Pergamon

Polyhedron Vol. 14, No. 11, pp. 1487–1494, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 \$9.50+0.00

0277–5387(94)00409–9

SYNTHESES AND PROPERTIES OF THE NICKEL COMPLEXES OF 1,2-DITHIOLATES MEDT AND PHDT. THE CRYSTAL STRUCTURE OF $[Bu_4N][Ni(MEDT)_2]$

YAO TIAN-MING, ZUO JING-LIN and YOU XIAO-ZENG*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry,
Nanjing University, Centre for Advanced Studies in Science and Technology of
Microstructures, Nanjing 210008, P.R.C.

and

HUANG XIAO-YING

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science,
Fuzhou 350002, P.R.C.

(*Received* 29 *March* 1994; *accepted* 7 *October* 1994)

Abstract—The syntheses and characterizations of the nickel(III) complexes, $[Bu_4N][Ni(MEDT)_2]$ (MEDT = 5-methyl-6-hydro-1,4-dithiin-2,3-dithiolate) and $[Bu_4N][Ni(PHDT)_2]$ (PHDT = 5-phenyl-6-hydro-1,4-dithiin-2,3-dithiolate) are reported. Both complexes show characteristic IR and UV–vis absorptions of transition metal dithiolate complexes. The cyclic voltammograms contain two waves, indicating a two-step electrochemical process $[ML_2]^0 = [ML_2]^{1-} = [ML_2]^{2-}$. The solid powder ESR spectra show three broad signals. The frozen glass ESR spectra yielded g value assignments of $g_1 = 2.102$, $g_2 = 2.049$ and $g_3 = 2.004$ for $[Ni(MEDT)_2]^-$ and $g_1 = 2.104$, $g_2 = 2.048$ and $g_3 = 2.004$ for $[Ni(PHDT)_2]^-$. Both complexes are semiconductors with electrical conductivities of the order of 10^{-8} S cm^{-1}. Single-crystal structure analysis revealed that the gross geometry of the $[Ni(MEDT)_2]^-$ anion is planar with the exception of the external unit —$CH_2CH(Me)$—. There are two different kinds of anions. The anions form stacks along the *b*- and *c*-axes. The nearest intermolecular S—S distance is 5.104 Å.

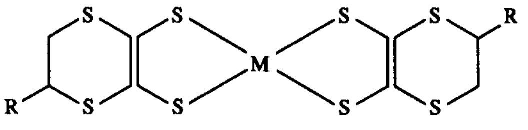
Since the discovery of metallic behaviour in tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ),[1] there has been extensive research on molecular metals.[2] The preparation of totally sulphur-based organic molecular conductors or even superconductors, such as bis-(ethylenedithiolotetrathiafulvalenium), κ-$(ET)_2Cu[N(CN)_2]Cl$, which possesses the highest T_c ($T_c = 12.8$ K, 0.3 kbar) of its kind,[3] has further increased the interest in this area.[4] Crystal analysis elucidated that the TTF framework and sulphur–sulphur network in the solid state may be the key structural requirement for the conduction of electrons.

On the other hand, the multi-sulphur 1,2-dithiolene complexes of $[Ni(DMIT)_2]^{n-}$ (DMIT) = 1,3-dithiol-2-thione-4,5-dithiolate) were also found to be molecular conductors.[6] This prompted many laboratories to explore new complexes in the area.[7] A scheme to combine the inorganic systems and the "TTF-type" organosulphur molecules was designed.[8] The multi-sulphur 1,2-dithiolene complexes of $[M(DDDT)_2]^{n-}$ (DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolate, M = Ni, Pd, Pt, Cu, Au, Co and V), which are similar in structure to ET salts, were synthesized.[9,10] Systematic investigations on the effects of cation on the crystal packing motif and the intermolecular S—S contact for $[Ni(DDDT)_2]^{n-}$ were undertaken.[11,12] Quite recently, the complexes of $[M(PDDT)_2]^{n-}$

---

*Author to whom correspondence should be addressed.

