a new family of the near-IR absorbing dye as a light absorber in a laser diode.[4] There is another example of a ferrocenyl Ni(edt)$_2$ complex which shows a strong near-IR absorption at λ_{max} = 1250 nm and in which the Ni(edt)$_2$ moiety is not linked directly to ferrocenyl groups as in complexes **II** and **III**, but *via* a –CH_2S– spacer.[5] These latter complexes are observed to absorb at considerably lower energy compared to that of complex **I** (λ_{max} = 720 nm in hexane).[6]

Recently, we have reported the synthesis and properties of diferrocenyl-VT (VT: bis(vinylenedithio)tetrathiafulvalene) and its radical salts.[7] Here, we report the synthesis and X-ray crystal structures of the di- and tetra-ferrocenyl Ni(ddt)$_2$ complexes (**1** and **2**; ddt: 1,4-dithiin-2,3-dithiolate), in which the ferrocenyl ddt ligands can be regarded as an extended multisulfur system compared to the ferrocenyl edt ligands in complex **II** and **III**. The properties of complexes **1** and **2** such as EPR, cyclic voltammetry and near-IR absorption are also discussed in relation to the complexes being potent candidates for molecular conductors and infrared dyes for absorbing low energy.

I: X = Y = H; Ni(edt)$_2$
II: X = H, Y = Fc
III: X = Y = Fc

IV: Ni(ddt)$_2$

Scheme 1 Structures of some nickel-bis(dithiolene)s.

Experimental

Measurements

Infrared spectra were recorded by the KBr method on a MIDAC FT-IR spectrometer, UV-vis spectra in acetonitrile on a HP 8452A diode array spectrometer, near-IR in CH_2Cl_2 on a Shimadzu UV-3100. EPR measurements on polycrystalline samples were carried out at the Korea Basic Science Institute (KBSI) in Seoul, by using a BRUKER ER 200D-SRC X-band spectrometer (9.79 GHz) at 300 K and 77 K. Cyclic voltammetry (CV) measurements of the nickel complexes were performed with a BAS 100B system in THF with (n-Bu$_4$N)·BF$_4$ as the supporting electrolyte (0.1 M). The working electrode was a glassy carbon disc (diameter = 3.0 mm) or a carbon fiber ultramicroelectrode (diameter = 10 μm) and the counter electrode was platinum wire. The reference electrode was Ag/Ag$^+$ (0.01 M $AgNO_3$ in THF with the same electrolyte) and the measured potentials are reported *versus* the Fc/Fc$^+$ couple ($E_{1/2}$ = 0.22 V). Voltammograms were run at a scan rate of 0.05 V s^{-1}. Electrical conductivities were measured on pressed pellets of microcrystalline samples by the two-probe method at room temperature.

X-Ray crystal structure determination

All the X-ray diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The structures were solved and refined using SHELXS-86 and SHELXL-93.[8] Hydrogen atoms in acetone and the tetrabutylammonium cation of complex **2**·[Me$_2$CO] were not fixed because of the high disorder problem. Crystal parameters and experimental details are collected in Table 1.

CCDC reference number 1145/226. See http://www.rsc.org/suppdata/jm/b0/b001829p/ for crystallographic files in .cif format.

Table 1 Crystal data and structure refinement for (n-Bu_4N)[Ni(fcvdt)$_2$]·[Me_2CO]$_{0.5}$ and (n-Bu_4N)[Ni(dfcvdt)$_2$]·[Me_2CO]

Compound	TBA[Ni(fcvdt)$_2$]·[Me_2CO]$_{0.5}$	TBA[Ni(dfcvdt)$_2$]·[Me_2CO]
Empirical formula	$C_{45.5}H_{59}Fe_2NNiO_{0.5}S_8$	$C_{67}H_{78}Fe_4NNiOS_8$
Formula weight	1054.83	1451.89
Crystal system	monoclinic	orthorhombic
Space group	*P*2(1)/*a*	*Pnma*
a/Å	19.503(4)	20.457(14)
b/Å	10.841(3)	39.220(13)
c/Å	24.137(5)	8.496(2)
β/degrees	97.13(3)	90
Volume/Å^3	5064(2)	6817(5)
Z	4	4
Abs. coeff./mm^{-1}	1.296	1.388
Reflections collected	4697 [*R*(int) = 0.0659]	3052
*R*1, *wR*2^a	0.0772, 0.1971 [$I > 2\sigma(I)$]	0.0861, 0.2515 [$I > 3\sigma(I)$]

$^a R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR2 = \Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma wF_o{}^4)^{1/2}$, where $w = 1/\{\sigma^2F_o{}^2+(aP)^2+bP$ where $P = \{\max(F_o{}^2,0)+2F_c{}^2\}/3$.

