Synthesis and characterization of the nickel and copper complexes of the new dithiolene, 1,3-propanediyldithioethylene-1,2-dithiolate (PDDT)

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(Received January 17, 1992; revised September 11, 1992)

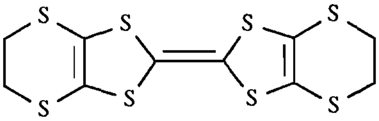
Abstract

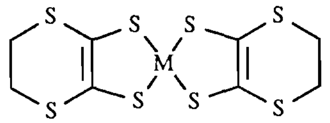
Nickel and copper complexes in the formal oxidation state three of the new 1,2-dithiolene ligand, 1,3-propanediyldithioethylene-1,2-dithiolate, were prepared and characterized. Electrochemical, ESR and IR characterizations indicate that the electronic structures are different for the 1,2-ethane analog. X-ray structures for the tetraethylammonium salts of both complexes were obtained. Both belong to the monoclinic space group $P2_1/c$. Each complex is planar through the tetrathioethylene portion of each ligand with the propane moiety forming a chair configuration. Packing diagrams reveal an unusual double layer array. Details of the molecular structures and packing are discussed.

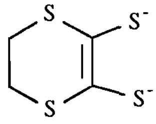
Introduction

Since the discovery of metal-like conductivity in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) was reported in the early 1970s [1, 2], a rather massive research effort has centered on the design and synthesis of organic superconductors. The first actual observation of an *organic* superconducting material was reported in 1979 as bis(tetramethyltetraselenafulvalenium) hexafluorophosphate, $(TMTSF)_2PF_6$ [3]. Other TMTSF salts $(TMTSF)_2X$ ($X=TaF_6^-$, SbF_6^-, AsF_6^-, ReO_4^-, FSO_6^-, CiO_4^-) were later shown to have similar properties [4]. $(BEDT\text{-}TTF)_2ReO_4$ (bis(ethylenedithio)-tetrathiafulvaleneperrhenate) was later found to be a superconductor at 1.5 K and 7 Kbar [5] and represented the first example of a sulfur based organic superconductor. Very recently, it has been shown that an analogue containing oxygen, $(BEDO\text{-}TTF)_3Cu_2(SCN)_3$, behaves as a superconductor at 1.06 K and at ambient pressure (where (BEDO-TTF) is bis(ethylenedioxy)-tetrathiafulvalene) [6].

As suggested by Wudl [7] very early and later by others, the 'TTF' framework possesses the prerequisite properties necessary to yield an 'organic metal'. Due to the apparent importance of the tetrathioethylene unit in the TTF series of superconductors, the design of inorganic complexes of ligands containing this subunit has been of interest in our laboratories. An example of the attractiveness of this area is $M(DDDT)_2^-$ ($DDDT^{2-}$ is the dianion 5,6-dihydro-1,4-dithiin-2,3-dithiolate [8]) which represents an 'inorganic analogue' of the 'organic salt BEDT-TTF'. Detailed studies of this ligand complexed with Ni [8–10], Pd [11], Pt [11, 12], Cu [13] and Co [14] with the general formula $M(DDDT)_2^-$ have been reported.


BEDT-TTF


$M(DDDT)_2^-$


$DDDT^{2-}$

A number of similarities exist between some $M(DDDT)_2^-$ salts and BEDT-TTF [8, 13]. This is particularly true in the nickel complex. Both molecules are planar and are approximately the same size. Both molecules have a two dimensional layered type structure with close sulfur··· sulfur contacts. In addition, BEDT-TTF exists as a partially oxidized radical cation while $Ni(DDDT)_2^-$ is a full oxidized radical anion [8]. We have also studied the 1,2-dithioethylene ligand, 1,2-

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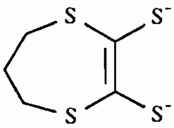
0020-1693/93/$6.00

bis(methylthio)-1,2-dithiolene, which contains the tetrathioethylene unit [11].

We report here the study of a new dianion, 1,3-propanediyldithioethylene-1,2-dithiolate, $PDDT^{2-}$, which represents a new dithiolene ligand also containing the tetrathioethylene subunit. (During the preparation of this manuscript, Williams and co-workers [15] reported the structure of the neutral nickel complex of this ligand.) This report also discusses the syntheses of the formally Ni(III) and Cu(III) complexes and their molecular structures. The apparent minor modification in ligand design when compared to $DDDT^{2-}$ was prompted by several factors. The properties of tetramethyltetrathiafulvalene are quite different from those of tetrathiafulvalene. Second, Whangbo and co-workers [16] recently reported a study on BPDT-TTF (bis(1,3-propanediyldithio)tetrathiofulvalene), first synthesized by Mizuno *et al.* in 1978 [17]. Finally, BPDT-TTF has been shown to form charge-transfer salts with InI_4^- [16], I_3^- [18], PF_6^- [19] and ICl_2^- [20].



$PDDT^{2-}$

Experimental

Reagents

2,6,8,10-Tetrathiobicyclo[5,3,0]dec-1(7)-en-9-one (TTDEO) was prepared by a literature method [21] and characterized by NMR, IR and element analysis. Interestingly, the melting point (m.p. 86 °C) was not the same as reported (m.p. 130 °C). Nickel chloride hexahydrate was purchased from Matheson, Coleman and Bell, Inc. Cupric chloride dihydrate was purchased from J. T. Baker Chemical Co. Tetraethylammonium bromide and potassium metal were obtained from Aldrich Chemical Company, Inc. Argon was purchased from Air Products, Inc. All chemicals were used without further purification. All solvents were dried by standard techniques. The solvent THF was dried over molecule sieves and freshly distilled from Na/benzophenone prior to use. Methanol, ethanol and water used in the synthesis of the complexes were degassed with argon for 45 min prior to use.

Procedure

All reactions were carried out under argon using standard Schlenk techniques. Element analyses were performed by Atlantic Microlabs, Atlanta, GA.