(PDDT = 6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolate, M = Ni, Cu, Pt), which are analogous to [M(DDDT)$_2$]$^{n-}$ but differ in the external ligand unit, were also prepared.[13,14] In our previous work, the role of the external ligand unit on the molecular structure and crystal packing was discussed.[15]



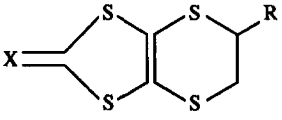
[M(DDDT)$_2$]$^-$: R = H
[M(MEDT)$_2$]$^-$: R = Me
[M(PHDT)$_2$]$^-$: R = Ph

In continuation of this work and investigation into the electronic and structural effects of the substitution on the external ligand unit of DDDT, new multi-sulphur 1,2-dithiolate ligands MEDT (5-methyl-6-hydro-1,4-dithiin-2,3-dithiolate) and PHDT (5-phenyl-6-hydro-1,4-dithiin-2,3-dithiolate), were synthesized. We report here the characterization and properties of the nickel complexes of [Bu$_4$N][Ni(MEDT)$_2$] and [Bu$_4$N][Ni(PHDT)$_2$]. The single crystal structure of [Bu$_4$N][Ni(MEDT)$_2$] is also determined.

EXPERIMENTAL

Reagents

All the chemicals used were analytically pure. Solvents were purified and dried by standard techniques. [Bu$_4$N]$_2$[Zn(DMIT)$_2$] was prepared by a literature method[16] and recrystallized from acetone. 1,2-Dibromoethylbenzene was obtained by the addition reaction of phenylethene with bromine.



(1) R = Me, X = S
(2) R = Ph, X = S
(3) R = Ph, X = O

2,3 - dihydro - 2 - methyl - 1,3 - dithiolo - [4,5-e] [1,4]dithiin-6-thione (**1**) and 2,3-dihydro-2-phenyl-1,3-dithiolo [4,5-e] [1,4]dithiin-6-thione (**2**) were synthesized by treatment of [Bu$_4$N]$_2$[Zn(DMIT)$_2$] with 1,2-dibromopropane or 1,2-dibromoethylbenzene in acetone. The crude products were recrystallized in ethanol to give yellow needle crystals.

The thione compound **2** was then converted to the anlogue **3** by a modification of a reported procedure.[17] To the thione compound **2** (1.0 g) in chloroform (35 cm^3) was added mercury(II) acetate (3.0 g) in glacial acetic acid (40 cm^3. The mixture was stirred at 40°C (water bath) for 5 h. After filtration, the filtrate was washed with an aqueous solution (250 cm^3) of NaHCO$_3$ (60.0 g) and then with water. The organic phase was dried with CaCl$_2$ and concentrated in a rotary evaporator. A yellow solid was then collected. Pale yellow crystals of compound **3** were obtained by recrystallization from ethanol–chloroform (3 : 1). Found: C, 46.2; H, 2.8. Calc. for $C_{11}H_8OS_4$: C, 46.4; H, 2.8%.

Syntheses

[Bu$_4$N][Ni(MEDT)$_2$]. A mixture of ethanol (10 cm^3), potassium hydroxide (1.0 g) and the thione compound **1** (0.5 g) was stirred for 1 h at 40°C (water bath) under nitrogen. The resulting pale yellow microcrystals of the potassium salt were isolated by centrifugation. The salt was then dissolved instantly in methanol (20 cm^3). A methanol solution (20 cm^3) of $NiCl_2 \cdot 6H_2O$ (0.15 g) was added dropwise to the solution under nitrogen with the colour changing from amber to brown. The solution was then stirred in air for 30 min and the colour further changed to dark green. After filtration, to the filtrate was added tetrabutylammonium bromide (1.0 g) and a dark green solid was precipitated immediately. The solid was then collected by filtration, washed with methanol, and dried in air. Crude product was recrystallized in acetone through slow evaporation. Dark green crystals suitable for X-ray determination were obtained in 2 weeks. Found: C, 44.7; H, 7.0; N, 1.5. Calc. for $C_{26}H_{48}NNiS_8$: C, 45.2; H, 7.0; N, 2.0%. IR (KBr): 1443 (m), 1365 (s), 1172 (m), 865 (m) and 449 (m) cm^{-1}.

[Bu$_4$N][Ni(PHDT)$_2$]. The procedure followed was identical to that described above with the exception of using compound **3** (0.5 g) instead of compound **1**. A dark green solid was obtained. Found: C, 52.6; H, 6.3; N, 1.5. Calc. for $C_{36}H_{52}NNiS_8$: C, 53.1; H, 6.4; N, 1.7%. IR (KBr): 3026, 1962, 1883, 1598, 1468 (m), 1450 (m), 1365 (s), 1179 (m), 858 (m), 696 (m) cm^{-1}.

