

Synthesis, crystal structure and electrochemical properties of $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$: a potential precursor for new materials (mdt = 1,3-dithiole-4,5-dithiolate)

Yvonne S. J. Veldhuizen,^a (the late) Nora Veldman,^b Anthony L. Spek,^{†,b} Patrick Cassoux,^c Roger Carlier,^d Martijn J. J. Mulder,^a Jaap G. Haasnoot^{*,a} and Jan Reedijk^a

^a Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

^b Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

^c Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex, France

^d Laboratoire d'Electrochimie, UA 439, Université de Rennes 1, Beaulieu, 35042 Rennes Cedex, France

Reaction of methylenedithio-1,3-dithiol-2-one with sodium methanolate resulted in the anionic ligand mdt^{2-} (mdt = 1,3-dithiole-4,5-dithiolate) which has been co-ordinated to nickel. The salt $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$ was successfully crystallised and its crystal structure showed that the $\text{Ni}(\text{mdt})_2$ unit is significantly distorted from planarity. Electrochemical studies showed that $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$ can be further oxidised in two steps *via* the neutral $[\text{Ni}(\text{mdt})_2]$ complex to a partially oxidised positively charged complex. The neutral complex has also been successfully synthesized by oxidation with TCNQ. The redox potential of the oxidation from the neutral to the partially oxidised positive $\text{Ni}(\text{mdt})_2$ complex is relatively low, +0.60 V, making this compound a promising precursor for the preparation of conducting materials, based on derived cation radical salts.

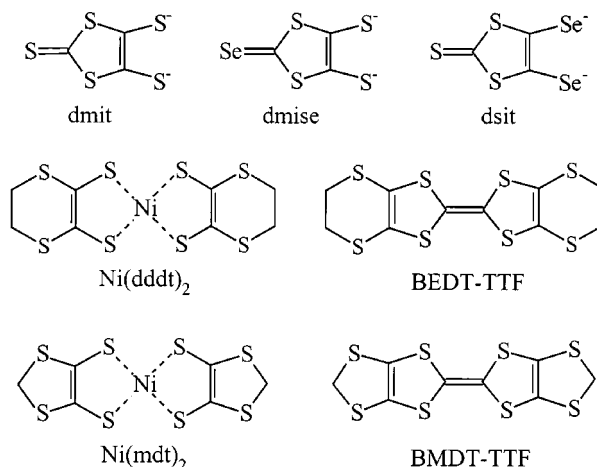
1 Introduction

The crystallisation of the first partially oxidised $\text{Ni}(\text{dmit})_2$ compound (dmit = 4,5-disulfanyl-1,3-dithiole-2-thionate), $[\text{NBu}_4]_2[\text{Ni}(\text{dmit})_2] \cdot 7\text{MeCN}$, by Valade *et al.* in 1983,¹ initiated a real impetus to the investigation of transition-metal complexes of sulfur donor ligands as possible conducting materials. Variants were synthesized by substitution of the cation, the ligand and the metal.

Substitution of Bu_4N^+ by other cations resulted in a rich variety of $[\text{Cation}]_x[\text{M}(\text{dmit})_2]$ combinations ($0 < x < 1$; M = Ni, Pd or Pt), which were extensively reviewed in 1991 and 1992.^{2,3} The Bu_4N cation has been substituted by mostly spherical tetraalkylammonium-type cations and alkali metals. A few compounds using planar cations such as guanidinium, acridinium and phenazinium have also been synthesized.⁴ Among the $\text{M}(\text{dmit})_2$ compounds are seven superconductors of which α -[EDT-TTF][Ni(dmit)₂] [EDT-TTF = ethylenedithiotetrathiafulvalene] is the only compound which becomes superconducting at ambient pressure at a T_c of 1.3 K.⁵

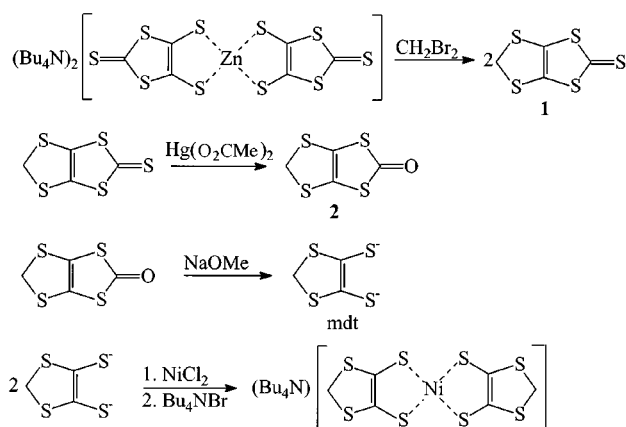
A variation on the dmit ligand can be made by substituting one or more of the sulfur atoms by the larger selenium atoms. The greater size and polarisability of selenium might diminish the Coulomb repulsion in a system. The selenium-containing ligands dmise and dsit are among the most studied (dmise = 4,5-disulfanyl-1,3-dithiole-2-selenonate; dsit = 4,5-diselanyl-1,3-dithiole-2-thionate). Comparison of the conducting properties of $[\text{NMe}_4][\text{Ni}(\text{dmise})_2]$,⁶ and $[\text{NMe}_4][\text{Ni}(\text{dsit})_2]$,⁷ with the properties of $[\text{NMe}_4][\text{Ni}(\text{dmit})_2]$,⁸ shows, however, that in these compounds the substitution does not improve the conducting properties of the compounds: both selenium compounds show a semiconducting behaviour, while the dmit compound is a metallic conductor down to 100 K. On the contrary, the con-