Syntheses

$K_2(C_5H_6S_4)$: potassium 1,3-propanediyldithioethylene-1,2-dithiolate (K_2(PDDT))

Potassium ethoxide was prepared by adding 3.6 g (9×10^{-2} mol) of sliced potassium metal to 10 ml (excess) of absolute ethanol under argon. Then approximately 200 ml of freshly distilled THF were added to this solution, followed by the addition of 5 g (2.2×10^{-2} mol) TTDEO. A light-cream colored precipitate formed after a few minutes. The mixture was stirred for about 15 h, then the precipitate was filtered, washed with ethyl ether, dried and stored in a Schlenk tube for further use. An elemental analysis of K_2(PDDT) was not obtained because of the extreme air sensitivity of the material. Yield 5.3 g (88%). ^1H NMR (d_6-DMSO): δ 1.0 (quintet) $-CH_2-$, 3.6 (triplet) $-SCH_2-$.

$[(C_2H_5)_4N][Ni(C_5H_6S_4)_2]$

A solution of 0.44 g (1.9×10^{-3} mol) of $NiCl_2\cdot6H_2O$ in 50 ml CH_3OH was added dropwise to 1.0 g (3.7×10^{-3} mol) of K_2PDDT in 100 ml CH_3OH. The color changed from amber to dark brown as the reaction proceeded. The solution was stirred for 1 h and then filtered to remove any byproduct. One equivalent of tetraethylammonium bromide was added; a brown precipitate formed which was collected by filtering. Single crystals were obtained by careful recrystallization from dry acetonitrile. Yield 0.45 g (38%). m.p. 202 °C. IR (KBr pellet): 2970(m), 2930(m), 2875(m), 1475(s), 1415(m), 1390(s), 1380(vs), 1270(s), 1170(s), 1000(s), 895(m), 875(w), 860(s), 775(m), 620(2), 455(m), 385(m) cm^{-1}. *Anal.* Calc. for $NiC_{18}H_{32}S_8N$: C, 37.43; H, 5.58; S, 44.30; N, 2.42. Found: C, 37.50; H, 5.58; S, 44.33; N, 2.42%.

$[(C_2H_5)_4N][Cu(PDDT)_2]$

A solution of 0.26 g (1.5×10^{-3}mol) of $CuCl_2\cdot2H_2O$ in 25 ml of H_2O was added dropwise to 0.7 g (2.6×10^{-3} mol) of K_2PDDT in 50 ml of 1:1 ethanol/water solution basic with KOH. The color changed from amber to purple immediately. The solution was stirred for 1 h and then filtered to remove the solid byproduct. A solution of 0.3 g (excess) of tetraethylammonium bromide in water was added and a dark purple precipitate formed. The solid was collected by filtering. The yield was 0.36 g (25%) of dark purple powder. A single crystal was obtained by recrystallization from acetonitrile/isopropanol. m.p. 176–177 °C. IR (KBr pellet): 2960(m), 2935(m), 2880(m), 1475(s), 1410(m), 1385(s), 1270(s), 1170(s), 1000(s), 895(m), 880(s), 860(m), 775(m), 620(2), 425(m), 370(m) cm^{-1}. ^{13}C NMR (d_6-DMSO): δ 7.16; 33.30, 36.43, 51.44, 132.88. *Anal.* Calc. for $CuC_{18}H_{32}S_8N$: C, 37.11; H, 5.54; S, 44.04; N, 2.40. Found: C, 36.89; H, 5.47; S, 44.21; N, 2.34%.

Physical measurements

IR spectra were recorded on a Perkin-Elmer 521 spectrometer over the range 4000–300 cm^{-1}. ESR spectra were recorded on a Varian E-3 spectrometer at 132 K in a DMF glass. ^{1}H NMR spectrum was obtained on a GE 300 MHz Omega FT-NMR spectrometer using TMS as an internal standard.

Electrochemical data were obtained with the use of a BAS CV-27 potentiostat. A platinum wire was used for both the working and auxiliary electrode and an Ag/AgCl electrode was used as the reference electrode. The solution contained 0.1 M tetraethylammonium perchlorate as the supporting electrolyte in DMF with the metal complex concentration of 10^{-3} M. ^{13}C NMR spectra were obtained on a GE 300 MHz Omega FT-NMR spectrometer.

Single-crystal X-ray analysis

Unit cell dimensions were determined by rotation photographs and obtained from 15 reflections (2θ range 9.7–23°). A data set was collected on a Nicolet R3m/μ diffractometer equipped with a graphite monochromator and using molybdenum radiation ($\lambda = 0.71069$ Å). All diffractometer data were collected at room temperature. No corrections for absorption were applied due to the small absorption coefficients.

$[(C_2H_5)_4N][Ni(C_5H_6S_4)_2]$

A representative crystal grown from anhydrous acetonitrile was surveyed. Systematic absences indicated that the crystal belongs to the monoclinic space group $P2_1/c$ ($h0l$, $l = 2n+1$; $0k0$, $k = 2n+1$). Two standard reflections collected after every 48 reflections revealed no unexpected variation in intensity. Atomic scattering factors for all atoms were taken from the International Tables for X-ray Crystallography [22]. Relevant crystallographic information is given in Table 1.

TABLE 1. X-ray crystallographic parameters of $[(C_2H_5)_4N][M(PDDT)_2]$

Crystal parameters		
Formula	$NiC_{18}H_{32}S_8N$	$CuC_{18}H_{32}S_8N$
Molecular weight	577.68	582.51
Crystal size (mm)	$0.8 \times 0.5 \times 0.4$	$0.6 \times 0.4 \times 0.3$
Crystal color	brown	purple
Crystal habit	rhombic prism	rhombic prism
Cell dimensions		
a (Å)	18.956(7)	19.001(7)
b (Å)	7.437(2)	7.424(2)
c (Å)	20.715(11)	20.794(9)
β (°)	116.68(3)	116.48(3)
Volume (Å^3)	2609.5(18)	2625.3(17)
Space group	$P2_1/c$	$P2_1/c$
Molecules/unit cell	4	4
Density (calc.) (g/cm^3)	1.47	1.47
$F(000)$	1212	1216
Data collection parameters		
Radiation (Mo Kα), λ (Å)	0.71069	0.71069
Temperature	ambient	ambient
2θ range (°)	3–55	3–40
Scan type	θ–2θ	θ–2θ
No. reflections	5732	6716
No. reflections used ($I > 3\sigma(I)$)	4085	3870
Linear absorption coefficient (cm^{-1})	13.70	14.53
Refinement parameters		
Final R index		
R[a]	0.0285	0.0340
R_w[b]	0.0377	0.0407
Goodness of fit[c]	1.343	1.106
Largest Δ/σ	0.065	0.081
Data/parameter ratio	15.2	10.1

[a] $R = \Sigma \| F_o| - |F_c \| / \Sigma F_o$. [b] $R_w = [\Sigma w(\Delta F)^2 / \Sigma F_o^2]^{1/2}$. [c] $GOF = [\Sigma w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$.