Physical measurements

Cyclic voltammetry was performed using a model 79-1 V-A analyser, with an electrochemical cell with a platinum wire as the working electrode, a platinum plate as the auxiliary electrode and an SCE as reference. ESR spectra were recorded on a Bruker ER 200-D-SRC spectrometer. IR spectra were recorded on a Nicolet FT IR 170SX spectrophotometer using KBr pellets. Electronic spectra were recorded on a UV3100 spectrophotometer. Electrical conductivities for compacted pellets were measured by the two-probe technique. Elemental analyses were performed using a Perkin–Elmer 240 analytical instrument.

Single-crystal analysis

A representative crystal of $[Bu_4N][Ni(MEDT)_2]$ was surveyed and cell dimensions were obtained by a least-squares fit of 25 reflections (2θ range: 2–50°). A data set was collected on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator and molybdenum radiation ($\lambda = 0.71069$ Å). Three standard reflections were monitored every hour. The structure was refined with anisotropic thermal factors by full-matrix least-squares using the MSC/Rigaku TEXSAN 3.1 program package on Micro-vax 3100 computer. All non-hydrogen atoms were solved by Patterson and Fourier synthesis. The quantity minimized was $\Sigma W(\Delta F)^2$, where $W = 1/\sigma^2(|F_o|)$. All hydrogen atoms were refined with a fixed bond distance of 0.95 Å. Absorption correction was made using the DIFABS program. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (Vol. IV).[18] Pertinent crystal survey, data collection and refinement parameters are summarized in Table 1.

Table 1. Single-crystal X-ray crystallographic analysis

Crystal parameters	
Formula	$C_{26}H_{48}NNiS_8$
Molecular weight	689.85
Crystallization medium	acetone
Crystal size (mm)	$0.1 \times 0.1 \times 0.4$
Crystal colour	dark green
Crystal habit	prism
Cell dimensions	$a = 9.405(7)$ Å
	$b = 13.659(4)$ Å
	$c = 13.817(3)$ Å
	$\alpha = 84.06(2)°$
	$\beta = 78.32(4)°$
	$\gamma = 87.11(5)°$
Volume	1728(2) Å^3
Space group	$P\bar{1}$(no. 2)
Molecules/unit cell	2
D_{calc}	1.33 g cm^{-3}
$F(000)$	734
Data collection parameters	
Radiation	Mo-K_α
Temperature	296 K
2θ range	2–50.0°
Scan type	ω
Scan speed	Variable, $< 16.48°$ min^{-1}
Scan width	$0.50 + 0.35 \tan\theta$
Reflections collected	6476
Independent reflections	6071
Observed reflections	1588
Refinement parameters	
Final R index	$R = 0.073$
	$R_w = 0.079$
Goodness of fit	GOF = 1.59
Max. shift in final cycle	0.05
Largest peak in final diff. map	0.46 e Å^{-3}

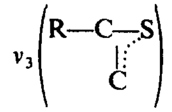
The data fit criteria [based on reflections having $F > 3.0\sigma(F)$] were $R = \Sigma||F_o| - |F_c||/\Sigma F_o$; $R_w = [\Sigma w(\Delta F)^2/\Sigma F_o^2]^{0.5}$; $\mathrm{GOF} = \Sigma(w[||F_o| - |F_c||]^2/[N_o - N_v]^{0.5}$.

RESULTS AND DISCUSSION

For the preparation of the dipotassium salt K$_2$MEDT, hydrolysis of compound **1** with hot ethanolic potassium hydroxide was used. However, the hydrolysis of compound **2** under the same conditions did not produce K$_2$PHDT. Upon converting compound **2** to the corresponding carbonyl derivative, compound **3**, followed by hydrolysis with ethanolic potassium hydroxide, the dipotassium salt K$_2$PHDT was successfully obtained.

The dipotassium salts are extremely sensitive to air, but stable for a short period of time in methanol solution. We could only obtain the formally nickel(III) complexes, although we used nickel(II) complexes as the starting material. As might be expected, the brown nickel(II) dithiolate complexes were rapidly oxidized to the green nickel(III) dithiolate complexes when the solution was exposed to air.

The IR spectra of both complexes contain characteristic absorptions of monoanionic nickel dithiolenes:[19] ν_1(C=C) around 1445 cm^{-1}; ν_2(C—S) around 1175 cm^{-1};



$$\nu_3\left(\begin{array}{c}\mathrm{R{-}C{-}S}\\ \vdots\\ \mathrm{C}\end{array}\right)$$

around 857 cm^{-1}. The absorptions of [Bu$_4$N][Ni(PHDT)$_2$] at 3026, 1962, 1883, 1598, 1468 and 696 cm^{-1} confirm the presence of the phenyl group.

