Bis(tetraphenylphosphonium) bis[*cis*-1,2-bis(methoxycarbonyl)ethylene-dithiolato-$\kappa^2 S,S'$]nickelate(II) and bis(tetraphenylphosphonium) bis[*cis*-1,2-bis(methoxycarbonyl)ethylene-dithiolato-$\kappa^2 S,S'$]nickelate(III) iodide

Stéphane A. Baudron and Patrick Batail*

Laboratoire Chimie Inorganique, Matériaux et Interfaces, FRE 2447 CNRS, Université d'Angers, Bâtiment K, 2, Boulevard Lavoisier, Angers, France
Correspondence e-mail: patrick.batail@univ-angers.fr

The crystal structures of the title compounds, $(C_{24}H_{20}P)_2[Ni(C_6H_6O_4S_2)_2]$, (I), and $(C_{24}H_{20}P)_2[Ni(C_6H_6O_4S_2)_2]I$, (II), in the diamagnetic reduced (2–) and paramagnetic oxidized (1–) states, are reported at 200 and 293 K, respectively. In both compounds, the Ni atom lies on an inversion centre and the NiS_4 coordination is thus required to be exactly planar. In the diamagnetic complex, (I), the Ni—S distances are 2.1818 (7) and 2.1805 (6) Å, while they are 2.1481 (6) and 2.1392 (5) Å in the paramagnetic complex, (II). This results from both the different complex core oxidation states and the different conformations of the methoxycarbonyl groups.

Comment

In the course of our study of the flexibility of functional groups with respect to redox-active conjugated cores (Baudron *et al.*, 2002), we became interested in studying nickel dithiolene complexes, $[Ni(S_2C_2R_2)_2]^x$ (Robertson & Cronin, 2002). These compounds are very attractive for the construction of magnetic or conducting materials (Cassoux, 1999). We became interested in the $[Ni\{S_2C_2(CO_2Me)_2\}_2]^-$ anion, which has been shown to display several conformations in the solid state as a result of rotation of the ester groups (Brown *et al.*, 1983). In an attempt to prepare this compound, we were able to isolate the reduced (2−) complex $(PPh_4)_2[Ni\{S_2C_2(CO_2Me)_2\}_2]$, (I). This compound, which is air-stable in the crystalline state, is oxidized in hot acetonitrile. When it is oxidized with iodine in acetonitrile, a new crystalline form is identified incorporating the I^- anion, namely $(PPh_4)_2[Ni\{S_2C_2(CO_2Me)_2\}_2]I$, (II).

In both compounds, the Ni atoms lie on an inversion centre, requiring an exactly planar arrangement of the NiS_4 core. The Ni—S bond lengths are longer in (I) than in either (II) or the

reported crystal structure of $(AsPh_4)[Ni\{S_2C_2(CO_2Me)_2\}_2]$ [2.129 (6) Å; Brown *et al.*, 1983]. This is normally observed for
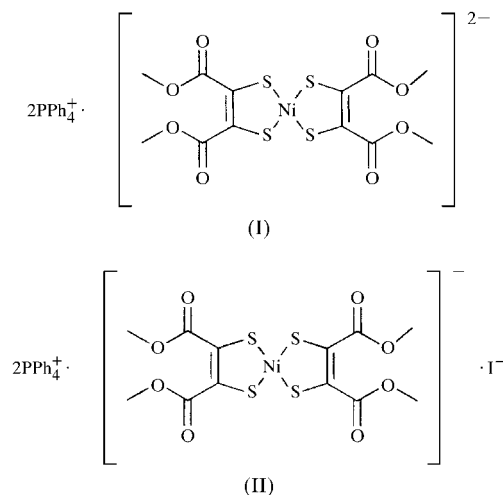
nickel dithiolene complexes with different oxidation states (Lim *et al.*, 2001). These values compare favourably with the Ni—S bond lengths in $[Ni(mnt)_2]^{n-}$ [mnt is maleonitriledithiolate; 2.174 (2) Å when $n = 2$ and 2.147 (3) Å when $n = 1$; Mahadevan *et al.*, 1984; Kobayashi & Suzuki, 1977].