The nickel and sulfur atoms were located by the direct method program SOLV of the crystallographic program package SHELXTL [23]. The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. This trial structure was refined by the block-diagonal least-squares technique using SHELXTL on a Data General Microeclipse computer. The quantity to be minimized was $\Sigma w(\Delta F)^2$, where w is the weight to be assigned to an observation $w = 1/(\sigma^2(F) + 0.00033F^2)$. Non-hydrogen atoms were refined with anisotropic temperature factors. Refinement with the hydrogen atoms which were placed at calculated positions 0.96 Å away from the attached carbon atom gave a final R value of 0.0285. A final difference Fourier map revealed no missing or misplaced electron density. The thermal ellipsoid drawing of the molecule was plotted using the SHELXTL graphics package. The stereoview of the cell packing was plotted using the program ORTEP [24]. Bond lengths and bond angles are given in Tables 2 and 3, respectively. See also 'Supplementary material'.

$[(C_2H_5)_4N][Cu(C_5H_6S_4)_2]$

A purple crystal was grown by vapor diffusion from acetonitrile/isopropanol. Systematic absences indicated that the crystal belongs to the monoclinic space group $P2_1/c$ ($h0l$, $l = 2n+1$; $0k0$, $k = 2n+1$). Two check reflections collected after every 48 reflections revealed no unexpected variation in intensity. Of the 6716 unique reflections recorded in the range $3 < 2\theta < 40°$, 3870 ($I > 3\sigma(I)$) were used in the structure analysis. Atomic scattering factors for all atoms were taken from the International Tables for X-Ray Crystallography [22]. Relevant crystal, data collection and refinement parameters are given in Table 1.

A trial structure with non-hydrogen atoms was obtained by the isomorphous replacement method using all atom coordinates of the $[(C_2H_5)_4N][Ni(PDDT)_2]$

TABLE 2. Bond lengths (Å) of $[(C_2H_5)_4N][Ni(PDDT)_2]$

Ni(1)–S(1a)	2.141(1)	Ni(2)–S(1b)	2.136(1)
Ni(1)–S(4a)	2.145(1)	Ni(2)–S(4b)	2.145(1)
Ni(1)–S(1a′)	2.141(1)	Ni(2)–S(1b′)	2.136(1)
Ni(1)–S(4a′)	2.145(1)	Ni(2)–S(4b′)	2.145(1)
S(1a)–C(1a)	1.728(2)	S(1b)–C(1b)	1.720(3)
S(2a)–C(1a)	1.761(2)	S(2b)–C(1b)	1.758(2)
S(2a)–C(5a)	1.807(3)	S(2b)–C(5b)	1.807(3)
S(3a)–C(2a)	1.759(2)	S(3b)–C(2b)	1.755(3)
S(3a)–C(3a)	1.810(3)	S(3b)–C(3b)	1.812(3)
S(4a)–C(2a)	1.729(2)	S(4b)–C(2b)	1.728(2)
C(1a)–C(2a)	1.351(3)	C(1b)–C(2b)	1.363(4)
C(3a)–C(4a)	1.512(4)	C(3b)–C(4b)	1.526(4)
C(4a)–C(5a)	1.511(4)	C(4b)–C(5b)	1.510(5)
N–C(6)	1.510(3)	C(6)–C(7)	1.517(5)
N–C(8)	1.513(4)	C(8)–C(9)	1.508(4)
N–C(10)	1.523(4)	C(10)–C(11)	1.486(4)
N–C(12)	1.511(3)	C(12)–C(13)	1.507(5)

TABLE 3. Bond angles (°) of $[(C_2H_5)_4][Ni(PDDT)_2]$

S(1a)–Ni(1)–S(4a)	91.5(1)	S(1b)–Ni(2)–S(4b)	91.3(1)
S(1a)–Ni(1)–S(1a′)	180.0(1)	S(1b)–Ni(2)–S(1b′)	180.0(1)
S(4a)–Ni(1)–S(1a′)	88.5(1)	S(4b)–Ni(2)–S(1b′)	88.7(1)
S(1a)–Ni(1)–S(4a′)	88.5(1)	S(1b)–Ni(2)–S(4b′)	88.7(1)
S(4a)–Ni(1)–S(4a′)	180.0(1)	S(4b)–Ni(2)–S(4b′)	180.0(1)
S(1a′)–Ni(1)–S(4a′)	91.5(1)	S(1b′)–Ni(2)–S(4b′)	91.3(1)
Ni(1)–S(1a)–C(1a)	104.5(1)	Ni(2)–S(1b)–C(1b)	104.9(1)
C(1a)–S(2a)–C(5a)	103.4(1)	C(1b)–S(2b)–C(5b)	102.9(1)
C(2a)–S(3a)–C(3a)	103.3(1)	C(2b)–S(3b)–C(3b)	103.3(2)
Ni(1)–S(4a)–C(2a)	104.0(1)	Ni(2)–S(4b)–C(2b)	104.8(1)
S(1a)–C(1a)–S(2a)	116.2(1)	S(1b)–C(1b)–S(2b)	116.0(2)
S(1a)–C(1a)–C(2a)	119.4(2)	S(1b)–C(1b)–C(2b)	119.9(2)
S(2a)–C(1a)–C(2a)	124.3(2)	S(2b)–C(1b)–C(2b)	124.1(2)
S(3a)–C(2a)–S(4a)	115.9(1)	S(3b)–C(2b)–S(4b)	116.4(2)
S(3a)–C(2a)–C(1a)	123.9(2)	S(3b)–C(2b)–C(1b)	124.5(2)
S(4a)–C(2a)–C(1a)	120.2(2)	S(4b)–C(2b)–C(1b)	119.1(2)
S(3a)–C(3a)–C(4a)	115.2(2)	S(3b)–C(3b)–C(4b)	116.5(2)
C(3a)–C(4a)–C(5a)	115.4(2)	C(3b)–C(4b)–C(5b)	116.0(2)
S(2a)–C(5a)–C(4a)	117.1(2)	S(2b)–C(5b)–C(4b)	116.1(2)
C(6)–N–C(8)	111.8(2)	C(6)–N–C(10)	105.6(2)
C(8)–N–C(10)	112.2(2)	C(6)–N–C(12)	111.6(2)
C(8)–N–C(12)	104.4(2)	C(10)–N–C(12)	111.4(2)
N–C(6)–C(7)	115.3(3)	N–C(8)–C(9)	115.0(3)
N–C(10)–C(11)	115.8(3)	N–C(12)–C(13)	116.0(3)