Preparation of 1,2-di(ferrocenyl)ethylene: 3b

To a 30 ml THF suspension containing $TiCl_4$ (1.95 ml, 18 mmol) was added ferrocenecarboxaldehyde (2.5 g, 12 mmol) and then Zn powder (2.35 g, 40 mmol) at ice temperature, and the mixture was refluxed for 4 h. After cooling to room temperature, the black mixture was poured into ice (50 g), hydrolyzed with saturated aqueous $NaHCO_3$ (30 ml) and extracted with CH_2Cl_2 (100 ml). The extract was dried over $MgSO_4$ and evaporated under reduced pressure.

Yield 76%; mp 163–165 °C (decomp.); ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.13 (5H, C_5H_5, s), 4.24 (2H, C_5H_4, t), 4.39 (2H, C_5H_4, t), 6.41 (1H, CH, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 66.232, 68.580, 69,194, 156.347; FT-IR (KBr, cm^{-1}) 1633.8, 1385, 1253.8, 1107.2, 1051.3, 1028.1, 1001.1, 947.1, 908.5, 819.8, 763.9, 493.8 (Fc); UV-vis (CH_3CN, nm) 214(st), 244(m), 276(m), 312(m), 460(vw).

Preparation of 5,6-dihydro-5,6-diferrocenyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione: 5b

A 40 ml benzene suspension of oligomeric trithione **4** (0.43 g, 2.2 mmol) and **3b** (0.87 g, 2.2 mmol) was refluxed for 3.5 h. The hot solution was filtered and decolourized with activated carbon. The product was purified by column chromatography on a silica gel support using chloroform as the eluent, and recrystallized from $CHCl_3$/MeOH in a freezer.

Yield 70%; mp 203–204 °C; FABMS (*m*/*z*) 592 (M$^+$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.63 (2H, C_5H_4, s), 4.01 (2H, C_5H_4, s), 4.20 (5H, C_5H_5, s), 4.27 (1H, CH, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 52.670, 66.022, 67.832, 68.710, 69,206, 70.181, 212.097; FT-IR (KBr, cm^{-1}) 1654.2, 1481.2, 1405.8, 1388.9 (C=C), 1265.9, 1105.8, 1062.0 (C=S), 996.4, 923.8, 887.1, 823.8, 805.4 (Ar C–H), 483.8 (Fc); UV-vis (CH_3CN, nm) 212(st), 276(sh), 312(sh), 412(m).

Preparation of 5,6-diferrocenyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-thione: 6b

25 ml benzene with **5b** (1.78 g, 3 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 0.68 g, 3 mmol) was refluxed for 1 h. The hot solution was filtered and decolourized with activated carbon. The product was purified by column chromatography on a silica gel support using chloroform as the eluent, and recrystallized from $CHCl_3$/EtOH in a freezer.

Yield 44%; mp >190 °C (decomp.); FABMS (*m*/*z*) 590 (M$^+$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.19 (5H, C_5H_5, s), 4.25 (2H, C_5H_4, t), 4.39 (2H, C_5H_4, t); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 68.920, 69.869, 70.353, 130.463; FT-IR (KBr, cm^{-1}) 1654.3, 1560.2, 1488.3, 1407.9 (C=C), 1264.0, 1105.2, 1064.6, 1046.8 (C=S), 1001.2, 911.7, 885.7, 817.6 (Ar C–H), 493.3 (Fc); UV-vis (CH_3CN, nm): 214(st), 244(sh), 274(sh), 310(m), 406(w).

Preparation of 5,6-diferrocenyl-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-one: 7b

To a 50 ml $CHCl_3$ solution of **6b** (0.74 g, 1.26 mmol) were added acetic acid (50 ml) and $Hg(OAc)_2$ (1.27 g, 4 mmol), and the mixture was stirred for 30 min at room temperature. The white precipitate was filtered off, and the filtrate was washed with H_2O, saturated aq. $NaHCO_3$, finally with H_2O, and then dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on a silica gel support using chloroform as the eluent.

Yield 40%; mp >175 °C (decomp.); ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.18 (5H, C_5H_5, s), 4.20 (2H, C_5H_4, s), 4.24 (2H, C_5H_4, s); FT-IR (KBr, cm^{-1}) 1676.2 (C=O), 1626.1, 1375.3, 1265.4 (C=C), 1105.3, 1064.8, 1047.4, 1001.1, 910.5, 873.8, 817.9, 758.1 (Ar C–H), 493.8 (Fc); UV-vis (CH_3CN, nm) 216(st), 250(sh), 294(m), 382(w), 468(vw).

Preparation of (n-Bu_4N)[Ni(dfcvdt)$_2$]: 2

To an EtOH suspension of **7b** (144 mg, 0.25 mmol) was added KOH (28.1 mg, 0.5 mmol) dissolved in EtOH (5 ml) with continuous stirring under a dry N_2 atmosphere. To this solution were added $NiCl_2$ (16.9 mg, 0.13 mmol) and (n-Bu_4N)·Br (80.6 mg, 0.25 mmol), each dissolved in 5 ml ethanol, and the mixture stirred for an additional 1 h. The brown-coloured product was filtered off, washed successively with EtOH, H_2O and diethyl ether in the presence of air, and then recrystallized from acetone/ethyl acetate.