ducting properties of $[\text{NHMe}_3][\text{Ni}(\text{dmise})_2]$ and $[\text{Me}_3\text{NH}][\text{Ni}(\text{dmit})_2]$ are very similar.^{9,10} Tight-binding band-structure calculations show that the selenium atoms in the dmise compound give this compound a three-dimensional electronic structure, whereas the dmit compound has only a one-dimensional electronic structure. So, in this example, the larger selenium atoms improve the dimensionality of the conducting properties of the compound. Apparently, the conducting properties of $\text{Ni}(\text{dmit})_2$ can be improved as well as deteriorated by substituting sulfur atoms by selenium atoms.



Another way for the preparation of new complexes as possible precursors for new inorganic molecular conductors is the synthesis of the inorganic analogues of successful donor molecules. As a d^8 metal ion (M^{2+}) is isolobal to a (C_2^{4+}) unit,¹¹ substitution of the C=C bond of a donor molecule by a d^8 metal ion results in the isolobal inorganic analogue of the donor molecule. A successful example of this strategy is the complex

[†] To whom correspondence pertaining to the crystallographic studies should be addressed.



Scheme 1

$M(\text{ddd}t)_2$, first synthesized in 1985.¹² This complex is the inorganic analogue of the successful donor BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene], which is the precursor donor for a large number of organic superconductors.¹³ Several metallic conductors with $M(\text{ddd}t)_2$ have been reported, among which $[\text{Ni}(\text{ddd}t)_2][\text{HSO}_4]_2$ is the best synthesized with this complex so far [$\sigma(\text{RT}) = 60\text{--}300 \text{ S cm}^{-1}$, metallic behaviour down to 25 K].¹⁴

Here, the synthesis and characterisation of $[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$ ($\text{md}t = 1,3\text{-dithiole-4,5-dithiolate}$), a new variation of a bis-(dithiolene) nickel complex, is reported; $\text{Ni}(\text{md}t)_2$ is isolobal to the organic donor BMDT-TTF [bis(methylenedithio)tetrathiafulvalene], first synthesized in 1984.¹⁵ One of the most interesting conductors synthesized with this donor is $[\text{BMDT-TTF}]_2[\text{Au}(\text{CN})_2]$ [$\sigma(\text{RT}) = 300 \text{ S cm}^{-1}$, metallic behaviour down to 80 K].¹⁶ The complex $[\text{Ni}(\text{md}t)_2]$ can also be considered as a variation on $[\text{Ni}(\text{ddd}t)_2]$ and their properties may therefore be expected to be comparable. Parts of these results have been published as a preliminary communication.¹⁷

2 Experimental

2.1 Synthesis of $[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$

The route to the synthesis of $[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$ is shown in Scheme 1. All reactions were carried out under a dinitrogen atmosphere. Ligand precursors **1** and **2** were synthesized by a combination of the methods described by Papavassiliou *et al.*¹⁸ and Nigrey *et al.*¹⁹ The final product was synthesized according to the method described by Faulmann *et al.*²⁰ for $M(\text{ddd}t)_2$ compounds.

Methylenedithio-1,3-dithiole-2-thione 1. The complex $[\text{NBu}_4]_2[\text{Zn}(\text{dmit})_2]$ (4.72 g, 5 mmol) was dissolved in acetone *p.a.* (75 cm^3). Dibromomethane (*ca.* 7 cm^3 100 mmol) was added and the resulting solution brought to reflux and heated for 4 h. A change from red to brown occurred during the reaction and a yellow-orange solid precipitated. The mixture was concentrated under vacuum until almost dry after cooling. The residue was washed with hot dichloromethane to extract the product until the washings were colourless (approximately 300 cm^3 of dichloromethane were necessary). The yellow-brown solution was concentrated under vacuum to a small volume. The product was filtered off and washed with methanol. Purity was checked by infrared spectroscopy for the presence of Bu_4N^+ (characteristic pattern between 3000 and 2800 cm^{-1}). If necessary the product was further purified by suspending and stirring it in a small amount of methanol, filtration and drying. Yield $\approx 65\%$. IR (KBr): 3002w, 2930w, 1741w, 1667s, 1603m, 1495m, 1402w, 1388w, 1190w, 1072m, 962m, 876m, 852m, 743m, 710w, 688w, 552w, 536w, 506w, 472m, 400m, 376w and 338w cm^{-1} .