crystal except changing Ni to Cu. This trial structure was refined by SHELXTL on a Data General Microeclipse computer. The quantity minimized was $\Sigma w(\Delta F)^2$, where $w = 1/(\sigma^2(F) + 0.00055F^2)$ is the weight to be assigned to an observation. Non-hydrogen atoms were refined with anisotropic temperature factors. Refinement with the hydrogen atoms (most were placed by assigning the peaks near the carbon atoms and the rest at calculated positions 0.96 Å away from the attached carbon atoms) gave the final R value 0.0340. A final difference Fourier revealed no missing or misplaced electron density. The thermal ellipsoid drawing of the molecule was plotted using the SHELXTL graphics package. The stereo view of the cell packing was plotted by using the program ORTEP [24]. Bond lengths and bond angles are given in Tables 4 and 5, respectively. See also 'Supplementary material'.

Results and discussion

The synthesis of a new 1,2-dithiolene ligand which contains the tetrathioethylene unit, dipotassium 1,3-propanediyldithioethylene-1,2-dithiolate (K_2(PDDT)), has been achieved. This light-cream colored salt is extremely air sensitive and must be stored under an

TABLE 4. Bond lengths (Å) of $[(C_2H_5)_4N][Cu(PDDT)_2]$

Cu(a)–S(1a)	2.177(1)	Cu(b)–S(1b)	2.176(1)
Cu(a)–S(4a)	2.189(1)	Cu(b)–S(4b)	2.184(1)
Cu(a)–S(1a′)	2.177(1)	Cu(b)–S(1b′)	2.176(1)
Cu(a)–S(4a′)	2.189(1)	Cu(b)–S(4b′)	2.184(1)
S(1a)–C(1a)	1.750(3)	S(1b)–C(1b)	1.744(4)
S(2a)–C(1a)	1.761(3)	S(2b)–C(1b)	1.754(3)
S(2a)–C(5a)	1.820(4)	S(2b)–C(5b)	1.814(4)
S(3a)–C(2a)	1.750(3)	S(3b)–C(2b)	1.752(4)
S(3a)–C(3a)	1.813(4)	S(3b)–C(3b)	1.812(5)
S(4a)–C(2a)	1.750(3)	S(4b)–C(2b)	1.752(3)
C(1a)–C(2a)	1.336(4)	C(1b)–C(2b)	1.338(5)
C(3a)–C(4a)	1.499(5)	C(3b)–C(4b)	1.510(6)
C(4a)–C(5a)	1.500(5)	C(4b)–C(5b)	1.505(7)
N–C(6)	1.509(4)	C(6)–C(7)	1.523(8)
N–C(8)	1.522(5)	C(8)–C(9)	1.502(6)
N–C(10)	1.518(5)	C(10)–C(11)	1.495(5)
N–C(12)	1.509(4)	C(12)–C(13)	1.492(6)

TABLE 5. Bond angles (°) of $[(C_2H_5)_4N][Cu(PDDT)_2]$

S(1a)–Cu(a)–S(4a)	91.6(1)	S(1b)–Cu(b)–S(4b)	91.4(1)
S(1a)–Cu(a)–S(1a′)	180.0(1)	S(1b)–Cu(b)–S(1b′)	180.0(1)
S(4a)–Cu(a)–S(1a′)	88.4(1)	S(4b)–Cu(b)–S(1b′)	88.6(1)
S(1a)–Cu(a)–S(4a′)	88.4(1)	S(1b)–Cu(b)–S(4b′)	88.6(1)
S(4a)–Cu(a)–S(4a′)	180.0(1)	S(4b)–Cu(b)–S(4b′)	180.0(1)
S(1a′)–Cu(a)–S(4a′)	91.6(1)	S(1b′)–Cu(b)–S(4b′)	91.4(1)
Cu(a)–S(1a)–C(1a)	102.8(1)	Cu(b)–S(1b)–C(1b)	103.6(1)
C(1a)–S(2a)–C(5a)	102.7(1)	C(1b)–S(2b)–C(5b)	102.6(1)
C(2a)–S(3a)–C(3a)	102.7(2)	C(2b)–S(3b)–C(3b)	103.2(2)
Cu(a)–S(4a)–C(2a)	102.7(1)	Cu(b)–S(4b)–C(2b)	103.3(1)
S(1a)–C(1a)–S(2a)	114.9(2)	S(1b)–C(1b)–S(2b)	114.5(2)
S(1a)–C(1a)–C(2a)	121.2(2)	S(1b)–C(1b)–C(2b)	120.9(2)
S(2a)–C(1a)–C(2a)	123.9(2)	S(2b)–C(1b)–C(2b)	124.6(2)
S(3a)–C(2a)–S(4a)	114.7(2)	S(3b)–C(2b)–S(4b)	115.0(2)
S(3a)–C(2a)–C(1a)	124.8(2)	S(3b)–C(2b)–C(1b)	124.6(2)
S(4a)–C(2a)–C(1a)	120.5(2)	S(4b)–C(2b)–C(1b)	120.5(3)
S(3a)–C(3a)–C(4a)	115.3(2)	S(3b)–C(3b)–C(4b)	116.7(3)
C(3a)–C(4a)–C(5a)	115.9(3)	C(3b)–C(4b)–C(5b)	117.2(3)
S(2a)–C(5a)–C(4a)	116.7(3)	S(2b)–C(5b)–C(4b)	115.6(2)
C(6)–N–C(8)	111.3(3)	C(6)–N–C(10)	105.9(3)
C(8)–N–C(10)	111.7(3)	C(6)–N–C(12)	111.5(3)
C(8)–N–C(12)	105.7(3)	C(10)–N–C(12)	110.8(2)
N–C(6)–C(7)	115.7(4)	N–C(8)–C(9)	116.5(4)
N–C(10)–C(11)	116.5(4)	N–C(12)–C(13)	117.0(3)

