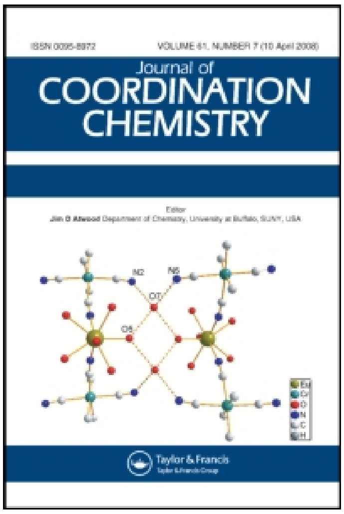

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE SYNTHESIS AND CHARACTERIZATION OF NEW NEUTRAL METAL COMPLEXES CONTAINING THE TETRATHIOETHYLENE UNIT

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To cite this Article Proctor, Kimberly A. , Boyle, Paul D. and Bereman, Robert D.(1996) 'THE SYNTHESIS AND CHARACTERIZATION OF NEW NEUTRAL METAL COMPLEXES CONTAINING THE TETRATHIOETHYLENE UNIT', Journal of Coordination Chemistry, 39: 1, 43 — 58

To link to this Article: DOI: 10.1080/00958979608028174

URL: http://dx.doi.org/10.1080/00958979608028174

J. Coord. Chem., 1996, Vol. 39, pp. 43–58
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THE SYNTHESIS AND CHARACTERIZATION OF NEW NEUTRAL METAL COMPLEXES CONTAINING THE TETRATHIOETHYLENE UNIT

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S-alkylated derivatives of $[Ni(DDDT)_2]^{2-}$ ($DDDT_2^{2-}$ = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) and $[Ni(PDDT)_2]^{2-}$ ($PDDT_2^{2-}$ = 1,3-propanediyldithioethylene-1,2-dithiolate) were synthesized and characterized. The syntheses were carried out by alkylation (CH_3I) of the dianions under inert atmospheric conditions. Crystals of $[Ni(CH_3\text{-}S_4C_4H_4)_2]$ were grown at 25°C from saturated CH_2Cl_2. The structure was determined by X-ray crystallography. The crystals were monoclinic, space group $P2_1/c$, a = 7.1860(20) Å, b = 10.3930(9)Å, c = 11.831(6)Å, β = 107.12(4)°, V = 844.4(5) $Å^3$, and Z = 2. Variable temperature ^1H-NMR studies revealed evidence of dynamic behavior in solution. Cyclic voltammetry showed the presence of an electrochemically reversible (chemically irreversible) reduction product.

Keywords: thioether; tetrathioethylene; nickel(II)

INTRODUCTION

Studies of a wide range of organic metals and inorganic dithiolene complexes have demonstrated that the TTF "framework" can be a key prerequisite to highly conductive materials (Figure 1).[1] It is possible to synthesize ligand systems containing this fragment which possess a number of structural and electronic properties of organic sulfur-containing donor molecules. The combination of these new ligand systems and suitable metal ions may be used to form species with properties of poten-

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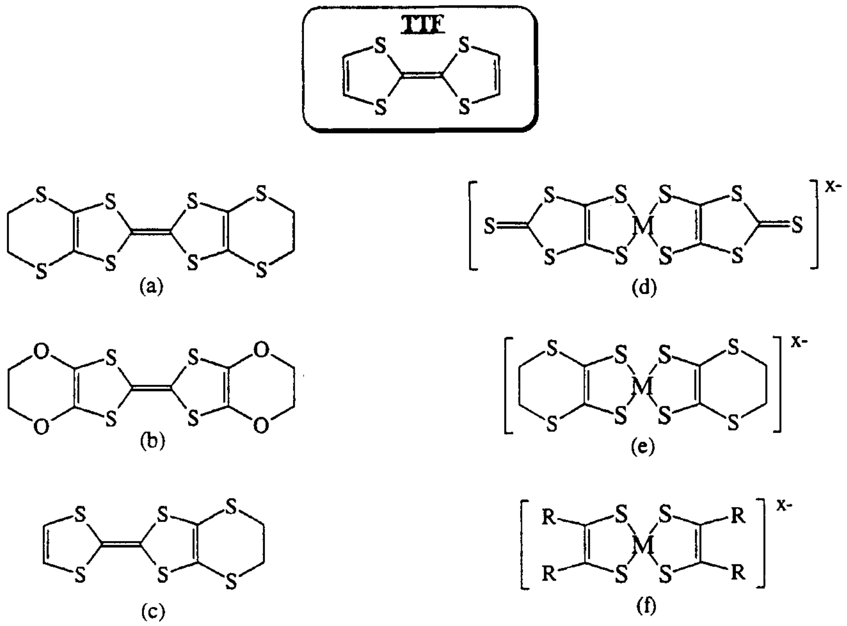