Another structural feature is the relative orientation of the ester groups, which are almost orthogonal in both compounds. The salient difference lies in the position of the ester group that is in the NiS_4 plane. While it is in a *cis* position with respect to the C=C bond of the dithiolene ring in (I), it is in a *trans* position in (II). This shows the solid-state expression of the free rotation of these functional groups that exists in solution. This feature is observed for other related compounds (Beswick *et al.*, 2002) and it is of interest to note that it has an influence on the S—C bond lengths. Indeed, in both compounds, one S—C bond is shorter than the other, revealing the existence of a mesomeric form involving the ester group in the NiS_4 plane along the S1—C2=C3—C4=O3 conjugated path. As a consequence, this S—C bond has a partial double-bond nature. This phenomenon has been highlighted in amide-functionalized tetrathiafulvalene (Heuzé *et al.*, 1999; Batsanov *et al.*, 1995). A closer look at other coordination compounds involving this kind of ligand, such as $(PPh_4)_2[Fe_2\{S_2C_2(CO_2Me)_2\}_4]\cdot 2DMF$ (DMF is dimethylform-
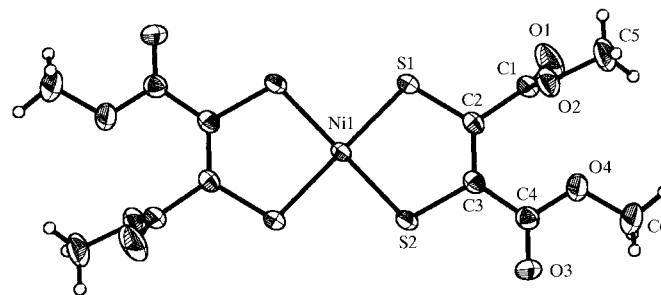

Figure 1
The molecular structure of the $[Ni\{S_2C_2(CO_2Me)_2\}_2]^{2-}$ anion in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

metal-organic compounds

amide; Kanatzidis & Coucouvanis, 1984), (Et$_4$N)[NbO-{S$_2$C$_2$(CO$_2$Me)$_2$}$_2$(S$_2$)(bpy)]·DMF (bpy is 2,2'-bypyridine; Kim *et al.*, 2001), (Pr$_4$N)$_2$[W$_2$(μ-S)$_2${S$_2$C$_2$(CO$_2$Et)$_2$}$_4$] (Umakoshi *et al.*, 2000) and (Et$_4$N)[W(S$_2$CNMe$_2$){S$_2$C$_2$(CO$_2$Me)$_2$}$_2$] (Lim *et al.*, 2000), reveals the same phenomenon.

In compound (II), the paramagnetic centres are well separated and no short S···S contact is observed. As a consequence, the temperature evolution of the magnetic susceptibility obeys a Curie law, with $\mu_{eff} = 1.79\mu_B$, which is close to the $S = \frac{1}{2}$ value of $1.73\mu_B$.
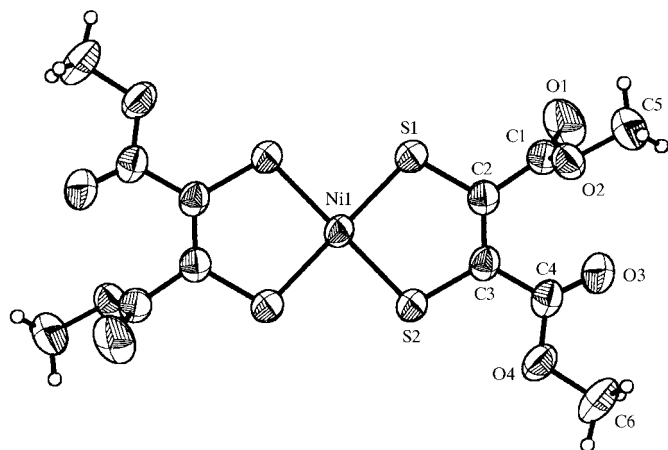

Figure 2
The molecular structure of the [Ni{S$_2$C$_2$(CO$_2$Me)$_2$}$_2$]$^-$ anion in (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

4,5-Bis(methoxycarbonyl)-2-oxo-1,3-dithiole (3 g) was added to a solution of sodium methanolate (0.6 g Na in 100 ml MeOH); the mixture turned yellow. Upon addition of NiCl$_2$ (0.84 g), the solution turned orange and it was then stirred for 90 min. A solution of tetraphenylphosphonium bromide (5.4 g) in water (100 ml) was added. The methanol was then evaporated, affording red needles of (I) (yield 4.81 g, 59%). Analysis calculated (found) for C$_{60}$H$_{52}$NiO$_8$PS$_4$: C 62.67 (62.63), H 4.56 (4.55)%. A single crystal was prepared by ether vapour diffusion into an acetonitrile solution. For the preparation of (II), I$_2$ (0.11 g) was added to a solution of (I) (1 g) in methanol (200 ml) and the solution stirred overnight, before being evaporated to dryness. The product was washed with water and ether. The remaining solid was recrystallized from hot acetonitrile, affording dark-red prisms of (II) (yield 0.78 g, 70%). Analysis calculated (found) for C$_{60}$H$_{52}$INiO$_8$PS$_4$: C 56.44 (56.46), H 4.10 (4.07), S 10.04 (9.74)%.