argon atmosphere. The formally nickel(III) and copper(III) complexes of this ligand were synthesized by mixing metal(II) salts and the ligand.

The IR spectra of both complexes contain the characteristic absorptions of transition metal complexes of 1,2-dithiolenes [25]. Table 6 shows the IR data and absorption assignments for $Cu(PDDT)_2^-$. The IR spectrum of $Cu(PDDT)_2^-$ has all bands of $Ni(PDDT)_2^-$ but some bands show a modest frequency shift and slight intensity differences.

The DMF frozen glass ESR spectrum of the Ni(III) monoanion shows three peaks characteristic of $g_1 = 2.156$, $g_2 = 2.070$, $g_3 = 2.013$. This spectrum like that of $Ni(DDDT)_2^-$ and $Ni(MTDT)_2^-$ shows a rhombic g tensor. Table 7 lists the spin Hamiltonian parameters for the Ni(III) complexes of $PDDT^{2-}$, $DDDT^{2-}$, $MTDT^{2-}$ as well as $dmit^{2-}$ and MNT^{2-}.

A cyclic voltammogram of $Ni(PDDDT)_2^-$ reveals two well defined reversible waves. The first is at +0.30 V versus Ag/AgCl and represents the monoanion to neutral complex oxidation; the second, at −0.60 V, represents the monoanion to dianion reduction. The potentials indicate the ability of the ligand to accept or donate electron density as the charge on the complex changes. Table 8 contains the cyclic voltammetric data for the nickel dithiolenes which were listed in Table 7.

In order to make a comparison of the relative ability of this new ligand to accept or donate electron density, the voltammetric data of the nickel complexes can be utilized. We find the relative ability to accept electron density to be: $MNT^{2-} > PDDT^{2-} > MTDT^{2-} > DDDT^{2-}$. This trend follows the electron withdrawing ability of neutral dithiolene ligand complexes [30], i.e. the greater the electron attracting ability of the ligand, the more electron density the complex can accommodate and the higher the voltammetric value.

TABLE 6. Frequencies (cm^{-1}) and assignments of the bands observed in the IR spectra of the complexes $[(C_2H_5)_4N]$-$[Cu(PDDT)_2]$ and $[(C_2H_5)_4N][Ni(PDDT)_2]$

$[(C_2H_5)_4N][Cu(PDDT)_2]$	$[(C_2H_5)_4N][Ni(PDDT)_2]$	Assignments
1445 (m)	1445 (m)	C=C
1270 (m)	1270 (m)	C=S
880 (s)	875 (2)	S | R–C–C
860 (w)	860 (s)	
425 (2)	455 (m)	
370 (m)	385 (m)	M–S

TABLE 7. ESR data of selected nickel dithiolenes

Compound	g_1	g_2	g_3	Reference
$Ni(PDDT)_2^-$	2.156	2.070	2.013	this work
$Ni(DDDT)_2^-$	2.119	2.057	2.022	8
$Ni(MTDT)_2^-$	2.093	2.051	2.014	11
$Ni(dmit)_2^-$	2.105	2.041	2.001	26
$Ni(MNT)_2^-$	2.160	2.042	1.988	27

TABLE 8. Cyclic voltammetry parameters for some selected nickel 1,2-dithiolene compounds

Ligand	Neutral–anion	Anion–dianion	Reference
$PDDT^{2-}$	+0.30	−0.60	this work
$DDDT^{2-}$	+0.014	−0.81	8
$MTDT^{2-}$	+0.10	−0.67	11
$dmit^{2-}$	not reported	−0.19	28
MNT^{2-}	+1.05	+0.259	29

TABLE 9. Half-wave potential of monoanion-to-dianion couple of the copper dithiolenes

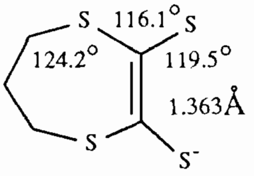
Ligand	$E_{1/2}$ (V)	Reference
$PDDT^{2-}$	−0.56	this work
$DDDT^{2-}$	−0.49	13
$dmit^{2-}$	−0.07	28
MNT^{2-}	+0.37	29

A cyclic voltammogram over the scan range of +1.0 to −1.0 V for $Cu(DDDT)_2^-$ reveals an irreversible redox pair and a reversible one. The peak at $E_{1/2} = -0.56$ V is a classic one-electron reversible redox peak. We assign this to a monoanion to dianion couple which is typical of metal dithiolenes. A summary of some electrochemical results concerning these redox couples of selected copper dithiolenes is given in Table 9.

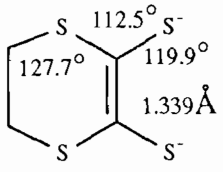
$Cu(PDDT)_2^-$ has a lower reduction potential than $Cu(DDDT)_2^-$. This trend is opposite to the nickel complexes of $PDDT^{2-}$ and $DDDT^{2-}$. Careful inspection of the molecular structures of copper complexes of both ligands reveals that the equivalent bond angles on double bonded carbons are almost equal. Therefore unlike nickel complexes of these ligands, there is no difference in sp^2 orbital distortions on the C=C group between $Cu(PDDT)_2^-$ and $Cu(DDDT)_2^-$. In this case, we can only consider the inductive effect of substituent groups on 1,2-dithiolenes affecting the electron donating/withdrawing ability of the ligand, that is, the $-SCH_2CH_2CH_2S-$ unit in $PDDT^{2-}$ is more electron donating than the $-SCH_2CH_2S-$ unit in $DDDT^{2-}$. The order of electron withdrawing ability is $DDDT^{2-} > PDDT^{2-}$. The greater the electron accepting ability of the ligand, the more easily the complexes can accommodate the excess electron density [30]. Thus $Cu(PDDT)^-_2$ is more difficult to be reduced to the dianion than is $Cu(DDDT)^-_2$.