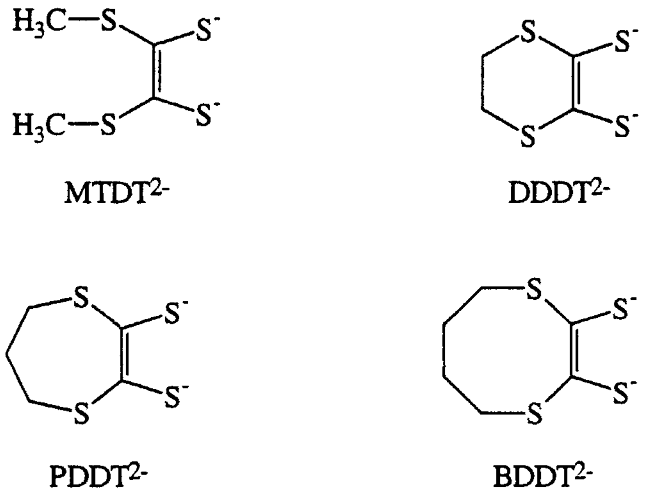
FIGURE 1 Organic conductors and ligand systems based on the modification of the TTF molecule: a) BEDT-TTF; b) BEDO-TTF; c) EDT-TTF; d) [M(dmit)$_2$]; e) [M(DDDT)$_2$; f) [M(bdt)$_2$]; R = CF_3 or CN.

tial molecular metals and even superconductors. This has encouraged a number of studies on fragments of TTF-type molecules as ligands in conjunction with transition metals in order to enhance the potential conducting properties.[2,3] $(H_3O)_{0.33}Li_{(0.82)}[Pt(S_2C_2(CN)_2] \cdot 1.67H_2O$ was the first transition metal complex of the metal bisdithiolenes series in which metal-like behavior was not related to the TTF-like donor molecule, but due to intermolecular interactions of the metal complex anions.[4]

Much work has focused on synthesis and characterization of metal complexes of dmit (dmit^{2-} = 1,3-dithiol-2-thione-4,5-dithiolate).[5,6] One breakthrough resulting from this work was the discovery of superconductivity in $[Me_4N][Ni(dmit)_2]_2$.[7] This metal complex demonstrates the ability of dithiolene complexes to form superconducting materials which are dependent solely upon the dithiolate complexes of the inorganic acceptor.

Efforts in a number of laboratories, including ours, have been made to study the relationships between structural and electronic properties of dithiolene ligands by synthesizing, characterizing and examining further modifications of these systems.[8] It is difficult to predict which structural changes to a ligand produce significant stereoelectronic differences in metal complexes. Following dmit and its derivatives, the most widely studied dithiolene for the preparation of synthetic metals has been DDDT (5,6-dihydro-1,4-dithiin-2,3-dithiolate) (Figure 2). This ligand is the structural inorganic analog to fragments of BEDT-TTF (Figure 1a). Detailed analyses of a number of metal complexes with this ligand, $[M(DDDT)_2]^{0,1-,2-}$ (M = Ni,[9–12] Pd,Pt,[13–15] Cu,[16] Au,[17] Co[18]), have been reported. Additional examples with modifications to the ethylene unit yielding inorganic analogs to the BEDT-TTF for which metal complexes were synthesized and characterized include 1,2-bis(methylthio) 1,2-dithiolate (MTNT), 1,3-propanediyldithioethylene-1,2-dithiolate (PDDT) and 1,4-butanediyldithioethylene-1,2-dithiolate (BDDT).[19–23]

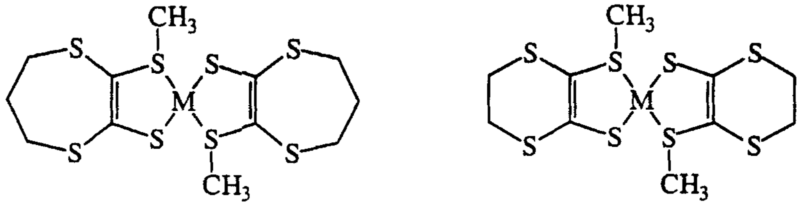
Most metal complexes of these ligands have been isolated as alkyl ammonium salts. As in the case of complexes of $M(dmit)_2^{n-}$, crystal structures revealed that bulky cations are often positioned between stacks of the anions resulting in large S···S contacts. This problem could be addressed by synthesis and characterization of neutral complexes; surprisingly, little attention has been given to this area. Examples of such attempts have included complexes such as: $[Ni(dmit)_2]$, $[Au(DDDT)_2]$, $[Ni(DDDT)_2]$, and $[Ni(PDDT)_2]$.[24–26]



$MTDT^{2-}$ $DDDT^{2-}$

$PDDT^{2-}$ $BDDT^{2-}$

FIGURE 2 Examples of "TTF-Type" 1,2-Dithiolene Ligands.



