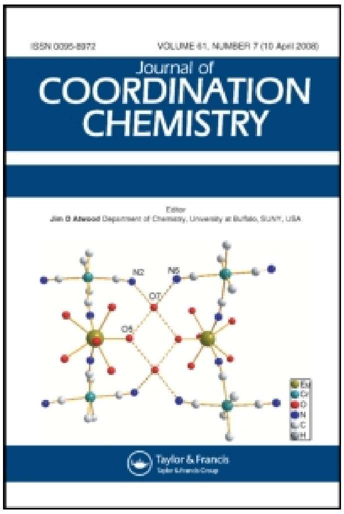

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SYNTHESIS AND CHARACTERIZATION OF THE FORMAL Ni(III) AND Cu(III) COORDINATION COMPLEXES OF THE NEW 1,2-DITHIOLENE, 1,4-BUTANEDIYLDITHIOETHYLENE-1,2-DITHIOLATE

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SYNTHESIS AND CHARACTERIZATION OF THE FORMAL Ni(III) AND Cu(III) COORDINATION COMPLEXES OF THE NEW 1,2-DITHIOLENE, 1,4-BUTANEDIYLDITHIOETHYLENE-1,2-DITHIOLATE

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The new 1,2-dithiolene, 1,4-butanediyldithioethylene-1,2-dithiolate, has been isolated. In addition, new monoanionic bis-complexes with nickel and copper have been prepared and isolated. The formal Ni(III) complex crystallizes in the orthorombic space group, P_{bca}, with a = 9.762(9), b = 12.53(2), and c = 23.166(3) Å, with 4 molecules in the unit cell. The structure was refined to an R = 9.01% (R_w = 8.95%). The formal Cu(III) complex crystallizes in the monoclinic space group, $C_{2/c}$, with a = 25.567(6), b = 8.011(3), c = 14.504(3) Å, and β = 106.17(2)° with 4 molecules in the unit cell. The structure refined to R = 4.2% with R_w = 4.3%. Comparisons to similar 1,2-dithiolenes suggest this ligand produces only modest structural and electronic differences when compared to the 1,3-propanediyldithioethylene-1,2-dithiolate complexes. The oxidation (to a neutral complex) and reduction (to a dianion) for the Ni(III) and Cu(III) complexes show large differences from those of maleonitriledithiolate. Other physical data are presented as well.

KEYWORDS: dithiolene, Ni(III), Cu(III), sulfur containing ligands

INTRODUCTION

During the past twenty years, one of the most interesting areas of "interdisciplinary" inorganic chemistry which has been developed is that of the coordination chemistry of 1,2-dichalcogenolenes. Prompted by the early work of Schrauzer and Gray,[1-3] it was recognized that 1,2-dithiolenes could stabilize an extended series of *formal* oxidation states or an extended redox series with a particular transition element. [For an excellent review of Ni, Pd, and Pt maleonitriledithiolate complexes, see reference 4].

There have been a number of studies attempting to understand the formal metal oxidation states and formal ligand electronic structures of not only maleonitriledithiolate (I), but of several other 1,2-dithiolenes as well. Extended Huckel

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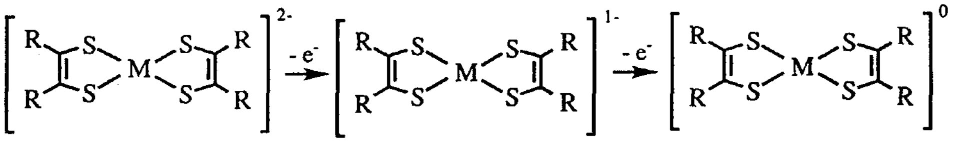
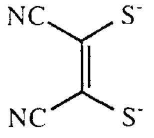
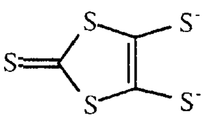
calculations on several systems support the following formalization, that is, the oxidation is primarily ligand based.[5–7]