Yield 10%; Anal. Calc. for $C_{67}H_{78}Fe_4NNiOS_8$: C 55.43, H 5.41, S 17.66; Found: C 54.80, H 5.37, S 17.13%; FT-IR (KBr, cm^{-1}) 3094 (Fc C–H), 2963, 2932, 2874 (C–H), 1543, 1561, 1458 (Fc C–C), 1389 (C=C), 885, 820, 762 (Fc C–H), 498 (Fc Ar); UV-vis (CH_3CN, nm) 218(st) 252(m) 318(m), 460(sh).

Preparation of (n-Bu_4N)[Ni(fcvdt)$_2$]: 1

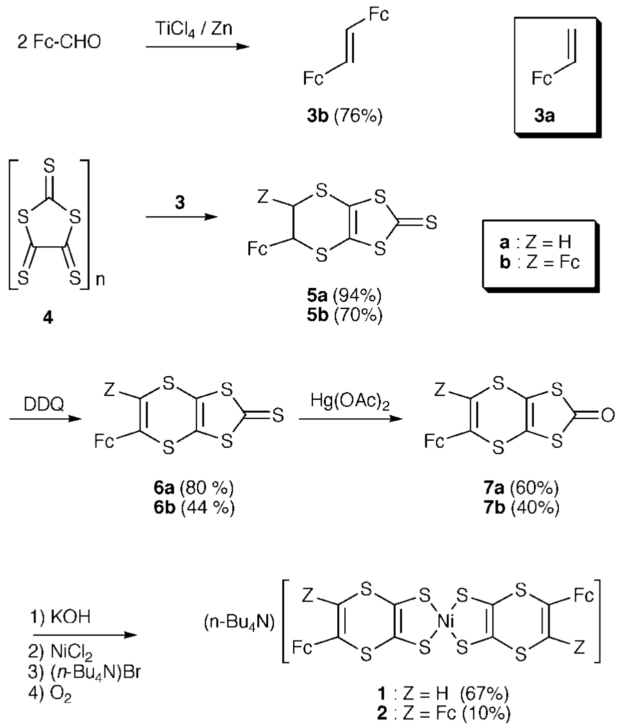
Syntheses and analytical data of the monoferrocenyl analogues **5a**, **6a** and **7a** were reported previously.[7] Complex **1** was prepared by using compound **7a**, and recrystallized according to the procedure for complex **2**.[9]

Yield 67%; Anal. Calc. for $C_{45.5}H_{59}Fe_2NNiO_{0.5}S_8$: C 51.81, H 5.64, S 24.31; Found: C 51.31, H 5.29, S 23.96%; FT-IR (KBr, cm^{-1}) 1630, 1464 (Fc C–C), 1377 (C=C), 999, 819, 498 (Fc Ar); UV-vis (CH_3CN, nm) 216(st) 246(sh) 316(m), 460(sh).

Results and discussion

Synthesis

The synthetic route to multiferrocenyl ligand precursors and their nickel complexes is outlined in Scheme 2. As a ferrocenyl dienophile, 1,2-diferrocenylethylene **3b** was synthesized by the McMurry coupling method[10] using ferrocenecarboxaldehyde



Scheme 2 Synthesis of multiferrocenyl nickel complexes.

(Fc-CHO) and a low-valent titanium compound prepared in a $TiCl_4$ and Zn powder mixture, while vinylferrocene **3a** was purchased (Aldrich) and used without further purification. Diels–Alder type [2+4] cycloaddition reaction of **3** with oligomeric 1,3-dithiol-2,4,5-trithione **4**[11] yielded **5**, which was successively treated with DDQ (2,3-dichloro-5,6-dicyano-benzo-1.4-quinone) to produce ferrocenyldithiolene ligand precursor **6** totally connected by the π-electron system. The formation of compounds **5** and **6** was clearly confirmed by X-ray structural analysis[12] as well as spectroscopic methods. The oxo derivative **7**, which was obtained according to the standard method[13] using $Hg(OAc)_2$, was treated with KOH in EtOH in order to generate the dithiolate ligands. The monoanionic complexes, **1** and **2**, with formally nickel(III) ions were prepared by adding $NiCl_2$ and TBA·Br successively to the ethanolic solution of dithiolate and concomitant exposure to air. Air oxidation in solution was also observed during the synthesis of the $Ni(dddt)_2$[14] and $Ni(ddt)_2$[15] complexes which also have a six-membered 1,4-dithiin ring on the ligand. Complexes **1** and **2** appear to be stable in the solid state.