Compound (I)

Crystal data

(C$_{24}$H$_{20}$P)$_2$[Ni(C$_6$H$_6$O$_4$S$_2$)$_2$]	$Z = 1$
$M_r = 1149.91$	$D_x = 1.393$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.2994$ (14) Å	Cell parameters from 8000
$b = 11.1508$ (16) Å	reflections
$c = 13.8197$ (19) Å	$\theta = 1.7$–$26.1°$
$\alpha = 68.023$ (16)°	$\mu = 0.62$ mm^{-1}
$\beta = 68.730$ (15)°	$T = 200$ (2) K
$\gamma = 80.092$ (17)°	Prism, red
$V = 1370.3$ (3) Å^3	$0.63 \times 0.23 \times 0.15$ mm

Data collection

Stoe IPDS diffractometer	4966 independent reflections
Oscillation scans, $\Delta\varphi = 1.4°$	3899 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.052$
(*FACEIT* in *IPDS*; Stoe &	$\theta_{max} = 25.9°$
Cie, 1995)	$h = -11 \rightarrow 12$
$T_{min} = 0.777$, $T_{max} = 0.928$	$k = -12 \rightarrow 13$
14 269 measured reflections	$l = 0 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
$R(F) = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2]$
$wR(F^2) = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{max} = 0.001$
4966 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
340 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}

Compound (II)

Crystal data

(C$_{24}$H$_{20}$P)$_2$[Ni(C$_6$H$_6$O$_4$S$_2$)$_2$]I	$Z = 1$
$M_r = 1276.81$	$D_x = 1.479$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.4071$ (3) Å	Cell parameters from 25
$b = 10.2501$ (6) Å	reflections
$c = 15.4642$ (7) Å	$\theta = 2.2$–$30°$
$\alpha = 85.671$ (4)°	$\mu = 1.13$ mm^{-1}
$\beta = 77.541$ (4)°	$T = 293$ (2) K
$\gamma = 80.240$ (4)°	Prism, dark red
$V = 1433.75$ (12) Å^3	$0.60 \times 0.45 \times 0.45$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.017$
diffractometer	$\theta_{max} = 30°$
Non-profiled $\omega/2\theta$ scans	$h = -13 \rightarrow 13$
Absorption correction: ψ scan	$k = -14 \rightarrow 0$
(North *et al.*, 1968)	$l = -21 \rightarrow 21$
$T_{min} = 0.529$, $T_{max} = 0.601$	3 standard reflections
8773 measured reflections	frequency: 120 min
8343 independent reflections	intensity decay: 14%
6177 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0550P)^2$
$R(F) = 0.032$	$+ 0.1901P]$
$wR(F^2) = 0.097$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
8343 reflections	$\Delta\rho_{max} = 0.64$ e Å^{-3}
347 parameters	$\Delta\rho_{min} = -0.63$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	(Sheldrick, 1997)
	Extinction coefficient: 0.0107 (9)

Table 1
Comparison of selected geometric parameters in (I) and (II) (Å, °).

Parameter	(I)	(II)
Ni1—S1	2.1818 (7)	2.1481 (6)
Ni1—S2	2.1805 (6)	2.1392 (5)
S1—C2	1.7322 (19)	1.710 (2)
S2—C3	1.7562 (19)	1.730 (2)
C2—C3	1.361 (3)	1.367 (3)
C1—O1	1.198 (3)	1.196 (3)
C4—O3	1.210 (2)	1.192 (3)
S1—Ni1—S2	91.24 (2)	92.21 (2)

H atoms were treated as riding, with C—H distances in the range 0.93–0.96 Å.

For compound (I), data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1995); cell refinement: *SELECT* and *CELL*, both in *IPDS*; data reduction: *INTEGRATE* in *IPDS*. For compound (II), data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995). For both compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1015). Services for accessing these data are described at the back of the journal.

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