The oxidation peaks of the monoanion of this compound show a very unusual and interesting redox behavior. There are three peaks in the −1.0 to 0.0 V region, one very sharp anode peak at +0.55 V and two cathode peaks at +0.48 and +0.29 V. The current of this anode peak is three times higher than that of the anode peak for the monoanion to dianion reversible couple and may indicate more than a one electron oxidation in this step.

The structure related data of $[(C_2H_5)_4N][Ni(PDDT)_2]$ and $[(C_2H_5)_4N][Ni(DDDT)_2]$ are listed in Table 10. Both complex salts have been characterized with the same cation and show approximately the same unit cell size. Both have a square planar core consisting of the $Ni(S_2C_2S_2)_2$ unit. It is expected that C(1) and C(2) make up the double bond in the molecules and show sp^2 hybridization. The bond angle between ideal sp^2 hybridized orbitals of 120° is less than the average endocyclic angles on C(1) and C(2) of 124.2(2)° in the seven-membered ring of $Ni(PDDT)_2^-$ and of 127.7(5)° in the six-membered ring of $Ni(DDDT)_2^-$. The average exocyclic S–C–S angles are 116.1(2)° in $Ni(PDDT)_2^-$ and 112.5(4)° in $Ni(DDDT)_2^-$, as shown below.



$PDDT^{2-}$



$DDDT^{2-}$

As demonstrated by the bond angles, the sp^2 orbital distortion in the six-membered ring of $Ni(DDDT)_2^-$ is actually greater than in the seven-membered ring of $Ni(PDDT)_2^-$. The larger bond angle is a result of more s-character in the bonding orbital [31]. The greater strain in the six-membered ring results in more s-character in the C(1)–C(2) bond and more p-character in exocyclic C–S bond. Therefore, the orbital on the ring carbon near the exocyclic sulfur atom (i.e. C–S bond), in the seven-membered ring of $PDDT^{2-}$ must in turn exhibit greater s-character than that in $DDDT^{2-}$. The corresponding increased s-character in the bond to the exocycic sulfur atom results in a greater electronegativity [31]. The explanation can be further confirmed by observing the longer C=C double bond in $PDDT^{2-}$ (1.363(4) Å in $PDDT^{2-}$, 1.339(11) Å in $DDDT^{2-}$) brought about by the increased p-character and the shorter exocyclic C–S bond (1.726(3) Å in $PDDT^{2-}$, 1.735(8) Å in $DDDT^{2-}$) caused by more s-character. The exocyclic sulfur in $PDDT^{2-}$ is therefore less basic and more electronegative than that in $DDDT^{2-}$. Thus the complex of $PDDT^{2-}$ can accommodate more electron density and this is displayed by a higher reduction potential than the complex of $DDDT^{2-}$.

TABLE 10. Key bond angles and distances in $[(C_2H_5)_4N][Ni(PDDT)_2]$ and $[(C_2H_5)_4N][Ni(DDDT)_2]$

	PDDT	DDDT
Average endocyclic angle (°)		
C=C–S	124.2(2)	127.7(5)
Average exocyclic angle (°)		
S–C–S	116.1(2)	112.5(4)
C=C–S	119.5(3)	119.9(5)
Bond distances (Å)		
C=C	1.363(4)	1.339(11)
C–S (coordinated S)	1.726(3)	1.735(8)

The molecular structure of $Ni(PDDDT)_2^-$ is shown in Fig. 1. The four sulfurs surrounding the nickel atom yield a square planar structure with an average Ni–S bond length 2.148(1) Å and an average S–Ni–S angle 91.4(2)°. The average S–C bond length is 1.726(3) Å in the five-membered ring containing the nickel atom. These values indicate the modest nature of the electron delocalization in the metal ligand coordination ring characteristic of transition metal dithiolenes. The $Ni(S_2C_2S_2)_2$ core is planar and the seven-membered ring consisting of the 1,3-propanediyl group and the dithioethylene group exists in a chair configuration with an average C–S–C bond angle of 103.2(2)°, an average S–C–C angle of 116.2(2)° and an average C–C–C angle of 115.7(2)°.

There are four tetraethylammonium cations and four complex anions in each unit cell. The nickel atom lies on an inversion center of the cell. A packing diagram is shown in Fig. 2 (looking down the *a* axis). Inspection of the stereo view of the packing reveals a layer structure

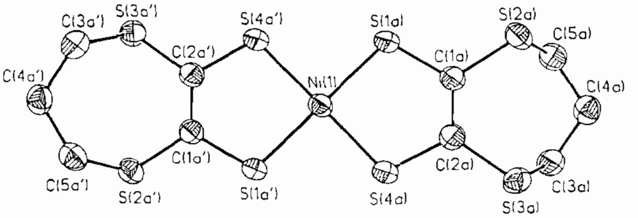


Fig. 1. Structure of $Ni(PDDT)_2^-$ with the atom-labeling scheme.

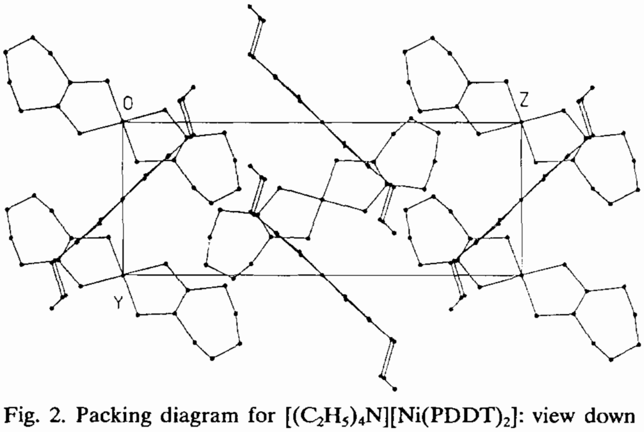


Fig. 2. Packing diagram for $[(C_2H_5)_4N][Ni(PDDT)_2]$: view down *a* axis with tetraethylammonium cations removed.