As is the case with [Ni(DDDT)$_2$]$^-$, both [Bu$_4$N][Ni(MEDT)$_2$] and [Bu$_4$N][Ni(PHDT$_2$)] show intense absorption at 1180 nm. This low energy visible or near-IR absorption is due to the electron i.e. $\pi \rightarrow \pi$ transition.[20] The rather weak absorption at 610 nm of the complexes may be attributed to the electron $\pi \rightarrow$ M transition. The substitution on the DDDT external unit has no effect on the electronic spectrum.

In order to make a comparison, cyclic voltammograms of [Bu$_4$N][Ni(MEDT)$_2$] and [Bu$_4$N][Ni(PHDT)$_2$], together with other related dithiolate complexes, were recorded. The elecrochemical data are given in Table 2. As expected, the cyclic voltammograms of the title complexes reveal two reversible waves. The first, around −0.68 V (vs SCE), represents the mono- to dianion reduction. The second, around +0.05 V (vs SCE), represents the neutral to monoanion reduction. From Table 2 it is concluded that substitution on the external unit of DDDT has a small effect on the reduction potentials. The potential is indicative of the ability of the dithiolate ligands to accept or donate electron density as the charge on the complex changes. The relative ability to accept electron density is PHDT > DDDT > MEDT, although the difference is very small. This trend follows the electron withdrawing ability of the substitution group: Ph > H > Me.

Table 2. Cyclic voltammetry results ($E_{1/2}$) for nickel complexes of 1,2-diothiolate

Complex	Dianion–anion	Anion–neutral
[Ni(MEDT)$_2$]$^{n-}$	−0.70	+0.05
[Ni(PHDT)$_2$]$^{n-}$	−0.65	+0.06
[Ni(DDDT)$_2$]$^{n-}$	−0.68	+0.06
[Ni(PDDT)$_2$]$^{n-}$	−0.69	+0.17

Volts vs SCE, measured at a platinum wire electrode, sweeping rate 250 mV s^{-1}, 1.0×10^{-4} mol dm^{-3} in CH$_3$CN, containing 0.1 mol dm^{-3} TBAP.

The ESR spectra of [Bu$_4$N][Ni(MEDT)$_2$] and [Bu$_4$N][Ni(PHDT)$_2$] solid powder at room temperature are shown in Fig. 1. Three broad ESR signals can be detected, though they are partly overlapped. The broadening of the ESR signals is due to intermolecular interaction in the solid state.[21] The frozen glass ESR spectra of the title complexes in DMF at 128 K show a rhombic g tensor. The spin Hamiltonian parameters for the MEDT and PHDT nickel complexes, together with other related complexes, are listed in Table 3. The g values of [Ni(MEDT)$_2$]$^-$ and [Ni(PHDT)$_2$]$^-$ are slightly smaller than those of [Ni(DDDT)$_2$]$^-$ and [Ni(PDDT)$_2$]$^-$, but very close to that of [Ni(DMIT)$_2$]$^-$.

The structure, with the numbering scheme for the [Bu$_4$N]$^+$ cation and the [Ni(MEDT)$_2$]$^-$ anions, is

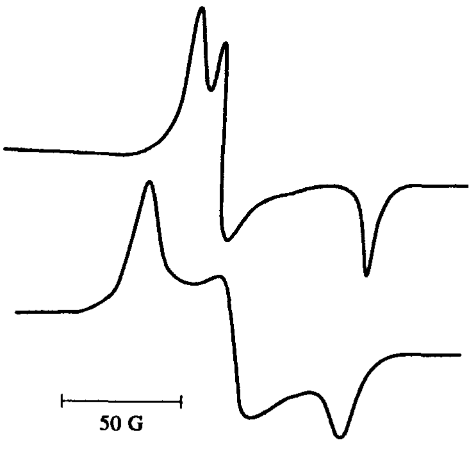


Fig. 1. Solid powder ESR spectra of [Bu$_4$N][Ni(MEDT)$_2$] and [Bu$_4$N][Ni(PHDT)$_2$].