Methylenedithio-1,3-dithiol-2-one 2. Compound **1** (1.05 g, 5 mmol) was dissolved in a mixture of chloroform (125 cm^3), glacial acetic acid (50 cm^3) and demineralised water (10 cm^3). After the solution was brought to reflux, $\text{Hg}(\text{O}_2\text{CMe})_2$ (1.60 g, 5 mmol) was carefully added to the boiling mixture. The resulting mixture was stirred under reflux for 20 h, while black HgS precipitated. After cooling the black precipitate was filtered off and the filtrate concentrated to dryness under vacuum. The yellow product was recrystallised from dichloromethane and methanol. Yield $\approx 72\%$. IR (KBr): 1466m, 1054m, 1036s, 1011m, 952m, 890w, 683w, 508m, 479w, 453w, 392w and 309w cm^{-1} .

$[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$. Compound **2** (0.194 g, 1 mmol) was suspended in methanol *p.a.* (4 cm^3) after which a solution (6 cm^3) of 1 M NaOMe was added slowly. After 1 h of stirring all **2** had reacted and a clear brown solution was formed. The compound $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.119 g, 0.5 mmol) in methanol (10 cm^3), was added using a transfer tube, resulting in a change to orange-red. After another hour of stirring a solution of NBu_4Br (0.17 g, 0.5 mmol) in methanol (5 cm^3) was added using a transfer tube. The product crystallised by standing overnight at -18°C . The orange-brown crystals were filtered off, washed with Pr^iOH and dried under vacuum. Yield $>85\%$. Recrystallisation from acetone- Pr^iOH (1:1) resulted in single crystals suitable for X-ray determination. The oxidation state of 1^- is in accord with the C=C stretching vibration at 1330 cm^{-1} in the infrared spectrum and was confirmed by elemental analysis (C, H, N, S) performed by the University College Dublin. IR (KBr): 2956m, 2920w, 2867m, 1472m, 1443w, 1435w, 1410w, 1385w, 1330s, 1030w, 927w, 739m, 455m and 352 cm^{-1} [Calc. (Found) for $\text{C}_{22}\text{H}_{40}\text{NNiS}_8$: C, 41.69 (41.72); H, 6.36 (6.34); N, 2.21 (2.02); S, 40.47 (39.44%)].

2.2 Synthesis of $[\text{Ni}(\text{md}t)_2]$

The complex $[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$ (0.158 g, 0.25 mmol) was dissolved in benzonitrile (10 cm^3) at 80°C and TCNQ (0.051 g, 0.25 mmol) was dissolved in boiling acetonitrile (10 cm^3). The hot TCNQ solution was added to the hot $[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$ solution using a transfer tube, resulting in a change from orange-brown from $[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$ to green from TCNQ^- . After cooling to room temperature the black precipitate of $[\text{Ni}(\text{md}t)_2]$ was filtered off, washed with hot acetonitrile and acetone and dried under vacuum. Yield $>95\%$. The neutral oxidation state was shown by the strong C=C stretching vibration at 1195 cm^{-1} in the infrared spectrum and confirmed by elemental analysis (C, H, S) performed by the Laboratoire de Chimie de Coordination for CNRS in Toulouse. IR (KBr): 2923w, 2522w, 2081w, 1338m, 1195s, 1054m, 964m, 684m, 553w, 466s and 364 cm^{-1} [Calc. (Found) for $\text{C}_6\text{H}_4\text{NiS}_8$: C, 18.42 (19.13); H, 1.03 (0.65); S, 65.55 (66.30%)]. Attempts to synthesize single crystals of $[\text{Ni}(\text{md}t)_2]$ by slow interdiffusion of solutions of $[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$ and TCNQ resulted in hair-thin needles, not suitable for X-ray determination.