Electron spin resonance results of nickel complexes utilizing enriched nickel 61 confirm the extensive delocalization in the formal Ni(III) material, the monoanion in the scheme above.[8] The recognition of ligand based oxidations for these dithiolenes has prompted a great deal of interest in these complexes as possible highly conducting materials.[9–11] Since that time, a new field has developed which has looked at the properties of such complexes as analogs to *organic metals*. While the field was initiated by the chemistry of maleonitriledithiolate (*mnt*) **I**, the more recent work has concentrated on the coordination chemistry of 1,3-dithiole-2-thione-4,5-dithiolate (*dmit*) **II**, to a lesser extent its isomer, 1,2-dithiole-3-thione-4,5-dithiolate (*dmt*) **III**, and 1,3-dithiole-2-one-4,5-dithiolate (*dmid*) **IV**. Both



(I)



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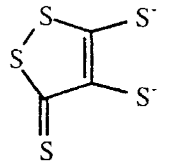

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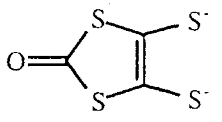


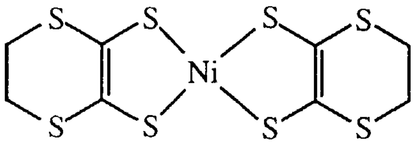
(IV)

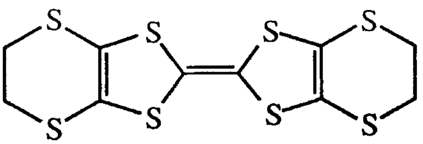
ligands **II** and **IV** share a unique structural feature, that is the presence of the tetrathioethylene unit. Thorough reviews of the coordination chemistry and applications of these materials have appeared recently.[9–11] Most work focuses on the conductivity of the transition element complexes especially since partially oxidized 'd^7' complexes have been shown to be superconducting. Nearly 200 research papers have been published on *dmit* complexes, focusing primarily on the structures of these complexes as well as their unique electrical and conductive properties.

A very important breakthrough involving inorganic superconductors containing dithiolene ligands was the discovery that the superconducting nature of these materials is dependent solely on the dithiolate ligands of the inorganic acceptor and not on the various "open" cationic donors such as tetrathiafulvalene[12] which participate in intermolecular electron transfer. $[Me_4N][Ni(dmit)_2]_2$ was the first superconducting complex of this type to have a "closed" cation.[13] (A "closed" cation is one which does not participate in intermolecular electron transfer.) The $Ni(dmit)_2$ units in this material are essentially planar, dimeric and stacked in one direction. The distances between the planes of the complexes alternate between 3.53 Å for individual members of a dimer and 3.58 Å between distinct dimer units. The cations line up between the stacks of the complex. The room temperature conductivity of $[Me_4N][Ni(\mathit{dmit})_2]_2$ is about 50 s cm^{-1} giving it metal-like conductivity. This material undergoes a transition to superconductivity at a temperature of 5 K at 7 *kbar*. It has been shown that superconductivity is possible with different cations and with different metals. Some of these molecular superconductors are $[Me_4N][Pd(\mathit{dmit})_2]_2$[14] with a T_c of 6.2 K at 6.5 *kbar*, and α-$[Me_2Et_2N][Pd(\mathit{dmit})_2]_2$,[15] with a superconducting transition at 4 K and 2.4 *kbar*.

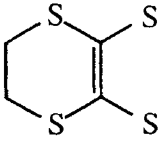
Alvarez *et al.*[16] have shown that bis(dithiolene) metal complexes tend to form stacks in a manner analogous to that of the tetrathiafulvalenes. The interaction of these molecules along the stack tends to be very weak for d^8 metals, but significantly stronger interactions exist for d^7 metals, leading to the formation of dimers. This difference in behavior is exactly analogous to that found in TTF derivatives; neutral TTF compounds form stacks of widely separated molecules, while the cationic species form dimers.[17] However, non-integral oxidation states lead to the formation of regular chains which exhibit high conductivity in the solid state.