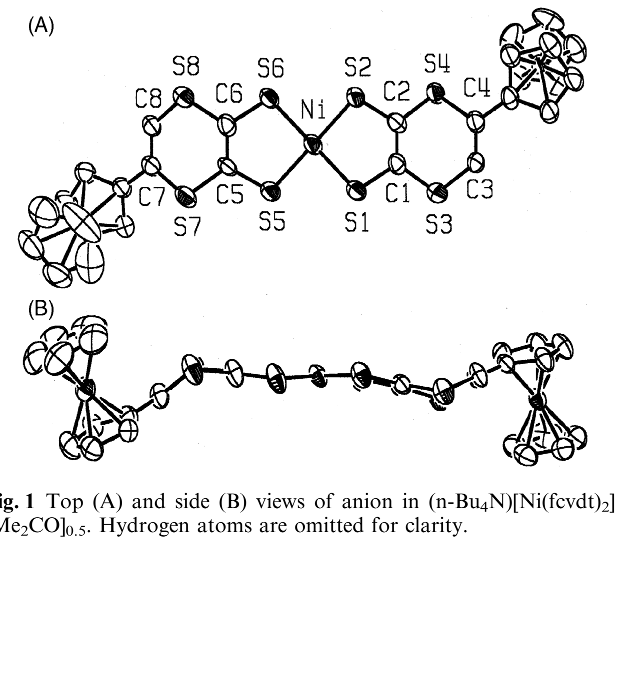


Fig. 1 Top (A) and side (B) views of anion in $(n\text{-}Bu_4N)[Ni(fcvdt)_2]\cdot[Me_2CO]_{0.5}$. Hydrogen atoms are omitted for clarity.

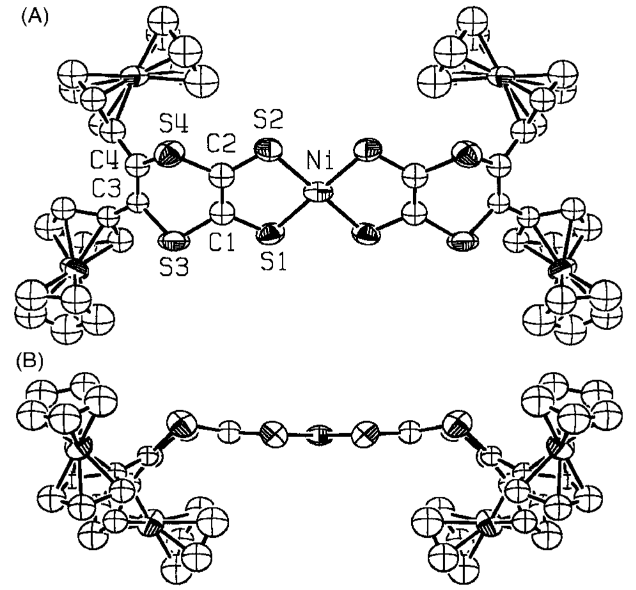


Fig. 2 Top (A) and side (B) views of anion in $(n\text{-}Bu_4N)[Ni(dfcvdt)_2]\cdot[Me_2CO]$. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) for $(n\text{-}Bu_4N)[Ni(fcvdt)_2]\cdot[Me_2CO]_{0.5}$ with estimated standard deviations (e.s.d.s) in parentheses

Ni–S(5)	2.147(3)	Ni–S(1)	2.147(3)
Ni–S(2)	2.155(2)	Ni–S(6)	2.156(3)
S(1)–C(1)	1.722(9)	S(2)–C(2)	1.729(9)
S(3)–C(1)	1.753(9)	S(3)–C(3)	1.750(9)
S(4)–C(2)	1.749(9)	S(4)–C(4)	1.777(9)
S(5)–C(5)	1.721(10)	S(6)–C(6)	1.724(9)
S(7)–C(7)	1.773(10)	S(7)–C(5)	1.753(8)
S(8)–C(8)	1.744(10)	S(8)–C(6)	1.765(9)
C(1)–C(2)	1.367(12)	C(3)–C(4)	1.352(12)
C(5)–C(6)	1.367(13)	C(7)–C(8)	1.337(13)
S(5)–Ni–S(1)	88.31(10)	S(5)–Ni–S(2)	174.63(13)
S(1)–Ni–S(2)	91.44(10)	S(5)–Ni–S(6)	91.45(10)
S(1)–Ni–S(6)	178.01(12)	S(2)–Ni–S(6)	88.98(10)
C(1)–S(1)–Ni	104.1(3)	C(2)–S(2)–Ni	104.0(3)
C(1)–S(3)–C(3)	103.2(4)	C(2)–S(4)–C(4)	102.6(4)
C(5)–S(5)–Ni	104.5(3)	C(6)–S(6)–Ni	104.0(3)
C(7)–S(7)–C(5)	103.0(4)	C(8)–S(8)–C(6)	101.8(5)
C(2)–C(1)–S(1)	120.3(7)	C(2)–C(1)–S(3)	123.6(7)
S(1)–C(1)–S(3)	116.1(5)	C(1)–C(2)–S(2)	119.2(6)
C(1)–C(2)–S(4)	124.1(7)	S(2)–C(2)–S(4)	116.6(5)
C(4)–C(3)–S(3)	125.2(7)	C(3)–C(4)–C(11)	122.2(8)
C(3)–C(4)–S(4)	122.6(7)	C(11)–C(4)–S(4)	115.1(7)
C(6)–C(5)–S(5)	119.6(7)	C(6)–C(5)–S(7)	123.2(7)
S(5)–C(5)–S(7)	117.2(5)	C(5)–C(6)–S(6)	120.1(7)
C(5)–C(6)–S(8)	122.7(7)	S(6)–C(6)–S(8)	117.2(6)