Table 3. DMF frozen glass ESR data of nickel complexes of 1,2-dithiolate

Complex	g_1	g_2	g_3	Ref.
$[Ni(MEDT)_2]^-$	2.102	2.049	2.004	this work
$[Ni(PHDT)_2]^-$	2.104	2.048	2.004	this work
$[Ni(DDDT)_2]^-$	2.119	2.057	2.022	9
$[Ni(PDDT)_2]^-$	2.156	2.070	2.013	14
$[Ni(MTDT)_2]^-$	2.093	2.051	2.014	22
$[Ni(DMIT)_2]^-$	2.105	2.041	2.001	23

shown in Fig. 2. There are two different kinds of anions on two inversion centres (anions A and B) in the $[Bu_4N][Ni(MEDT)_2]$ crystal. Selected bond lengths and bond angles are listed in Table 4.

The gross geometry of the $[Ni(MEDT)_2]^-$ anion is planar with the exception of the outer —$CH_2CH(Me)$— units. The mean deviation from the least-squares plane defined by the $Ni(S_2C_2S_2)$ core is 0.018 Å for anion A and 0.019 Å for anion B. The largest deviation from the plane is 0.047 Å [C(2)] for anion A and 0.038 Å [C(6)] for anion B.

The four sulphur atoms surrounding the nickel atom yield a square planar environment with an average S—Ni—S angle of 90.0°, identical to that in $[Bu_4N][Ni(DDDT)_2]$. The average C—S, Ni—S and C=C bond lengths in the $Ni(S_2C_2S_2)$ core are 1.73, 2.126 and 1.34 Å, respectively. The corresponding values in $[Bu_4N][Ni(DDDT)_2]$ are 1.74, 2.136 and 1.34 Å.[11] The similarities in bond angles and bond lengths reveal that the methyl substitution on the external unit has little structural effect on the $Ni(S_2C_2S_2)$ core. This may be a further explanation for observing small differences in electronic spectra and electrochemical data of the MEDT complex in comparison with the DDDT complex.

There are three types of C—S bonds in $[Ni(MEDT)_2]^-$. If the C—S bond lengths are averaged for each type, the values are 1.71, 1.76 and 1.77 Å, respectively. The C—S bonds become shorter the closer they are to the central metal atom. However, the C—S bonds in the five-membered coordination ring are much shorter than the others, indicating some double bond character. This means a slight incidence of electron delocalization in the coordination ring and also creates difficulty in the assignment of an oxidation state to the central metal atom.

The orientation of the external —CH_2CH_2— unit has been of interest for the square planar strucutre in DDDT complexes, or even in organomolecular superconductor (ET) salts. In the $[Bu_4N][Ni(MEDT)_2]$ complex, the two external —$CH_2CH(Me)$— units are *trans* orientated in anion A, with one C—C single bond lying above the mean plane at a distance of 0.58 Å, and the other lying below the mean plane at a distance of −0.58 Å. Quite differently in anion B, both the C—C single bonds are puckered, with one carbon atom lying above the mean plane at a distance of 0.29 Å, and the other lying below the mean plane at a distance of −0.24 Å. This orientation is believed to be random, most likely the result of

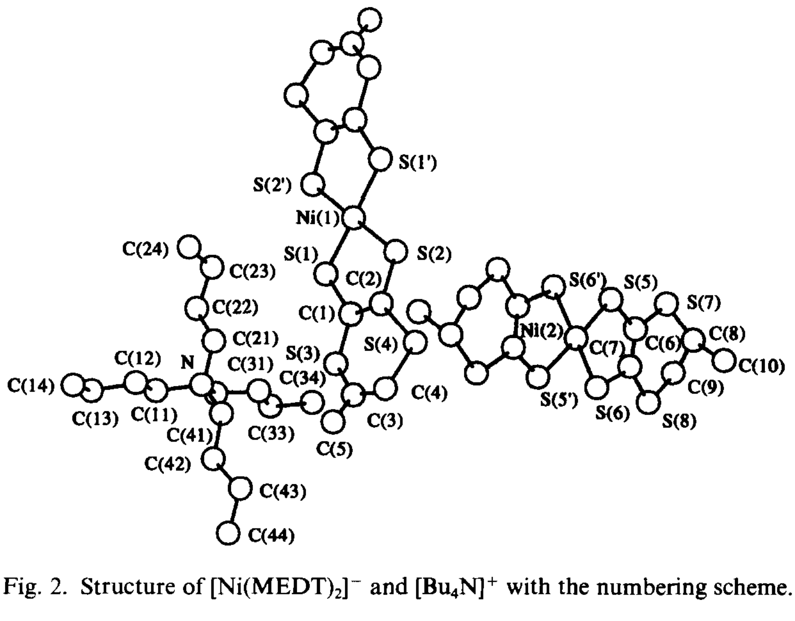


Fig. 2. Structure of $[Ni(MEDT)_2]^-$ and $[Bu_4N]^+$ with the numbering scheme.