$[M(CH_3\text{-}PDDT)_2]^0$
M=Ni, Pd

$[M(CH_3\text{-}DDDT)_2]^0$
M=Ni

FIGURE 3 Representation of target alkylated derivatives of $[M(PDDT)_2]^{2-}$ and $[M(DDDT)_2]^{2-}$.

We have chosen an alternate approach to neutral "dithiolene-like" complexes. We report here attempts to synthesize neutral complexes of the existing ligand systems, DDDT and PDDT, by direct alkylation (Figure 3). Alkylation of bisdithiolene metal complexes has already received some attention for a variety of applications. Schrauzer reacted the dianion $[MS_4C_4Ph_4]^{2-}$ (M = Ni, Pd, Pt; Ph = C_6H_5) with a variety of alkylating agents, yielding a new class of neutral sulfur ligand complexes.[27] The dimethyl, dibenzyl, trimethylene, and tetramethylene bis-*cis*-stilbene-1,2-dithiolato transition metal complexes (M = Ni, Pd, Pt) have been given attention due to their interesting structural and dynamic properties.[27b–d] Variable temperature ^{1}H NMR studies suggest the presence of dynamic behavior in solution for the dimethyl, dibenzyl, and tetramethylene derivatives. These alkylated products can no longer be classified as 1,2-dithiolenes but do contain the tetrathioethylene unit.

EXPERIMENTAL

Materials

2,5,7,9-Tetrathiabicyclo[4,3,0]non-1(6)-en-8-one (TTBEO) and 2,6,8,10-tetrathiobicyclo[5,3,0]dec-1(7)-en-9-one (TTDEO) were prepared according to literature methods.[28] As an alternate and more facile method, TTBEO and TTDEO were also prepared according to Muller and Ueba (in the case of TTDEO, however, 1,3-dibromopropane was substituted for 1,2-dibromoethane).[29] In both cases, the products were characterized by NMR and elemental analysis. Potassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate (K_2DDDT) and potassium 1,3-propanediyldithioethylene-1,2-

dithiolate (K_2PDDT) were prepared by literature methods.[30] Nickel chloride hexahydrate was purchased from Fisher Scientific. 1,3,4,6-Tetrathiapentalene-2,5-dione, bis(benzonitrile)-palladium(II)chloride and iodomethane were purchased from Aldrich Chemical Company. Potassium metal was purchased from Janssen Chimica. All chemicals were used without further purification. Ar(g) and N_2(g) were obtained from Air Products Inc. All solvents were dried using standard techniques. Methanol used in the syntheses of the nickel complexes were dried over Na, distilled and degassed prior to use. THF was dried over Na/benzophenone and was distilled prior to use.

Procedures

All reactions were carried out under Ar(g) or N_2(g) using standard Schlenk techniques unless otherwise stated.

Syntheses

[Ni($CH_3C_5H_6S_4$)$_2$]. A solution of 0.44 g (2.2×10^{-3} moles) of $NiCl_2 \cdot 6H_2O$ in 50 mL of methanol was added dropwise to 1.0 g (3.7×10^{-3} moles) of K_2PDDT in 100 mL methanol. The solution color changed from amber to dark reddish-brown as the reaction proceeded. The solution was stirred for two h and then filtered using standard Schlenk techniques to remove any byproduct. Two equivalents of iodomethane were added dropwise to the filtrate and stirred for 10 min. A brown precipitate formed after 72 h and was collected using standard Schlenk techniques. The product was extracted with methylene chloride yielding 0.05 g (5.2%) pure product as a dark brown powder. mp = 213°C. ^{1}H NMR ($CDCl_3$) = 2.87 ppm (t, *CH_2*-S-CH_3), 2.68 ppm (t, S-*CH_2*), 2.63 (s, S-*CH_3*), 2.34 ppm (q, CH_2-*CH_2*-CH_2). *Anal.* Calcd. for $NiC_{12}H_{18}S_8$: C, 30.19; H, 3.80; S, 53.72. Found: C, 30.23; H, 3.78; S, 53.65.