X-Ray structures

The molecular structures of $\mathbf{1}\cdot[Me_2CO]_{0.5}$ and $\mathbf{2}\cdot[Me_2CO]$ were determined by X-ray structural analysis of the single crystals obtained by recrystallization from acetone/ethyl acetate. Side and top views of $[Ni(fvcdt)_2]^-$ and $[Ni(dfcvdt)_2]^-$ are shown in Fig. 1 and Fig. 2, respectively. Selected bond distances (Å) and angles (°) for $\mathbf{1}\cdot[Me_2CO]_{0.5}$ and $\mathbf{2}\cdot[Me_2CO]$ are also summarized in Table 2 and Table 3, respectively. The structure of these complexes is nearly planar around the $[NiS_4]$ core with average Ni–S distances of 2.151 Å for complex **1** and 2.142 Å for complex **2**, which are close to those of other monoanionic nickel-bis(dithiolene)s such as $[Ni(dddt)_2]^-$ (2.137 Å),[14] $[Ni(ddt)_2]^-$ (2.142 Å),[15a] $[Ni(dmit)_2]^-$ (2.156 Å)[16] and $[Ni(mnt)_2]^-$ (2.149 Å).[17] Atoms (S1, S2, S5 and S6) lie in a plane (plane A) and atoms (S1, S2, S3, S4 or S5, S6, S7, S8) form a good plane (plane B) in complex **1** (Fig. 1) with the

Table 3 Selected bond distances (Å) and angles (°) for (n-Bu_4N)[Ni(dfcvdt)$_2$]·[Me_2CO] with estimated standard deviations (e.s.d.s) in parentheses[a]

Ni–S(1)	2.143(8)	Ni–S(1)#	2.143(8)
Ni–S(2)	2.140(7)	Ni–S(2)#	2.140(7)
S(1)–C(1)	1.72(2)	S(2)–C(2)	1.65(2)
S(3)–C(1)	1.75(3)	S(3)–C(3)	1.75(2)
S(4)–C(4)	1.72(2)	S(4)–C(2)	1.82(2)
C(1)–C(2)	1.39(3)	C(3)–C(4)	1.33(3)
S(1)#–Ni–S(1)	87.1(4)	S(1)#–Ni–S(2)	179.2(3)
S(1)–Ni–S(2)	92.1(3)	S(1)#–Ni–S(2)#	92.1(3)
S(1)–Ni–S(2)#	179.2(3)	S(2)–Ni–S(2)#	88.7(4)
C(1)–S(1)–Ni	104.5(9)	C(2)–S(2)–Ni	102.6(7)
C(1)–S(3)–C(3)	101.2(11)	C(4)–S(4)–C(2)	100.9(12)
C(2)–C(1)–S(1)	116(2)	C(2)–C(1)–S(3)	124(2)
S(1)–C(1)–S(3)	119.2(14)	C(1)–C(2)–S(2)	124.5(18)
C(1)–C(2)–S(4)	116(2)	S(2)–C(2)–S(4)	120.0(13)
C(4)–C(3)–S(3)	117.0(19)	C(3)–C(4)–S(4)	127(2)

[a]Symmetry transformation used to generate equivalent atoms: # x, $-y+1/2$, z.

dihedral angle (ϕ) between plane A and plane B being about 12°. The corresponding angle for complex **2** is about half that of complex **1** (6°); both of which are different from that of [Ni(ddt)$_2$]$^-$ ($\phi \simeq 0°$).[15a] The terminal 1,4-dithiin rings in complex **1** are folded up and down with the dihedral angle (ϕ) between plane B and plane C (made by atoms S3, S4, C3 and C4) being about 38° which is close to that of Ni(ddt)$_2$ ($\phi = 33.5°$).[15a] The corresponding angle (ϕ) for complex **2** is 52°, much bigger than the others. The variation of the dihedral angles seems to be related to the number of the peripheral ferrocenyl groups and directly affects the planarity of the nickel-bis(dithiolene)s. The two terminal vinylene groups of the 1,4-dithiin rings in complex **1** are folded in opposite directions with an inversion center at the Ni position, exhibiting the chair-