2.3 X-Ray data collection and structure determination of $[\text{NBu}_4][\text{Ni}(\text{md}t)_2]$

X-Ray data were collected on an Enraf-Nonius CAD-4T/rotating anode diffractometer for a dark, cut to size block-shaped crystal ($0.25 \times 0.25 \times 0.25 \text{ mm}$). Numerical data are collected in Table 1. Unit-cell dimensions were derived from the SET4 setting angles²¹ ($10 < \theta < 14^\circ$) and checked for higher lattice symmetry with LEPAGE.²² The structure was solved by automated Patterson techniques (DIRDIF 92²³) and refined on F^2 by full-matrix least-squares techniques (SHELXL 93²⁴). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms with fixed isotropic displacement parameters related to the value of the

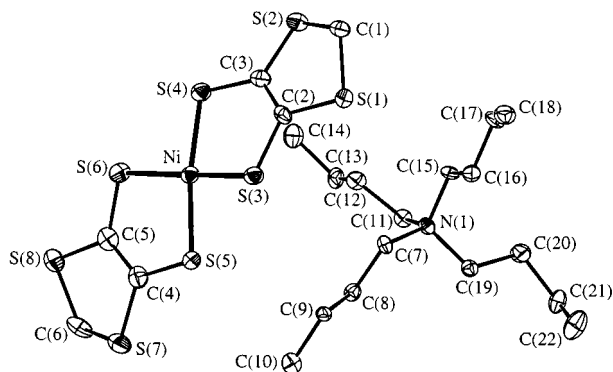


Fig. 1 An ORTEP 50% probability plot (PLATON)²⁷ of the crystallographically independent unit of $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$ with the labelling scheme of the heavy atoms. Hydrogen atoms have been omitted for clarity.

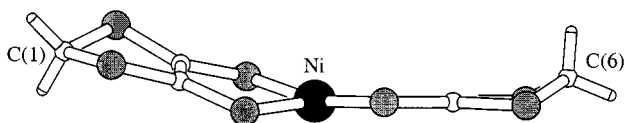


Fig. 2 Side view showing the distortion from planarity of the $\text{Ni}(\text{mdt})_2$ anion.

equivalent isotropic displacement parameter of the atom they are attached to, by a factor 1.5 for CH_3 and 1.2 for the other hydrogen atoms, respectively. The Flack absolute structure parameter refined to 0.02 (0.06).

CCDC reference number 186/1075.

2.4 Electrochemical experiments

The redox properties of $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$ and the possibility to synthesize partially oxidised $\text{Ni}(\text{mdt})_2$ compounds were studied by electrochemical experiments. Cyclic voltammetry (CV) was carried out in an air-tight three-electrode cell, using laboratory-made, microcomputer-controlled instrumentation with "interrupt method" ohmic resistance compensation.²⁵ A platinum wire auxiliary electrode was used in conjunction with a platinum disc working electrode (Tacussel EDI rotating electrode, 1 mm diameter). The measurement was performed on a 10^{-3} M solution of $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$ in nitrobenzene with NBu_4BF_4 (0.1 M) as supporting electrolyte, carried out in the region -0.70 to 0.85 V, starting at -0.20 V, with a potential scan rate of 0.1 V s^{-1} . All potentials were referred to a saturated calomel electrode (SCE) separated from the solution by a bridge compartment filled with the same solvent and supporting electrolyte solution as in the cell.

A linear voltammetry experiment was carried out with a 2 mm platinum disc working electrode, at a rotation speed of 1000 min^{-1} , and a scan rate of 5 mV s^{-1} . Coulometric measurements were performed on a platinum electrode with a large surface area at a potential slightly higher than the considered oxidation potential.

A thin-layer CV measurement was performed to study the possibility of the synthesis of a partially oxidised $\text{Ni}(\text{mdt})_2$ compound. With this special technique the CV experiment is carried out on a thin layer of solution, with an accurately known volume and concentration. The principle of the measurement is that during the different oxidation and reduction processes all the electroactive material present in the thin layer undergoes a charge transfer. Integration of the peak surfaces results in the exact amount of electrons transferred during the different reactions.²⁶ The thin-layer CV experiment was performed on a 2.5×10^{-4} M solution of $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$ in dichloromethane with NBu_4PF_6 (1 M) as supporting electrolyte. A platinum electrode with a surface of 1 mm^2 and a

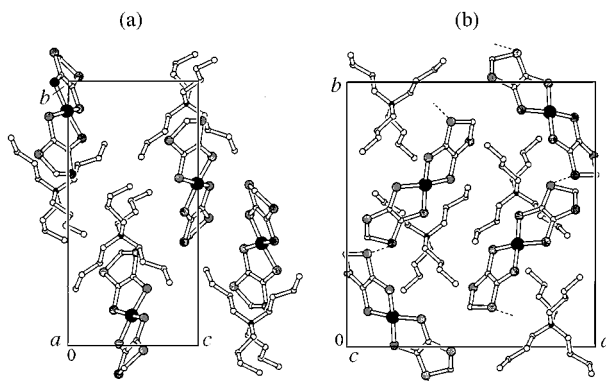


Fig. 3 Unit-cell contents of $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$ down the a and the c axis. Hydrogen atoms have been omitted for clarity.