[Ni($CH_3C_4H_4S_4$)$_2$]. A solution of 0.67g (2.9×10^{-3} moles) of $NiCl_2 \cdot 6H_2O$ in 50 mL of methanol was added dropwise to 1.0 g (3.9×10^{-3} moles) of K_2DDDT in 100 mL methanol. The solution color changed from amber to dark green as the reaction proceeded. The solution was stirred for two h and then filtered using standard Schlenk techniques to remove any byproduct. Two equivalents of iodomethane were added dropwise to the filtrate and stirred for 10 min. A brown precipitate formed after 72 h and was collected using standard Schlenk

techniques. The product was extracted with methylene chloride yielding 0.07 g (8%) pure product as a dark brown powder. The powder was recrystallized in methylene chloride and upon slow evaporation, afforded dark brown crystals. mp. = 166°C. ^{1}H NMR ($CDCl_3$) = 3.20 ppm (t, CH_2-$\mathit{CH_2}$-S-CH_3), 3.08 ppm (t, S-$\mathit{CH_2}$-CH_2), 2.61 ppm (s, S-$\mathit{CH_3}$). Mass spectral analysis and X-ray crystallographic analysis confirmed the product as pure $[Ni(CH_3C_4H_4S_4)_2]^0$. The product decomposes in aqueous solution: Me_2DDDT ($(CH_3)_2S_4C_4H_4$) as shown by ^{1}H NMR and mass spectral analysis.

Attempted synthesis of: $[Pd(CH_3C_5H_6S_4)_2]$. A solution of 0.80 g (2.1 × 10^{-3} moles) $(C_6H_5CN)_2PdCl_2$ in 50 mL THF was added dropwise to the suspension of 1.0 g (3.7 × 10^{-3} moles) of K_2PDDT in 100 mL THF. After 120 h the reaction was completed and the brown solution was filtered using Schlenk techniques to remove any byproducts. Two equivalents of iodomethane was added to the filtrate and the solution was stirred for 10 min. A white precipitate formed after 1 week. The product was filtered using standard Schlenk techniques. The filtrate was evaporated to dryness and separated on a silica column (the first band was kept) using a 50:50 mixture of chloroform:hexanes as elutant, yielding 0.07 g of pure product as a yellowish-red sticky solid. This resulting solid was identified as *cis*-1,2-di(methyl-1,3-propanediyldithioethylene)1,2-dithiolate = Me_2PDDT = $(CH_3S)_2C_5S_2H_6$ by mass spectral analysis. mp. = 72°C. ^{1}H NMR ($CDCl_3$) = 2.99 ppm (t, $\mathit{CH_2}$-S), 2.86 ppm (t, $\mathit{CH_2}$-S), 2.5 ppm (s, $\mathit{CH_3}$-S), 2.16 ppm (q, CH_2-$\mathit{CH_2}$-CH_2).

Physical Measurements

Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected. Room temperature nuclear magnetic resonance spectra were obtained with a Varian Gemini 300 spectrometer. Variable temperature nuclear magnetic resonance spectra were obtained with a G.E. GN 300 spectrometer. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Georgia. Mass spectroscopy results were obtained by FAB with a JEOL (Tokyo, Japan) HX110HF mass spectrometer. The ion source temperature was 51.8°C. The FAB$^+$ ion at 307.1810 m/z was used as a reference standard in a nitrobenzylalcohol matrix and was analyzed simultaneously with the samples. All electrochemical measurements were performed using a Bioanalytical Systems 100A electrochemical work station inside an inert atmosphere drybox. Solutions consisted of approximately 1 mM analyse in benzonitrile with 0.1 M tetrabutylammonium tetrafluoroborate. Ferrocene (0.5 mM) was added as an internal reference at the end of the experiment. The experimental setup consisted of a single-compartment cell with a Pt disc working electrode and a Pt wire counter electrode. A Ag wire immersed in a solution of 0.01 M $AgNO_3$ and 0.009 M tetrabutylammonium hexafluorophosphate (separated from the remainder of the cell by a ceramic tip) served as the reference electrode. The working electrode was polished using a 0.1 µm alumina slurry prior to each experiment. Benzonitrile (anhydrous) was obtained from Aldrich and used as received. Tetrabutylammonium tetrafluoroborate (Aldrich) was recrystallized three times from water/ethanol and dried in *vacuo* at 70°C. Ferrocene (Aldrich) was sublimed prior to use.

Crystallography

The crystal of neutral [$Ni(CH_3$-DDDT$)_2$] was found to belong to a primitive monoclinic space group. A full structural analysis was completed on a crystal grown from methylene chloride.