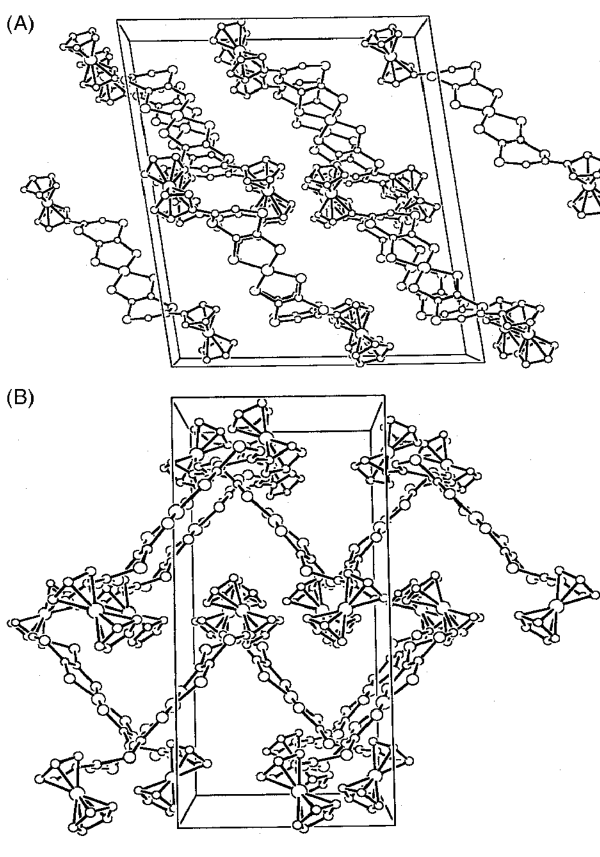


Fig. 3 Crystal structure of (n-Bu_4N)[Ni(fcvdt)$_2$]·[Me_2CO]$_{0.5}$ viewed normal to the (010) plane (A) and the (100) plane (B). Acetone molecules and n-Bu_4N cations are omitted for clarity.

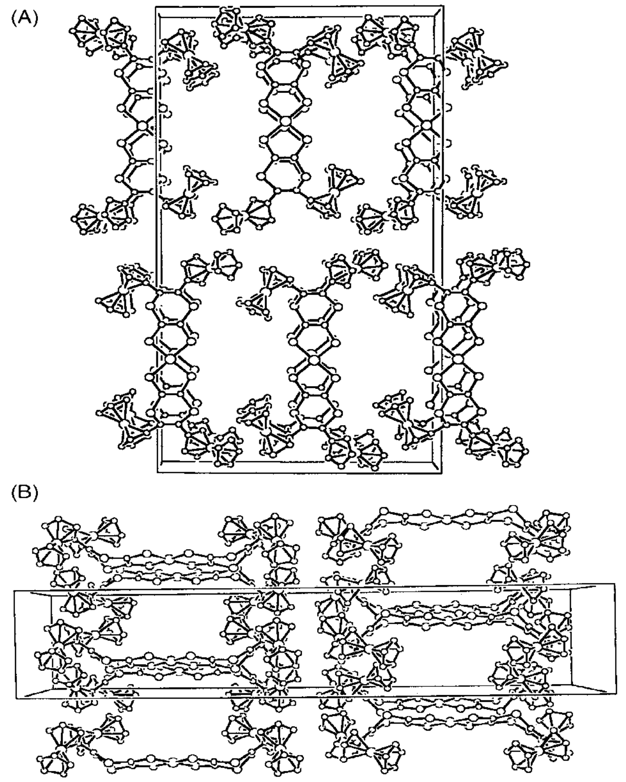


Fig. 4 Crystal structure of (n-Bu_4N)[Ni(dfcvdt)$_2$]·[Me_2CO] viewed normal to the (001) plane (A) and the (100) plane (B). Acetone molecules and n-Bu_4N cations are omitted for clarity.

like conformation (chair-form) found for many nickel-bis (dithiolene)s. In contrast, complex **2** has a boat-like conformation (boat-form) with the two terminal vinylene groups being folded up together. This complex possesses a mirror plane which is vertical to the [NiS_4] plane and passes through the Ni atom bisecting the dihedral angle of S(1)–Ni–S(1)# (#: x, $-y+1/2$, z). These two distinct conformations seem to originate simply from the number of the peripheral ferrocenyl groups which critically influence the crystal structure.