Table 1 Crystallographic data for $[\text{NBu}_4][\text{Ni}(\text{mdt})_2]$

Formula	$\text{C}_{22}\text{H}_{40}\text{NNiS}_8$
M	633.79
Space group	$Pna2_1$ (no. 33)
Crystal system	Orthorhombic
$a/\text{\AA}$	17.2633(6)
$b/\text{\AA}$	18.4274(9)
$c/\text{\AA}$	9.0116(8)
$V/\text{\AA}^3$	2866.8(3)
Z (formula units)	4
D / g cm^{-3}	1.4685(2)
μ/cm^{-1}	12.7 ^a
$F(000)$	1340
T/K	150
$\theta_{\text{min}}/\theta_{\text{max}}$	1.6, 26.5
Total data	5766
Total unique data (n)	2949
Observed data	2071 [$I > 2\sigma(I)$]
No. parameters (p)	294
$R1^b$	0.050
$wR2^c$	0.0825
S^d	1.00

^a Graphite monochromated Mo-K α radiation; $\lambda = 0.71073 \text{ \AA}$. ^b $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0233P)^2$, where $P = (F_o^2 + 2F_c^2)/3$. ^d $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$.

potential scan rate of 2 mV s^{-1} were applied and a EG&E potentiostat, Princeton Applied Research model 362, was used.

3 Results and discussion

3.1 Crystal structure

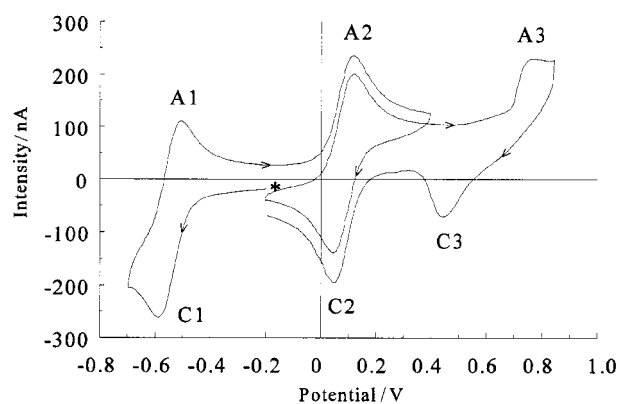
The asymmetric unit of the crystal structure contains one $\text{Ni}(\text{mdt})_2$ unit and one Bu_4N cation. Fig. 1 shows the labelling scheme used for the heavy atoms in the anion and the cation. It can be seen that the torsion angle of one of the butyl groups deviates from the expected antiperiplanar orientation. The torsion angle $\text{C}(19)\text{--}\text{C}(20)\text{--}\text{C}(21)\text{--}\text{C}(22)$ is $-60.2(8)^\circ$, *i.e.* a synclinal orientation, which is probably due to packing effects.

Table 2 lists the bond distances and bond angles of the $\text{Ni}(\text{mdt})_2$ unit. The observed Ni–S bond lengths vary from 2.154(2) to 2.170(2) \AA , slightly larger than those found in $[\text{NBu}_4][\text{Ni}(\text{ddd})_2]$, 2.130(6)–2.145(9) \AA ,²⁸ but are similar to those in $[\text{NBu}_4][\text{Ni}(\text{dmit})_2]$, 2.151(3)–2.160(3) \AA .²⁹

The large deviation from 180° for the angles $\text{S}(3)\text{--}\text{Ni}\text{--}\text{S}(6)$ and $\text{S}(4)\text{--}\text{Ni}\text{--}\text{S}(5)$, $173.37(10)$ and $166.53(10)^\circ$ respectively, indicates a large distortion from a square-planar configuration for the NiS_4 co-ordination geometry. This distortion is clearly illustrated by the side view of $\text{Ni}(\text{mdt})_2$ presented in Fig. 2. The twist between the planes $\text{S}(3)\text{--}\text{Ni}\text{--}\text{S}(4)$ and $\text{S}(5)\text{--}\text{Ni}\text{--}\text{S}(6)$ is $14.77(13)^\circ$, showing the distorting towards a tetrahedral geometry. Furthermore, the nickel centre is forming a plane together with the fragment $\text{S}(5)\text{--}\text{S}(6)\text{--}\text{C}(4)\text{--}\text{C}(5)\text{--}\text{S}(7)\text{--}\text{S}(8)$ [maximum

Table 2 Bond distances (Å) and angles (°) of the Ni(mdt)₂ unit in [NBu₄][Ni(mdt)₂] (estimated standard deviations in parentheses)