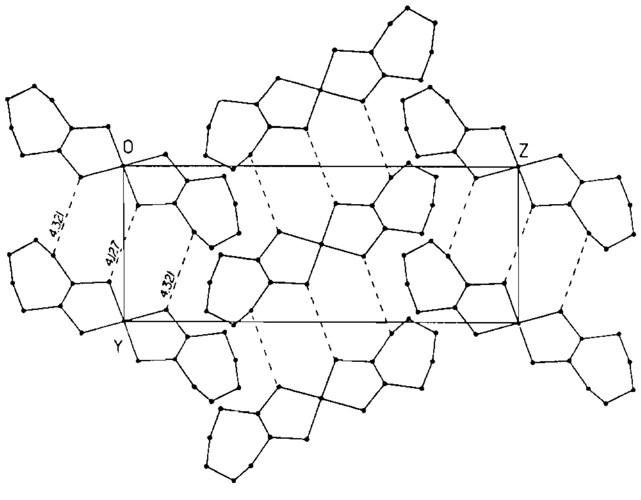


Fig. 3. Packing diagram of parallel anion layer for $[(C_2H_5)_4N]$-$[Ni(PDDT)_2]$.

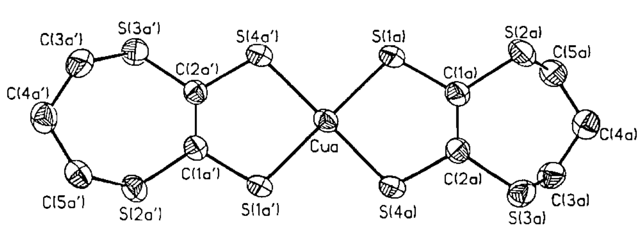


Fig. 4. Structure of $Cu(PDDT)_2^-$ with the atom-labeling scheme.

parallel to the *bc* plane. There are two kinds of layers packed two different ways. One consists of anions almost parallel to the *bc* plane of the crystal unit cell. We term this layer as the 'parallel layer'. It is shown in Fig. 3. Another layer is that of anions perpendicular to the *bc* plane. We call this layer the 'perpendicular layer'. In both layers the molecular contacts are anisotropic. In the 'parallel layer', anions are arranged as 'columns' along the *b* axis. The closest sulfur–sulfur contact is 4.127 Å for intra-column and 5.402 Å for inter-column. The anion plane, column plane and *bc* plane of the unit cell are not exactly parallel. Anions are oriented in the same manner within the column but are arranged in a zig-zag fashion between adjacent columns. In the 'perpendicular layer', anions are packed as 'stacks' along the *b* axis since they all have the same orientation. The anions in adjacent 'stacks' are tilted in different directions. This layer lies midway between two parallel layers. Here, the shortest intermolecular distance of double bonded carbon to sulfur (C(1b)· · ·S(4b)) is 5.331 Å intra-'stack'; sulfur to sulfur distances are 5.380 Å intra-'stack' and 4.891 Å inter-'stack'. The average separation of anion planes is 5.435 Å. From this data, it is clear that there is no intermolecular sulfur· · ·sulfur contact within this layer. The closest intermolecular sulfur· · ·sulfur contact in the entire structure is the 2.505 Å between parallel layers and perpendicular layers. Therefore, the anions in the perpendicular layer resembled bridges connecting two columns in two neighbor parallel layers. The shortest Ni· · ·Ni distance is 7.437 Å which is the length of the *b* axis. Table 11 presents more detail on these data. The tetraethylammonium counterions lie between the parallel layer and the perpendicular layer. The equivalent bond lengths and angles are slightly different between the molecules in both layers.

The molecular structure of $Cu(PDDT)_2^-$ is shown in Fig. 4. The gross geometry of $Cu(PDDT)_2^-$ is very similar to $Ni(PDDT)_2^-$. Like $Ni(PDDT)_2^-$, the four coordination sulfur atoms and copper atom yield a

TABLE 11. Close sulfur· · ·sulfur contact comparisons in $(C_2H_5)_4N[Cu(PDDT)_2]$ and $(C_2H_5)_4N[Ni(PDDT)_2]$

Molecule A	Molecule B	Distance (Å)		Operation of B
		$Cu(PDDT)_2^-$	$Ni(PDDT)_2^-$	
Parallel layer				
intra-column				
S(4a)	S(4a)	4.006	4.127	$-x,\ 1-y,\ -z$
S(3a)	S(1a)	4.353	4.321	$x,\ 1+y,\ z$
inter-column				
S(2a)	S(1a)	5.411	5.402	$-x,\ 0.5+y,\ 0.5-z$
Perpendicular layer				
intra-'stack'				
C(ab)	S(4b)	no	5.331	$1-x,\ -y,\ -z$
S(4b)	S(2b)	5.414	5.380	$1-x,\ -y,\ -z$
inter-'stack'				
S(3b)	S(3b)	4.860	4.896	$1-x,\ 0.5+y,\ 0.5-z$
S(3b)	S(3b)	4.860	4.896	$1-x,\ 0.5+y,\ 0.5-z$
Parallel layer to perpendicular layer				
S(2b)	S(3a)	3.500	3.505	$1-x,\ -0.5+y,\ 0.5-z$

TABLE 12. Bond data (Å) for some dithiolene complexes having square planar structure

Complex	M–S	S–C[a]	C=C	C–S[b]	ΔD[c]	Reference
$Cu(PDDT)_2^-$	2.182(1)	1.749(4)	1.337(5)	1.754(4)	0.005	this work
$Ni(PDDT)_2^-$	2.148(1)	1.726(3)	1.357(4)	1.758(3)	0.032	this work
$Cu(DDDT)_2^-$	2.185(3)	1.741(8)	1.320(13)	1.772(3)	0.031	13
$Ni(DDDT)_2^-$	2.148(2)	1.735(8)	1.339(11)	1.768(8)	0.033	8
$Cu(MNT)_2^-$	2.170(5)	1.720(10)	1.315(20)			32

[a] The bond length in five-membered coordination ring. [b] The bond length of sulfur with the carbon double bonded in non-coordination ring. [c] ΔD is the length difference of C–S bonds between both sides of C=C group.