Table 4. Selected bond distances (Å) and bond angles (°) in [Bu$_4$N][Ni(MEDT)$_2$]

Ni(1)—S(1)	2.126(5)	Ni(2)—S(5)	2.122(5)	N—C(11)	1.51(2)
Ni(1)—S(2)	2.136(5)	Ni(2)—S(6)	2.123(5)	N—C(21)	1.49(2)
S(1)—C(1)	1.70(2)	S(5)—C(6)	1.70(2)	N—C(31)	1.51(2)
S(2)—C(2)	1.73(2)	S(6)—C(7)	1.71(2)	N—C(41)	1.49(2)
C(1)—C(2)	1.32(2)	C(6)—C(7)	1.36(2)	C(11)—C(12)	1.56(3)
S(3)—C(1)	1.73(2)	S(7)—C(6)	1.75(2)	C(21)—C(22)	1.51(2)
S(4)—C(2)	1.79(1)	S(8)—C(7)	1.75(2)	C(31)—C(32)	1.45(3)
S(3)—C(3)	1.79(4)	S(7)—C(8)	1.79(3)	C(41)—C(42)	1.51(2)
S(4)—C(4)	1.70(3)	S(8)—C(9)	1.78(3)		
C(3)—C(4)	1.24(4)	C(8)—C(9)	1.37(3)		
C(3)—C(5)	1.16(4)	C(8)—C(10)	1.67(4)		

S(1)—Ni(1)—S(1′)	180.00	S(5)—Ni(2)—S(5′)	180.00
S(1)—Ni(1)—S(2′)	91.3(2)	S(5)—Ni(2)—S(6′)	91.3(2)
S(1)—Ni(1)—S(2)	88.7(2)	S(5)—Ni(2)—S(6)	88.7(2)
S(2)—Ni(1)—S(2′)	180.00	S(6)—Ni(2)—S(6′)	180.00
S(2)—Ni(1)—S(1′)	91.3(2)	S(6)—Ni(2)—S(5′)	91.3(2)
C(1)—S(1)—Ni(1)	105.3(6)	C(6)—S(5)—Ni(2)	105.1(7)
C(2)—S(2)—Ni(1)	103.0(5)	C(7)—S(6)—Ni(2)	104.8(6)
S(1)—C(1)—C(2)	119(1)	S(5)—C(6)—C(7)	119(2)
S(2)—C(2)—C(1)	121(1)	S(6)—C(7)—C(6)	120(1)
S(1)—C(1)—S(3)	116.3(9)	S(5)—C(6)—S(7)	115(1)
S(2)—C(2)—S(4)	111.8(9)	S(6)—C(7)—S(8)	113(1)
C(1)—C(2)—S(4)	127(1)	C(6)—C(7)—S(8)	127(2)
C(2)—C(1)—S(3)	125(1)	C(7)—C(6)—S(7)	126(2)
C(1)—S(3)—C(3)	101(1)	C(6)—S(7)—C(8)	105(1)
C(2)—S(4)—C(4)	103(1)	C(7)—S(8)—C(9)	105(1)
C(3)—C(4)—S(4)	129(3)	C(8)—C(9)—S(8)	121(3)
C(4)—C(3)—S(3)	126(3)	C(9)—C(8)—S(7)	120(3)
C(5)—C(3)—C(4)	106(5)	C(10)—C(8)—C(9)	97(3)
C(5)—C(3)—S(3)	128(4)	C(10)—C(8)—S(7)	107(2)
C(11)—N—C(21)	113(1)	C(21)—N—C(31)	109(1)
C(11)—N—C(31)	109(2)	C(21)—N—C(41)	107(1)
C(11)—N—C(41)	110(1)	C(31)—N—C(41)	108(1)

steric interaction in the crystal lattice. The lengths of the C—C single bonds in the external unit [—CH(Me)CH$_2$—] are highly uncharacteristic, which is possibly caused by disorder and/or thermal motion, evidenced in the large isotropic thermal factors.