Precise cell dimensions were obtained from 54 reflections with 2θ angle in the range of 40°-50°. The intensity data were collected on a Rigaku AFC 6S diffractometer using the $\theta/2\theta$ scan mode. Systematic absences indicated that the crystal belonged to the monoclinic space group $P2_1/c$. During data reduction the intensities were corrected for Lorenz and polarization effects. Absorption effects were corrected empirically using ψ scan data. The intensities of standard reflections showed negligible variation throughout the scan data collection. The structure was solved using SIR92.[31] The structure was refined using full matrix least squares. All non hydrogen atoms were included in the refinement using anisotropic displacement parameters. The hydrogen atom positions and isotropic displacement parameters were also refined. The final difference map was essentially featureless; the highest peak was 0.49 $e^-/Å^3$ located 0.82 Å away from S4. Data reduction, refinement and graphics were done using the NRCVAX[32] suite of programs. Analysis of the intermolecular packing and packing diagrams were performed using PLUTON and PLATON[31b,d] Weights based on counting-statistics were used. Atomic scattering factors for all atoms were taken from the International Tables for X-ray Crystallography and included anomalous dispersion terms for all atom types.[30] Pertinent crystal, data collections, and refinement parameters are summarized in Table 1. A diagram of the

TABLE 1 X-Ray Crystallographic Parameters

Crystal Parameters	
Formula	$NiC_{10}H_{14}S_8$
Molecular weight, g/mol	449.41
Crystallization medium	methylene chloride
Crystal size, mm	0.45 × 0.45 × 0.40
Crystal color	dark brown
Crystal habit	plate
Cell dimensions	$a = 7.1860\ (20)$ $b = 10.3930(9)$ $c = 11.831(6)$ $\beta = 107.12(4)$
Volume, A^3	844.4(5)
Space group	$P2_1/c$
Molecules/unit cell	2
Density calcd., $Mg * m^{-3}$	1.767
F(000)	462.42
Data Collection Parameters	
Radiation	Mo Kα
Temperature	298K
2θ range	0°–50°
Scan type	θ–2θ
Data collected	h = −9 to 8 k = 0 to 13 l = 0 to 15
No. of reflections measured	2862
No. of unique reflections (R merge = 0.042)	1944
No. of reflections with Inet > 0.5 sigma (Inet)	1862
Refinement Parameters[a]	
Final R index	R = 0.027 $R_w = 0.037$
Goodness of fit	1.35

[a] *Data fit criteria*: $R = \Sigma(F_o - F_c)/\Sigma F_o$ $Rw = [\Sigma(wF_o - F_c)^2)/\Sigma(wF_o{}^2)]^{0.5}$
$GOF = [\Sigma(w(F_o - F_c)^2)/(\text{No. of reflns} - \text{No. of params.})]^{0.5}$

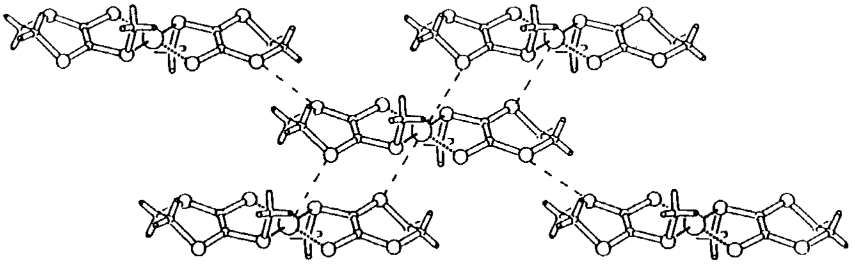


FIGURE 4 View along [001] of $[Ni(CH_3\text{-}DDDT)_2]$: Ni···S4 and S3···S3 interactions. (Hydrogen atoms have been removed for clarity).

entire molecule, S···S interactions, and Ni···S interactions are presented in Figure 4; a stick diagram of the unit cell is represented in Figure 5. Bond angles, bond distances and sulfur-sulfur distances are summarized in Tables 2–4.

TABLE 2 Bond Lengths, Å

Ni-S1	2.1750 (10)	S4-C4	1.8014 (22)
Ni-S1a	2.1750 (10)	C1-C2	1.340 (3)
Ni-S2	2.1793 (5)	C3-C4	1.502 (3)
Ni-S2a	2.1793 (5)	C3-H3a	0.933 (25)
S1-C1	1.7667 (18)	C3-H3b	0.89 (3)
S1-C5	1.812 (3)	C4-H4a	0.90 (3)
S2-C2	1.7526 (19)	C4-H4b	0.88 (3)
S3-C2	1.7522 (18)	C5-H5a	0.86 (5)
S3-C3	1.8089 (24)	C5-H5b	0.97 (4)
S4-C1	1.7552 (19)	C5-H5c	0.90 (4)

TABLE 3 Bond Angles (deg.)