Crystal structures of complex **1** and **2** are shown in Fig. 3 and Fig. 4, respectively. The [Ni(fcvdt)$_2$]$^-$ anions are stacked along the b-axis (Fig. 3A) in which the shortest intermolecular Ni···Ni distance is 10.841 Å corresponding to the b-axis cell parameter. The [Ni(dfcvdt)$_2$]$^-$ anions are, however, stacked along the c-axis (Fig. 4A) with the shortest intrastack Ni···Ni distance (8.496 Å) being identical to the c-axis distance. In addition, the interstack distances between sulfur atoms are much longer than 6 Å for both complexes, which is much greater than the sum of van der Waals radii of sulfur atoms (3.6 Å).[18] Close inter- and intra-stack contacts of the multi-sulfur-based molecules are commonly found in the crystal structures of molecular conductors such as the Ni(dmit)$_2$ family.[19] In complexes **1** and **2**, however, no significant close contacts are found because of the bulky ferrocenyl groups linked to the terminal of the molecule. In complex **2**, the [Ni(dfcvdt)$_2$]$^-$ anions with boat-like conformations stack along the c-axis and make two kinds of cavities as shown in Fig. 4; a valley made in between ferrocenyl groups and a tunnel made of [NiS_4] cores and ferrocenyl groups. These cavities are filled with acetone solvent molecules and n-Bu_4N cations, respectively. These structural characteristics will be reflected in the solid-state properties of the complexes discussed below.

EPR spectra

X-Band EPR spectra of microcrystalline complexes **1** and **2** were measured at 77 K and 300 K. They exhibited apparent orthorhombic symmetry with anisotropic g-values of

$g_1 = 2.096$, $g_2 = 2.036$ and $g_3 = 2.024$ for complex **1** and $g_1 = 2.104$, $g_2 = 2.041$ and $g_3 = 2.009$ for complex **2** at 77 K, and no significant temperature dependency was found at 300 K. These values are comparable to those of $[Ni(dphdt)_2]^-$ (dphdt = 5,6-diphenyl-1,4-dithiin-2,3-dithiolate; $g_1 = 2.096$, $g_2 = 2.038$ and $g_3 = 2.005$ at 77 K)[20] and $[Ni(dddt)_2]^-$ ($g_1 = 2.119$, $g_2 = 2.057$ and $g_3 = 2.022$ at 128 K),[14c] suggesting paramagnetic Ni^{3+} ions with the d^7 state ($S = 1/2$) and diamagnetic Fe^{2+} ions in ferrocene with the low-spin d^6 state ($S = 0$). Because these complexes contain two different kinds of redox active centres, there are two possible ways of reaction on further oxidation: the oxidation of Ni^{3+} ion to formally Ni^{4+} and the oxidation of ferrocene to ferrocenium. Further oxidation of the complexes is under investigation by controlling the amount of oxidant.

Strong near-IR absorption

Near-IR spectra of the complexes in dichloromethane show strong absorption bands at 1178 nm (log $\varepsilon = 3.99$) for complex **1** and at 1155 nm (log $\varepsilon = 4.06$) for complex **2**, corresponding to the $\pi \rightarrow \pi^*$ transition of nickel-bis(dithiolene)s. The absorption maxima are not significantly different for the two complexes and comparable to those of the monocationic complex **II** (1030 nm).[2] As the multisulfur system of the ligand is extended from that of complex **II** to that of complex **1** with the peripheral ferrocenyl groups being equal, the transition energy (ΔE_{NIR}) between the HOMO ($2b_{1u}$) and LUMO ($3b_{2g}$) levels[21] shifts to lower energy by *ca.* 1220 cm^{-1}. This means that the external 1,4-dithiin ring in complex **1** would destabilize the HOMO ($2b_{1u}$) level and thereby a lower energy transition would be observed. Complex **III**, which is supposed to be a neutral state, was reported to show an absorption maximum at 1310 nm.[3] The neutral complex **2**, $[Ni(dfcvdt)_2]^0$, which was prepared by mixing of acetonitrile solutions of complex **2** and iodine, showed the absorption at 1342 nm (log $\varepsilon = 3.63$).[9] This is lower in energy than that of complex **III** by *ca.* 182 cm^{-1} and the monocationic complex **2** by *ca.* 1206 cm^{-1}. Consequently, it can be concluded that the extension of the π-electron system of a multisulfur ligand can be a facile way to prepare the infrared dye absorbing lower energy.