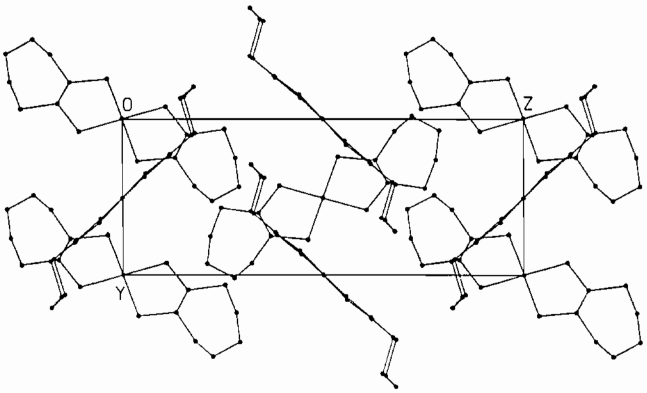


Fig. 5. Packing diagram for $[(C_2H_5)_4N][Ni(PDDT_2)]$: view down *a* axis with tetraethylammonium cations removed.

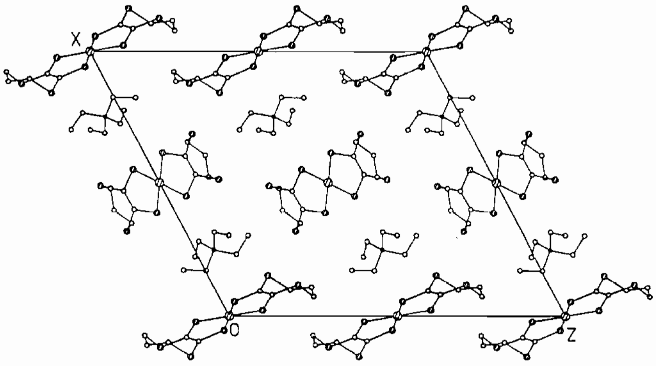


Fig. 6. Packing diagram for $[(C_2H_5)_4N][Ni(PDDT)_2]$: view down *b* axis.

square planar structure but with an average Cu–S bond length of 2.182 Å (Ni–S 2.148 Å in $Ni(PDDT)_2^-$) and an average S–Cu–S angle of 91.5° (S–Ni–S angle 91.4° in $Ni(PDDT)_2^-$). Unlike $Ni(PDDT)_2^-$, the average C–S bond lengths on both sides of the C=C group differ only by 0.005 Å (0.032 Å in $Ni(PDDT)_2^-$), that is, 1.749 Å C–S bond lengths in the five-membered ring containing a metal atom (1.726 Å in $Ni(PDDT)_2^-$) and 1.74 Å C–S bond lengths in the seven-membered ring containing a propanediyl group (1.758 Å in $Ni(PDDT)_2^-$). These values indicate that the $Ni(PDDT)_2^-$ complex has a greater electron delocalization in the metal ligand coordination ring than $Cu(PDDT)_2^-$. Some comparative structural data for selected dithiolene complexes are presented in Table 12.

Comparing $Ni(PDDT)^-_2$ to $Cu(DDDT)^-_2$, there is an almost equal electron delocalization in bonds on both sides of the C=C group. The $Cu(S_2C_2S_2)_2$ core is planar and the seven-membered ring consisting of the 1,3-propanediyl group and the dithioethylene group exists in a chair configuration with an average C–S–C bond angle of 102.8°, an average S–C–C angle of 116.1° and an average C–C–C angle of 116.6°.

Initial data collection indicated that $[(C_2H_5)_4N]$-$[Cu(PDDT)_2]$ had the same space group and almost the same unit cell constants as $[(C_2H_5)_4N]$-$[Ni(PDDT)_2]$. A cell packing diagram is shown in Fig. 5 (looking down the *a* axis). Like $Ni(PDDT)_2^-$, $Cu(PDDT)_2^-$ is a layer structure parallel to the *bc* plane of the unit cell. Again, there are two kinds of layers packed two different ways. We term the anions almost parallel to the *bc* plane as the 'parallel layer' and the anions perpendicular to the *bc* plane as the 'perpendicular layer'. In the 'parallel layer', anions are arranged as a 'column' along the *b* axis. As shown in Fig. 6, the closest intermolecular S···S contact is 4.006 Å for intra-column (shorter than the equivalent distance in $Ni(PDDT)_2^-$) and 5.411 Å for inter-column (longer than that in $Ni(PDDT)_2^-$). This indicates that the parallel layer in the $Cu(DDDT)_2^-$ structure has more 'column character' than that in $Ni(PDDT)_2^-$. In the perpendicular layer, the shortest intermolecular S···S distances are 5.414 Å in intra-'stacks' (longer than in $Ni(PDDT)_2^-$ and 4.860 Å for inter-'stack' (shorter than in $Ni(PDDT)_2^-$). It is clear that there is no intermolecular S···S contact within this layer. The closest S···S contact in the entire structure is 3.500 Å between the parallel layer and the perpendicular layer. This distance is slightly shorter than the van der Waals distance. Therefore the anions in perpendicular layers seem to bridge connecting columns in two neighboring parallel layers. The shortest Cu···Cu distance is 7.424 Å which is the length of the *b* axis. Table 11 lists intermolecular S···S contacts in crystals of Ni and Cu complexes.

Supplementary material

Tables of atomic coordinates, isotropic thermal parameters, anisotropic temperature parameters, and structure factors are available from author R.D.B.

Acknowledgements

This work was initiated with support from the Petroleum Research-Fund, administered by the American Chemical Society. Funds for the X-ray Diffractometer were obtained from the NSF (Grant CHE-8307022).

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