The paper by Alvarez *et al.* first discussed the "isolobal analogy" with reference to the similarity of certain transition metal dithiolenes and organic superconducting molecules where a metal replaces a C = C bond. Whangbo and co-workers extended this "analogy" to investigate the "Ni(IV)" complex of the ligand, $DDDT^{2-}$ (V).[17] When complexed with a transition element in the formal oxidation state of + 4 (and visualizing the isolobal analogy) this complex becomes the "equivalent" of BEDT-TTF.[16] Williams *et al.*[18] prepared and characterized $(TTF)[Ni(DDDT)_2]$ also with the objective of producing a superconductive material, but little work had addressed the possible conductivity of partially oxidized complexes of this ligand.



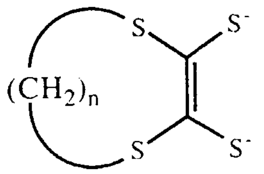


BEDT-TTF



(V)

It has been our *working hypothesis* that the potential exists to extend the class of transition element dithiolenes which are either highly conductive or superconductive by utilizing "sulfur-rich" dithiolenes and making use of the isolobal analogy as a synthetic guide. It is also difficult to predict which structural changes in a ligand might produce significant stereoelectronic differences in metal complexes. This manuscript reports the synthesis of a new 1,2-dithiolene which contains the tetrathioethylene unit, 1,4-butanediyldithioethylene-1,2-dithiolate ($n = 4$), the syntheses of the formal Ni(III) and Cu(III) complexes, and the characterization and structural study of these complexes. We view these materials as *precursors* to the ultimate syntheses of the partially oxidized materials.



n = 4

EXPERIMENTAL

Reagents: 2,7,9,11-tetrathiabicyclo[6.3.0]undec-1(8)-en-10-thione (TTUET) and its derivative, 2,7,9,11-tetrathiabicyclo[6.3.0]undec-1(8)-en-10 = -one (TTUEO), were prepared by literature methods[1] with some modifications and characterized by IR, NMR, elemental analysis and melting point (mp.). 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. THF was freshly distilled from Na/benzophenone prior to use. Methyl alcohol and acetonitrile were purchased from Fisher Chemical Company and stored over 4Å sieves for more than 24 h before use. Ethyl alcohol was purchased from Aaper Alcohol and Chemical Company. Ethyl alcohol and water used in the syntheses of the complexes were degassed with argon for 30 min prior to use.

General Procedure: All reactions were carried out under a static atmosphere of argon using standard Schlenk techniques. Transfers of liquid solvents and/or reagents were made using argon purged ground glass syringes with Luer-lock type stainless steel needles.

Syntheses: [$C_7H_8S_5$ (TTUET)]: To a stirred solution (0°C) of 200 mL CS_2 in 400 mL of DMF, 10 g of sliced potassium metal was added very slowly and carefully. After stirring for 1 h, 10 g of sliced potassium metal and 30 mL of CS_2 were added to the solution. This same addition was again repeated one hour later. To this solution, 50 mL of CS_2 was added and stirred for 3–4 h. To the reaction mixture, 100 mL of DMF and 1,4-dibromobutane (46 mL) were added slowly. The solution was allowed to warm to room temperature and stirred overnight. To destroy any unreacted potassium metal, approximately 20 mL of MeOH, followed by H_2O (200 mL) were added. To remove any by-product, the solution was filtered, extracted with chloroform and washed with H_2O. Organic extracts were dried over K_2CO_3 and concentrated to give orange-brown solid. The crude product was recrystallized to give orange crystals. : mp. 107–108°C; ^1H NMR ($CDCl_3$) δ 3.05 (t, 4H), 2.04 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 212.2, 140.2, 38.4, 27.4; IR (KBr pellet) 2920(m), 2900(s), 1440(s), 1400(s), 1288(s), 1055(vs), 1020(s), 880(m), 855(s), 800(m), 765(m), 505(m), 445(m), cm^{-1}; *Anal.* calcd. for $C_7H_8S_5$: C, 33.31; H, 3.19; S, 63.50. Found: C, 33.45; H, 3.13; S, 63.26.