S1-Ni-S1a	180.0	S4-C4-H4a	108.8 (16)
S1-Ni-S2	90.615 (20)	S4-C4-H4b	103.0 (17)
S1-Ni-S2a	89.385 (20)	C3-C4-H4a	108.9 (16)
S1a-Ni-S2	89.385 (20)	C3-C4-H4b	113.4 (17)
S1a-Ni-S2a	90.615 (20)	H4a-C4-H4b	110.1 (23)
S2-Ni-S2a	180.0	S1-C5-H5a	113 (3)
Ni-S1-C1	104.40 (6)	S1-C5-H5b	105.9 (20)
Ni-S-C5	104.73 (12)	S1-C5-H5c	111.7 (25)
C1-S1-C5	101.05 (13)	H5a-C5-H5b	113 (3)
Ni-S2-C2	102.86 (6)	H5a-C5-H5c	108 (4)
C2-S3-C3	105.37 (9)	H5b-C5-H5c	103 (3)
C1-S4-C4	99.26 (10)	C3-H3a-H3b	37.8 (14)
S1-C1-S4	114.41 (10)	C3-H3b-H3a	40.2 (14)
S1-C1-C2	117.71 (13)	C4-H4a-H4b	34.5 (15)
S4-C1-C2	127.85 (14)	C4-H4b-H4a	35.5 (15)
S2-C2-S3	111.44 (10)	C5-H5a-H5b	35.4 (22)
S2-C2-C1	122.15 (14)	C5-H5a-H5c	36.9 (24)
S3-C2-C1	126.39 (14)	H5b-H5a-H5c	59 (3)
S3-C3-C4	114.61 (15)	C5-H5b-H5a	30.9 (20)
S3-C3-H3a	111.6 (15)	C5-H5b-H5c	36.8 (20)
S3-C3-H3b	106.3 (17)	H5a-H5b-H5c	56 (3)
C4-C3-H3a	112.2 (15)	C5-H5c-H5a	34.8 (23)
C4-C3-H3b	109.1 (17)	C5-H5c-H5b	40.0 (21)
H3a-C3-H3b	102.0 (21)	H5a-H5c-H5b	63 (3)
S4-C4-C3	112.38 (15)		

TABLE 4 Sulfur-Sulfur Distances

Complex	S(I)···S(J)	Dist.,Å	Between/Thru Stack	Ref.
[Ni(CH_3-DDDT)$_2$]	S(1)···S(4)	3.584	between stack	
	S(3)···S(3)	3.449	between stack	
[Ni(DDDT)$_2$]	plane a	3.76	thru stack	20b
	plane b	3.74	thru stack	20b
[Me_4N] [Ni(DDDT)$_2$]	S(5)···S(7)	3.57	between stack	34
	S(5)···S(8)	3.70	between stack	34
	S(3)···S(6)	3.76	between stack	34
	S(2)···S(4)	3.78	between stack	34
	S(1)···S(7)	4.04	between stack	34
	S(2)···S(3)	4.22	between stack	34
	S(4)···S(6)	4.22	between stack	34
	S(1)···S(8)	4.49	between stack	34
[Et_4N] [Ni(DDDT)$_2$]	S(3)···S(3)	4.49	thru stack	9
	S(2)···S(3)	4.99	thru stack	9
	S(3)···S(4)	5.38	thru stack	9
	S(4)···S(3)	3.98	between stack	34
	S(3)···S(4)	3.98	between stack	34
	S(4)···S(4)	4.25	between stack	34
[Bu_4N] [Ni(DDDT)$_2$]	S(3)···S(4)	4.78	between stack	10,11,34
	S(7)···S(7)	3.43	between stack	10,11,34
	S(8)···S(1)	3.88	between stack	10,11,34
	S(8)···S(4)	4.33	between stack	10,11,34
	S(11)···S(14)	5.00	thru stack	12
	S(12)···S(13)	4.98	thru stack	12
	S(13)···S(14)	4.75	thru stack	12

DISCUSSION

X-ray Crystal Structure

The X-ray structural analysis of [Ni(CH_3-DDDT)$_2$] identifies the complex as having the preferred, stable *trans*-anti configuration in the solid state. The molecule sits on a crystallographic center of symmetry and is essentially square planar. The NiS_4 moiety has Ni-S bond lengths of 2.175 (10) and 2.179 (5) Å. The C-S(CH_3)(S1-C5) bond of 1.812 (3)Å is longer than the S1-C1 and S2-C2 bonds of 1.752(6) and 1.766(7) Å, all of which are clearly in the range of C-S single bonds. The C(1)-C(2) bond distance is 1.340(3) Å, which is typical of a C=C double bond. This is consistent with an electronically localized ground-state structure.