Ni–S(3)	2.167(2)	S(4)–C(3)	1.723(8)
Ni–S(4)	2.154(2)	S(5)–C(4)	1.727(8)
Ni–S(5)	2.155(2)	S(6)–C(5)	1.722(7)
Ni–S(6)	2.170(2)	S(7)–C(4)	1.756(7)
S(1)–C(1)	1.807(8)	S(7)–C(6)	1.821(8)
S(1)–C(2)	1.744(8)	S(8)–C(5)	1.759(8)
S(2)–C(1)	1.833(8)	S(8)–C(6)	1.800(7)
S(2)–C(3)	1.732(8)	C(2)–C(3)	1.372(11)
S(3)–C(2)	1.729(8)	C(4)–C(5)	1.349(10)
S(3)–Ni–S(4)	92.52(8)	S(1)–C(1)–S(2)	108.1(4)
S(3)–Ni–S(5)	88.08(8)	S(1)–C(2)–S(3)	122.0(4)
S(3)–Ni–S(6)	173.37(10)	S(1)–C(2)–C(3)	117.1(6)
S(4)–Ni–S(5)	166.53(10)	S(3)–C(2)–C(3)	120.7(6)
S(4)–Ni–S(6)	88.27(9)	S(2)–C(3)–S(4)	122.9(5)
S(5)–Ni–S(6)	92.69(8)	S(2)–C(3)–C(2)	116.8(6)
C(1)–S(1)–C(2)	95.0(3)	S(4)–C(3)–C(2)	120.1(6)
C(1)–S(2)–C(3)	94.6(4)	S(5)–C(4)–S(7)	122.2(4)
Ni–S(3)–C(2)	102.2(3)	S(5)–C(4)–C(5)	120.7(6)
Ni–S(4)–C(3)	102.8(3)	S(7)–C(4)–C(5)	117.0(6)
Ni–S(5)–C(4)	102.8(3)	S(6)–C(5)–S(8)	121.5(4)
Ni–S(6)–C(5)	102.3(3)	S(6)–C(5)–C(4)	121.4(6)
C(4)–S(7)–C(6)	93.5(4)	S(8)–C(5)–C(4)	117.0(5)
C(5)–S(8)–C(6)	93.9(3)	S(7)–C(6)–S(8)	108.9(4)

**Fig. 4** Cyclic voltammogram of [NBu₄][Ni(mdt)₂] in nitrobenzene; * = start of the scan.

atomic deviation 0.038(2) Å for S(6)], whereas a second plane is formed in the molecule by the fragment S(1)–S(2)–C(2)–C(3)–S(3)–S(4) [maximum atomic deviation 0.063(2) Å for S(2)]. The plane with S(1) is tilted 24.84(9)° from that with Ni(1), showing the large deviation from planarity of the anion. An inclination of 6.1° between the two ligands in Ni(dmit)₂ has been reported for [NBu₄][Ni(dmit)₂], but a large distortion as here has not been found in any comparable nickel dithiolene complex and donor molecule. However, the distortion may not be large enough to prohibit large orbital overlap and therefore good conducting properties in derived compounds. Moreover, this is the first crystal structure containing Ni(mdt)₂ and it is not clear at present whether the deviation is due to packing effects, or to internal tensions in the complex.

Fig. 3 shows the unit cell viewed down the *a* and the *c* axis. For clarity the four molecules on the right-hand side in Fig. 3(a) have been translated one step in the *c* direction. No stacking or dimerisation of Ni(mdt)₂ units is present in the structure. The shortest Ni···Ni distance found is 8.8806(19) Å, from the crystallographically independent Ni(mdt)₂ unit towards the Ni atom of the unit with a symmetry operation $-x, -y, 0.5 + z$. The shortest intermolecular S···S distance present is between the atoms S(1) and S(8) [with a symmetry operation of $0.5 - x, 0.5 + y, 0.5 + z$ on S(8)] and indicated with a dotted line in Fig. 3(b). This distance is 3.779(3) Å, which is slightly larger than the sum of the van der Waals radii,³⁰ *i.e.* 3.70 Å. Also the

Table 3 Comparison of electrochemical properties of several nickel bis(dithiolene) complexes *vs.* SCE ($0 < x < 1$)

Complex	Solvent, electrolyte	E_i/V			Ref.
		2–/1–	1–/0	0/x+	
[Ni(mdt) ₂]	Nitrobenzene, NBu ₄ BF ₄	–0.55	+0.08	+0.60	This work
[Ni(dddt) ₂]	Nitrobenzene, NEt ₄ BF ₄	–0.79	–0.11	+0.82	20
[Ni(pddt) ₂]	dmf, NEt ₄ ClO ₄	–0.66	+0.24	—	31
[Ni(mtdt) ₂]	dmf, NBu ₄ ClO ₄	–0.73	+0.04	—	32

structures of [NBu₄][Ni(dmit)₂] and [NBu₄][Ni(dddt)₂] do not show any S···S interactions shorter than 3.70 Å.^{28,29}