Figure 3 illustrates how the anions and cations are packed in the unit cell. As expected from the larger size of the substituted methyl group, the unit cell volume of [Bu$_4$N][Ni(MEDT)$_2$] is somewhat larger (78 Å^3) than that of [Bu$_4$N][Ni(DDDT)$_2$]. For clarity, the stereo diagram of Fig. 4 exhibits the stacking of anions with the cations removed. Unlike the case of [Bu$_4$N][Ni(DDDT)$_2$], where only one kind of anion forms stacks or [Bu$_4$N][Ni(PDDT)$_2$], where both stacks, and layers appear,[24] two kinds of anions form segregated stacks aligned along the *b*- or *c*-axis, but no layer is formed in the [Bu$_4$N][Ni(MEDT)$_2$] crystal. The anion A lies almost perpendicular to the anion B, with a dihedral angle between the least-squares planes of 83.71°.

The intermolecular atom–atom contact is a key parameter in the crystallographic analysis of a molecular conductor. In the crystal of [Bu$_4$N][Ni(MEDT)$_2$], the nearest Ni—Ni distance is 9.405 Å, the length of the *a*-axis. The nearest S—S contact is 5.104 Å between S(4) and S(7), while the corresponding value in [Bu$_4$N][Ni(DDDT)$_2$] is 4.75 Å. Finally, the electrical conductivities of [Bu$_4$N][Ni(MEDT)$_2$] and [Bu$_4$N][Ni(PHDT)$_2$] at room temperature are 2.62×10^{-8} and 1.36×10^{-8} S cm^{-1}, respectively. These values are consistent with the fact that there are no S—S contacts less than 3.70 Å in their crystals.

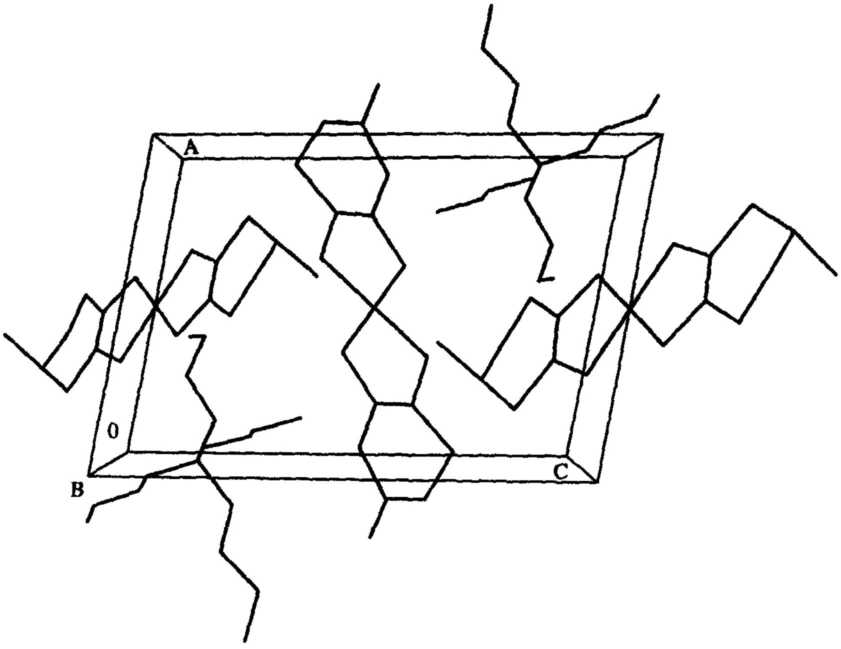
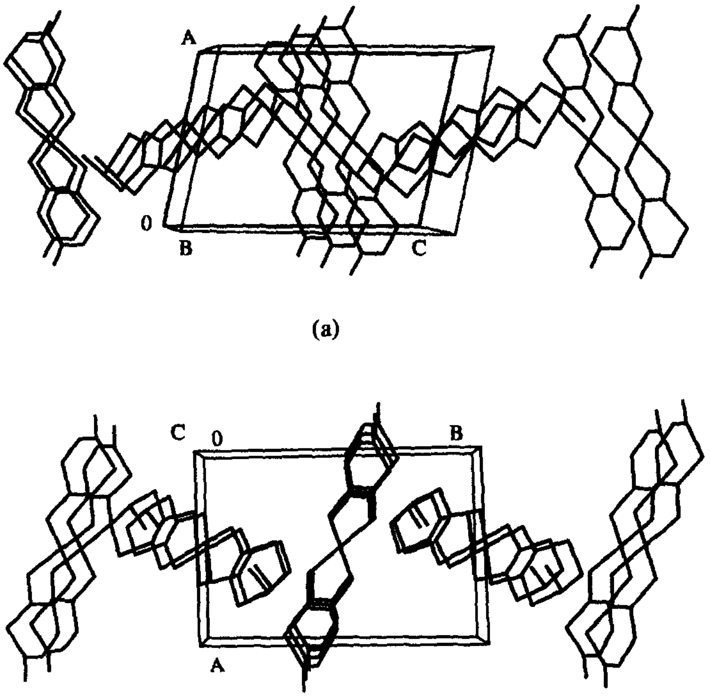