The bond lengths and angles of [Ni(CH_3-DDDT)$_2$][20b] are different from those of the previously published structures of [Ni(DDDT)$_2$] and [Ni(DDDT)$_2$]$^-$ (cation = [Bu_4N]$^+$ and [Et_4N]$^+$.[9–12] However, the neutral, alkylated derivative displays slight elongation of the Ni-S and S-C bonds. Elongation of these bonds is characteristic of non-oxidized d^8 bis-dithiolene metal complexes due to population of an antibonding orbital (HOMO). This differs greatly from simple bis-dithiolenes which are highly delocalized.[33] Accordingly, our observation agrees with Schrauzer's studies on bis(cis-(methylthio)stilbene-thiolato)nickel(II).[27b]

The crystal structure of [Ni(CH_3-DDDT)$_2$] reveals different stacking interactions than those published for the neutral and alkyl ammonium salts of Ni(DDDT)$_2$. For instance, the earlier published structures of [Ni(DDDT)$_2$]$^-$ (Et_4N^+ and Bu_4N^+ salts)[9–12] display two different types of stacking with the stacks aligning almost perpendicular to each other. No close S···S contacts indicative of π-stacking were observed in these complexes due to the presence of bulky cations between the stacks. In the case of [Me_4N][Ni(DDDT)$_2$],[34] anions form a zig-zag pattern down the **b** axis with overlap in the periphery of the ligand. The anions lie parallel to the one beneath them, and with the cations removed, appear to form stacks. The presence of cations between the anions within the stacks again prevents close S···S contacts among parallel anions. The shortest S···S contacts (8 contacts < 4.5Å) occur between anions in different

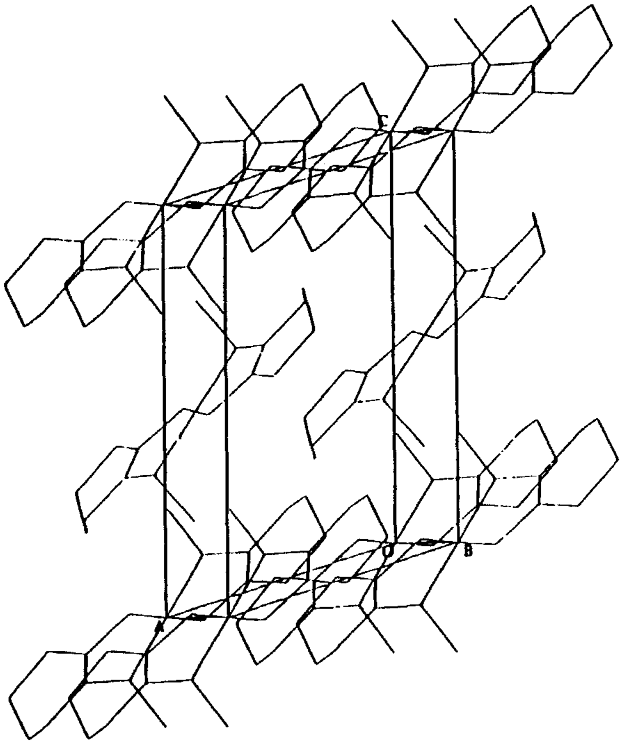


FIGURE 5 View of the molecular packing of [Ni(CH_3-DDDT)$_2$]. (Hydrogen atoms have been removed for clarity.)

TABLE 5 Cyclic Voltammetry Parameters for $[NiL_2]$[11] Complexes

		$E_{1/2}$,V	
	Compound	n: 0 ⇌ −1	n: −1 ⇌ −2
A	$[Ni(CH_3\text{-}DDDT)_2]^{0**}$	−1.18	
B	$[Ni(ETDT)_2]^0$	−0.47	−1.02
	$[Ni(PTDT)_2]^0$	−0.50	−1.07
	$[Ni(i\text{-}PTDT)_2]^0$	−0.37	−0.97
C	$[Ni(DDDT)_2]^-$	+0.01	−0.81
D	$[Ni(PDDT)_2]^-$	+0.30	−0.67

stacks. In contrast, the crystal structure of $[Ni(DDDT)_2]$ indicates two independent distances stacked along the **b** axis separately with interplanar distances of 3.76 Å and 3.74 Å; the Ni···Ni distance is given by the lattice constant of the **b** axis, 4.672.[20b] There are no short intermolecular S···S contacts within a stack (< 3.7 Å) nor between molecules of adjacent stacks.

The unit cell packing of the monoclinic form (Figure 5) reveals the association of this new neutral molecule which is quite different from previously observed packing motifs in the structures of $[Ni(DDDT)_2]$ and $[Ni(DDDT)_2]^-$ (Et_4N^+ and Bu_4N^+ salts). The stereoview of $[Ni(CH_3\text{-}DDDT)_2]$ indicates there is a primary stack that is aligned along the **a** axis which appears to form a step-like chain (or "slipped stack") with close Ni···S interactions (3.60 Å, considerably less than the sum of atomic radii, 4.10 Å).[35] There is also a chain with close S···S interactions (S3···S3′ = 3.45 Å) along the [110] direction. These S···S interactions, however, appear to be secondary, edge to edge interactions which are not beneficial to π-stacking. The stacking orientation and close Ni···S and S···S interactions are best viewed in Figure 4. The Ni···Ni distance within the stack is given by the lattice constant of the a-axis, 7.186 Å, and between stacks as 9.413 Å. Although beneficial π-overlaps are not observed, the close Ni···S contacts may warrant further investigation.