3.2 Electrochemical properties

Fig. 4 shows the cyclic voltammogram of [NBu₄][Ni(mdt)₂] in nitrobenzene recorded between –0.70 and 0.85 V at a potential scan rate of 0.1 V s^{–1}. The voltammogram shows the presence of three redox couples in the recorded region. The first reversible wave (A1, C1) at $E_i = -0.55$ V *vs.* SCE corresponds to the redox couple [Ni(mdt)₂]^{2–}–[Ni(mdt)₂][–], while the second reversible wave (A2, C2) at $E_i = 0.08$ V *vs.* SCE corresponds to the redox couple [Ni(mdt)₂][–]–[Ni(mdt)₂]. Linear voltammetry showed that the number of electrons transferred in the two reactions is the same and coulometry showed that one electron is transferred in each. The third wave (A3, C3) in the cyclic voltammogram at $E_i = 0.60$ V *vs.* SCE shows that the neutral complex [Ni(mdt)₂] can be further oxidised to a cationic species. However, the amount of electrons transferred in this oxidation could not be determined by either linear voltammetry, because of deposition of the product on the electrode, or by coulometry, because of the poor solubility of [Ni(mdt)₂] in nitrobenzene. The amount of electrons transferred was therefore determined by a thin-layer CV experiment, carried out in dichloromethane with NBu₄PF₆ as a supporting electrolyte. This experiment confirmed the transfer of one electron in the first two reactions and showed that 0.5 electron is transferred during the third reaction.

A comparison of the electrochemical properties of [NBu₄][Ni(mdt)₂], [Ni(dddt)₂], [Ni(pddt)₂] and [Ni(mtdt)₂] is presented in Table 3 [pddt = propane-1,3-diylthioethylene-1,2-dithiolate; mtdt = 1,2-bis(methylsulfanyl)-1,2-dithiolate].^{31,32} So far [Ni(mdt)₂] and [Ni(dddt)₂] are the only complexes for which oxidation to a partially oxidised positively charged complex has been reported; [Ni(mdt)₂] even shows a lower redox potential for this oxidation step, indicating that it should be easier to synthesize the positively charged Ni(mdt)₂ than the Ni(dddt)₂ complex.

4 Conclusion

A new nickel bis(dithiolene) complex, [Ni(mdt)₂], has been successfully synthesized. The crystal structure of [NBu₄][Ni(mdt)₂] shows that the Ni(mdt)₂ unit is largely distorted from planarity. However, the distortion may not be large enough to prohibit considerable orbital overlap and therewith good conducting properties in derived oxidised compounds.

An electrochemical study showed that [NBu₄][Ni(mdt)₂] can be further oxidised to a partially oxidised positively charged complex. Comparison of the electrochemical properties of [NBu₄][Ni(mdt)₂] and of [NBu₄][Ni(dddt)₂] shows that the redox potential for the final oxidation step is lower for Ni(mdt)₂ than for Ni(dddt)₂. This indicates that it should be easier to synthesize the positively charged Ni(mdt)₂ than the Ni(dddt)₂ complex, making [Ni(mdt)₂] a promising precursor for future conducting materials. Electrooxidation experiments to synthesize single crystals of partially oxidised Ni(mdt)₂ complexes are in progress.

5 Acknowledgements

Technical assistance by D. de Montauzon in carrying out cyclic voltammetry studies is gratefully acknowledged. This work was supported in part (A. L. S., N. V.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organisation for Scientific Research (Y. S. J. V.) and in part (Y. S. J. V., M. J. J. M., J. G. H., J. R.) by WFMO (Werkgroep Fundamenteel Materialen Onderzoek of Leiden University). Financial support by the European Community, allowing exchange of preliminary results with several European colleagues, under Contract ERBCHRXCT920080 is thankfully acknowledged. Also support and sponsorship concerted by COST Action D4/0001/95 (Chemistry of Molecular Materials) is kindly acknowledged.