Fig. 3. Stereoview of crystal unit cell of [Bu$_4$N][Ni(MEDT)$_2$].



(a)

(b)

Fig. 4. Stereoview of anion packing in the [Bu$_4$N][Ni(MEDT)$_2$] crystal.

Acknowledgements—This work was supported by a grant for the Key Research Project from the State Science and Technology Commission of China and the National Nature Science Foundation of China.

REFERENCES

1. L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito and A. J. Heeger, *Solid State Commun.* 1973, **12**, 1125.
2. J. Ferraris, D. O. Cowan, V. V. Walatka Jr. and J. H. Perlstein, *J. Am. Chem. Soc.* 1973, **95**, 948.
3. J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. L. Pyrka, D. M. Watkin, M. Kommers, S. J. Boryschuk, A. V. Streiby Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung and M. H. Whangbo, *Inorg. Chem.* 1990, **29**, 3272.
4. P. Cassoux and L. Valade, *Inorganic Materials.* Wiley, New York, (1991).
5. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M. H. Whangbo, *Organic Superconductors.* Prentice-Hall, Englewood Cliffs, NJ (1992).
6. M. Bousseau, L. Valade, J. P. Legros, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Am. Chem. Soc.* 1986, **108**, 1908.
7. P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.* 1991, **110**, 115.
8. C. T. Vance, R. D. Bereman, J. Bordner, W. E. Hatfield and J. H. Helms, *Inorg. Chem.* 1985, **24**, 2905.
9. C. T. Vance, J. H. Welch and R. D. Bereman, *Inorg. Chim. Acta* 1989, **164**, 191.
10. J. H. Welch, R. D. Bereman and P. Singh, *Inorg. Chem.* 1988, **27**, 2862.
11. A. J. Schultz, H. H. Wang, L. C. Soderholm, T. J. Stifter, J. M. Williams, K. Bechgaard and M. H. Whangbo, *Inorg. Chem.* 1987, **26**, 3757.
12. J. H. Welch, R. D. Bereman and P. Singh, *Inorg. Chim. Acta* 1989, **162**, 89.
13. R. Kato, H. Kobayashi, A. Kobayashi and Y. Sasaka, *Bull. Chem. Soc. Japan* 1986, **59**, 627.
14. R. D. Bereman and H. Lu, *Inorg. Chim. Acta* 1993, **204**, 53.
15. T. M. Yao, X. Z. You, C. Li, L. F. Li and Q. C. Yang, *Acta Cryst.* 1994, **C50**, 67.
16. Q. Fang, C. Li, Z. Qu and X. Z. You, *Acta Chim. Sinica* 1992, **50**, 365.
17. S. Larsen, T. Thorsteinsson, S. Bowadt, T. K. Hansen, K. S. Varma, J. Becher and A. E. Underhill, *Acta Chem. Scand.* 1991, 709.
18. *International Tables for X-ray Crystallography*, Vol. IV. Kynoch Press, Birmingham.
19. J. A. McCleverty, *Prog. Inorg. Chem.* 1968, **10**, 97.
20. G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.* 1965, **87**, 3585.
21. X. Z. You, *Structure and Properties of Coordination Compounds*, p. 315. Science Press, Beijing (1992).
22. C. T. Vance and R. D. Bereman, *Inorg. Chim. Acta* 1988, **149**, 229.
23. R. Kirmse, J. Stach, W. Dietsch, G. Steimecke and E. Hoyer, *Inorg. Chem.* 1980, **19**, 2679.
24. T. M. Yao, X. Z. You and Q. C. Yang, *Chin. J. Chem.* 1994, **12**, 248.