Variable Temperature ^{1}H-NMR

The room temperature ^{1}H-NMR spectrum of $[Ni(CH_3\text{-}DDDT)_2]$ (recrystallized from CH_2Cl_2) in $CDCl_3$ suggests the presence of at least two isomers. This is indicated by the appearance of two singlets in the methyl region (major: 2.61 ppm and minor: 2.42 ppm) and four triplets in the ethylene region (the peak at 2.42 ppm appeared after one hour in solution). Variable temperature ^{1}H NMR spectra of the methyl region, after heating to 45°C show broadening of the major signal and the development of a shoulder upon cooling to 0°C. This signal splits into two resonance (2.65 and 2.537 ppm) as the sample is cooled further. The original minor signal at 2.42 ppm is still present. The relative intensities of these peaks at -60°C are 1:1:1.

Based on the solid state results, we suggest the original peak at 2.61 ppm represents the complex in the trans-anti configuration. Upon cooling, there is evidence of an equilibrium between two possible isomers: *trans*-anti and the *trans*-syn. The *trans*-anti isomer interconverts to the *trans*-syn *via* sulfur inversion. The methyl peak at 2.42 ppm is attributed to formation of a new nickel complex where the metal is coordinated to one dithiolate ligand *and* one dithioether ligand (methyl groups coordinated to the same ligand). The signal at 2.42 ppm grows over time, demonstrating an eventual total conversion to this new compound, or even to the decomposition of this new product, in solution.

These results differ somewhat from Schrauzer's observations on bis-(*cis*-(methylthio)stilbenethiolato)nickel(II).[27b] For this complex, only a single methyl peak at 2.38 ppm was observed at room temperature; upon cooling, the peak split into three signals in a ratio of 7:1:11. Schrauzer attributed this to the presence of a dynamic equilibria between three isomers: *trans*-anti, *trans*-syn and the *cis*-anti. The two major signals have been attributed to the *tans*-anti and *trans*-syn isomers and are interconvertable by sulfur inversion. The third, minor signal is assigned to the *cis*-anti isomer which is generated by "backbone isomerization" or sulfur inversion followed by a ring flip.

Electrochemistry

Electrochemical studies of $[Ni(CH_3\text{-}DDDT)_2]$ were carried out to determine the ease and reversibility of oxidation and reduction of this compound. As anticipated, the cyclic voltammetric experiments carried out on the new, alkylated derivative of $[Ni(DDDT)_2]^{2-}$, $[Ni(CH_3\text{-}DDDT)_2]$ yielded very different redox characteristics from those of previously studied transition metal 1,2-dithiolenes. These differences provide experimental support that the electronic structures of these new neutral complexes (the alkylated derivatives) are quite distinct from those of 1,2-dithiolenes.

The cyclic voltammogram of $[Ni(CH_3\text{-}DDDT)_2]$ (100 mV/s scan) shows one electrochemically reversible reduction wave:

$$[Ni(CH_3\text{-}DDDT)_2] + e^- \rightarrow [Ni(CH_3\text{-}DDDT)_2]^- \quad E_{1/2} = -1.186\ V;$$
$$(E_{pa}-E_{pc})/n = 0.68\ V.$$

The cyclic voltammogram shows an apparently reversible electron transfer reaction coupled to a subsequent chemical reaction (possibly an EC mechanism). As the scan rate is decreased (1000 mV/s, 100 mV/s, 20 mV/s, 2 mV/s), the current of the anionic peak decreased significantly.

Table 5 compares the potentials required for reduction of this neutral complex to other neutral and anionic 1,2-dithiolenes.[14c, 23, 38] Inspection of these values shows that the metal complex of the alkylated derivative of 1,2-dithiolene $DDDT^{2-}$ does not undergo reduction as easily as the monoanionic and neutral bis dithiolene complexes. This could be due to electron localization within the MS_4 moiety created by alkylation of the bisdithiolene system.

Supplemental Material

Atomic coordinates, anisotropic displacement parameters, and structure factors (observed and calculated), are available upon request.

Acknowledgements

We wish to express sincerest gratitude to Dr. Sabapathy Sankar for his assistance in carrying out the variable temperature ^{1}H-NMR experiments. We also would like to express our appreciation to Dr. Ed Bowden and Dr. Brian Knight for helpful discussions concerning the electrochemical results.

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