References

- 1 L. Valade, M. Bousseau, A. Gleizes and P. Cassoux, *J. Chem. Soc., Chem. Commun.*, 1983, 110.
- 2 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115.
- 3 R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse and E. Hoyer, *Coord. Chem. Rev.*, 1992, **117**, 99.
- 4 Y. S. J. Veldhuizen, N. Veldman, A. L. Spek, C. Faulmann, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 1995, **34**, 140; Y. S. J. Veldhuizen, Ph.D. Thesis, Leiden University, 1997.
- 5 H. Tajima, M. Inokuchi, A. Kobayashi, T. Ohta, R. Kato, H. Kobayashi and H. Kuroda, *Chem. Lett.*, 1993, 1235.
- 6 J. P. Cornelissen, D. Reefman, J. G. Haasnoot, A. L. Spek and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1991, **110**, 345; J. P. Cornelissen, B. Pomarède, A. L. Spek, D. Reefman, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 1993, **32**, 3720.
- 7 M. A. Beno, A. M. Kini, U. Geiser, H. H. Wang, K. Douglas Carlson and J. M. Williams, in *The Physics and Chemistry of Organic Superconductors*, eds. G. Saito and S. Kagoshima, Springer, Berlin, 1990, p. 369.
- 8 A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, 1987, 1819.
- 9 T. Naito, A. Sato, K. Kawano, A. Tateno, H. Kobayashi and A. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1995, 351.
- 10 B. Pomarède, B. Garreau, I. Malfant, L. Valade, P. Cassoux, J.-P. Legros, A. Audouard, L. Brossard, J.-P. Ulmet, M.-L. Doublet and E. Canadell, *Inorg. Chem.*, 1994, **33**, 3401.
- 11 S. Alvarez, R. Vicente and R. Hoffmann, *J. Am. Chem. Soc.*, 1985, **107**, 6253.
- 12 C. T. Vance, R. D. Bereman, J. Bordner, W. E. Hatfield and J. H. Helms, *Inorg. Chem.*, 1985, **24**, 2905.
- 13 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, V. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, in *Organic Superconductors*, ed. R. N. Grimes, Prentice Hall, Englewood Cliffs, NJ, 1992, p. 400.
- 14 R. P. Shibaeva and V. E. Zavodnik, *Kristallografiya*, 1993, **38**, 84.
- 15 R. Kato, A. Kobayashi, Y. Sasaki and H. Kobayashi, *Chem. Lett.*, 1984, 993.
- 16 P. J. Nigrey, B. Morosin, J. F. Kwak, E. L. Venturini and R. J. Baughman, *Synth. Met.*, 1987, **19**, 617.
- 17 Y. S. J. Veldhuizen, N. Veldman, A. L. Spek, J. G. Haasnoot and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1995, **114**, 337.
- 18 G. C. Papavassiliou, V. C. Kakoussis, J. S. Zambounis and G. A. Mousdis, *Chem. Scri.*, 1989, **29**, 123.
- 19 P. J. Nigrey, B. Morosin, J. F. Kwak, E. L. Venturini and R. J. Baughman, *Synth. Met.*, 1986, **16**, 1.
- 20 C. Faulmann, P. Cassoux, E. B. Yagubskii and L. V. Vetoshkina, *New J. Chem.*, 1993, **17**, 385.
- 21 J. L. de Boer and A. J. M. Duisenberg, *Acta Crystallogr., Sect. A*, 1984, **40**, C410.
- 22 A. L. Spek, *J. Appl. Crystallogr.*, 1988, **21**, 578.
- 23 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
- 24 G. M. Sheldrick, SHELXL 93, Program for crystal structure refinement, University of Göttingen, 1993.
- 25 K. Hartke, T. Kissel, J. Quante and R. Matusch, *Chem. Ber.*, 1980, **113**, 1898; P. Cassoux, R. Dartiguepeyron, P. L. Fabre, D. de Montauzon and J.-B. Tomassino, *L'Actualité Chimique*, 1985, 79.
- 26 R. Carlier and J. Simonet, *Bull. Soc. Chim. Fr.*, 1988, 831; R. Carlier, A. Tallec, P. Frère, M. Sallé, M. Jubault, A. Gorgues and J. Cousseau, *Synth. Met.*, 1993, **55-57**, 2359; R. Carlier, P. Frère, M. Sallé, J. Roncali, M. Jubault, A. Tallec and A. Gorgues, *Adv. Mater.*, 1993, **5**, 445.
- 27 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
- 28 A. J. Schultz, H. H. Wang, L. C. Soderholm, T. L. Sifter, J. M. Williams, K. Bechgaard and M.-H. Wang, *Inorg. Chem.*, 1987, **26**, 3757; J. H. Welch, R. D. Bereman and P. Sing, *Inorg. Chem.*, 1988, **27**, 3680.
- 29 O. Lindqvist, L. Andersen, J. Sieler, G. Steimecke and E. Hoyer, *Acta Chem. Scand., Ser. A*, 1982, **36**, 855.
- 30 L. Pauling, *The Nature of the Chemical Bond*, 2nd edn., Cornell University Press, Ithaca, 1948.
- 31 R. D. Bereman and H. Lu, *Inorg. Chim. Acta*, 1993, **204**, 53.
- 32 C. T. Vance and R. D. Bereman, *Inorg. Chim. Acta*, 1988, **149**, 229.

Received 29th May 1998; Paper 8/04034F