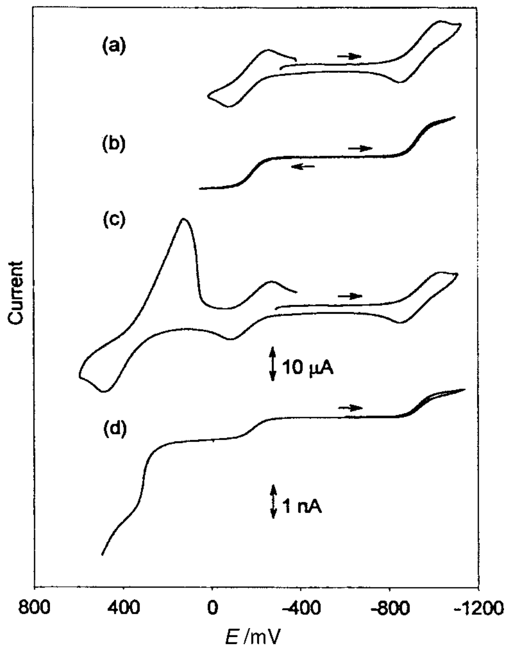


Fig. 5 Cyclic voltammograms of $(n-Bu_4N)[Ni(fcvdt)_2]$. The working electrode is a glassy carbon disc of 3.0 mm diameter (a and c) or a carbon fiber ultramicroelectrode of 10 μm diameter (b and d).

Table 4 Redox potentials of complexes **1**, **2** and **IV** (in V)[a]

Complex	E_{pa}^1	E_{pc}^1	ΔE^1	$E_{1/2}^1$	E_{pa}^2	E_{pc}^2	ΔE^2	$E_{1/2}^2$	ΔE_{pa}
1	−0.85	−1.04	0.19	−0.95	−0.04	−0.27	0.18	−0.18	0.76
2	−0.89	−1.06	0.17	−0.98	−0.11	−0.28	0.17	−0.20	0.78
IV[b]	−0.83	−1.02	0.19	−0.93	−0.07	−0.27	0.20	−0.17	0.76

[a] $\Delta E = |E_{pa} - E_{pc}|$; $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_{pa} = E_{pa}^2 - E_{pa}^1$. [b] Tetra-n-butylammonium salt.

Electrochemical properties

Cyclic voltammograms of complexes **1** and **2** were measured and compared with that of the TBA complex of **IV**.[15] These ferrocenyl complexes show similar CV patterns with two reversible redox peaks at around −0.9 V and −0.2 V, and one quasi-reversible peak around $E_{pa} = +0.5$ V. The CV of complex **1** is shown in Fig. 5 and the electrochemical parameters for these complexes are summarized in Table 4. The potential sweep was started from the resting potential (−0.30 V) in the negative direction and the voltammogram was obtained between −1.16 V and 0.00 V (Fig. 5a). Two reversible redox peaks with the half-wave potentials of $E_{1/2}^1 = -0.95$ V and $E_{1/2}^2 = -0.18$ V are exhibited for complex **1**. These peaks can be attributed, with no doubt, to the redox processes of $[NiS_4]^{2-/-}$ and $[NiS_4]^{-/0}$, respectively. Similar redox processes are found for complex **2** ($E_{1/2}^1 = -0.98$ V and $E_{1/2}^2 = -0.20$ V) and complex **IV** ($E_{1/2}^1 = -0.93$ V and $E_{1/2}^2 = -0.17$ V). The half-wave potentials ($E_{1/2}$) of complexes **1** and **2** are more cathodic than that of complex **IV** which has no ferrocenyl substitution, indicating that the electron density at the $[NiS_4]$ core is slightly increased due to the electron-donating property of the peripheral ferrocenyl groups and that complexes **1** and **2** can be more easily oxidized than complex **IV**. The ΔE_{pa} value of a complex is well known as a measure of the on-site Coulombic repulsion.[15,22] In the light of the ΔE_{pa} value only, electrical conductivities for the two ferrocenyl complexes are expected to be nearly equal to that of complex **IV** because the magnitude of the difference is not significant. If the complexes are oxidized further (Fig. 5c), one additional quasi-reversible oxidation peak was observed at about 0.48 V for complex **1** and 0.54 V for complex **2** with poor reproducibility. Compared with the half-wave potential of the ferrocenyl group in the tetra-n-butylammonium salt of complex **II** ($E_{1/2} = 0.76$ V),[2] this irreversible peak can be tentatively assigned to the redox process of ferrocenyl groups. It is noteworthy, however, that complex **II** shows just one reversible redox cycle for the ferrocenyl groups because the nickel-bis(dithiolene) core does not serve as an effective bridge for communication between the two ferrocenyl redox centres. An ultramicroelectrode was used to check whether a serious *iR* drop was involved in the normal CV measurements in THF solution (Fig. 5b and d). The half-wave potentials ($E_{1/2}$) of the complexes measured by using the ultramicroelectrode are almost identical to those obtained by normal CV experiments (Table 4), indicating no significant *iR* distortion in conventional CV measurements.

Electrical conductivity

Electrical conductivity was measured with the usual two-probe method on pressed pellets of complexes **1** and **2**. Room temperature conductivities are very low and in the order of 10^{-6} S cm^{-1}. This is consistent with the X-ray crystal structures of the complexes in which no significant close intermolecular S···S contacts were found. Further oxidation of the complexes beyond the $[NiL_4]^-$ state may result in several stages of oxidation state and is currently under investigation.

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