[$C_7H_8S_4O$ (TTUEO)] To a solution of 2.50 g(1.0×10^{-2} mol) of TTUET in 30 mL $CHCl_3$, 3.2 g of $Hg(OAc)_2$ in 50 mL HOAc was added. The solution was refluxed for about 6 h and the color changed to black. Approximately 8 g of anhydrous Na_2SO_4 was added and the reaction mixture was filtered to remove any by-product. To the filtrate, a saturated Na_2CO_3 aqueous solution was added slowly. Extraction with CH_2Cl_2, drying over $MgSO_4$ and concentration gave a yellow solid.

The crude product was recrystallized to yield light yellow crystals.: mp. 78-80°C; ^{1}H NMR ($CDCl_3$) δ 3.00 (t, 4H), 2.02 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 189.7, 131.6, 38.6, 27.5; IR (KBr pellet) 2950(m), 2930(m), 2910(s), 1755(m), 1750(vs), 1600(vs), 1440(m), 1420(s), 1408(s), 1295(s), 1275(m), 1170(m), 1005(m), 990(s), 880(vs), 805(s), 765(s), 730(s), 550(m), 455(m), 380(m) cm^{-1}; *Anal.* calcd. for

$C_7H_8S_4O$:C, 35.57; H, 3.41; S, 54.25. Found: C, 35.52; H, 3.37; S, 54.13.

[K_2(BDDT)]: Potassium ethoxide was prepared by adding 3.2 g (8×10^{-2} mol) of sliced potassium metal to 8 mL (excess) of absolute ethanol under argon. After approximately 200 mL of freshly distilled THF was added to this solution, 4.73 g (2×10^{-2} mol) TTUEO was added. A light-cream colored precipitate formed after a few minutes. The mixture was stirred for about 15 h, filtered, washed with ethyl ether, dried and stored in a Schlenk tube for further use.

$[(C_2H_5)_4N][Ni(C_6H_8S_4)_2]$: A solution of 0.25 g ($1.1 \times 10^{-3}$ mol) of $NiCl_2 \cdot 6H_2O$ in 20 mL CH_3OH was added dropwise to 0.58 g (2.0×10^{-3} mol) of K_2BDDT in 20 mL CH_3OH. The solution color changed from amber to dark brown as the reaction proceeded. The solution mixture was stirred for 3 h at room temperature and filtered to remove any by-product. To the filtrate, 0.25 g (1.1×10^{-3} mol) of tetraethylammonium bromide was added, and stirred for 30 min. A brown precipitate formed which was collected by filtration. Brown crystals suitable for X-ray analysis were obtained by careful recrystallization from dry acetonitrile. The product yield was 0.201 g (33%): mp. 187–189°C; ^{1}H NMR (DMSO-d^6) δ 3.33 (d, 8H), 3.20 (br. s, 8H), 1.17 (br. s, 12H); IR (KBr pellet) 2970(m), 2905(s), 2840(m), 1470(s), 1440(s), 1402(s), 1380(vs), 1285(s), 1165(s), 995(m), 880(m), 860(m), 800(s), 740(m), 445(m), 385(m) cm^{-1}; *Anal.* calcd. for $NiC_{20}H_{36}NS_8$: C, 39.66; H, 5.99; N, 2.31. Found: C, 39.70; H, 5.97; N, 2.37.

$[(C_2H_5)_4N][Cu(C_6H_8S_4)_2]$: A solution of 0.20 g ($1.2 \times 10^{-3}$ mol) of $CuCl_2 \cdot 2H_2O$ in 10 mL H_20 was added dropwise to 0.58 g (2.0×10^{-3} mol) of K_2BDDT in 20 mL 1:1 ethanol/water solution made basic with KOH. The color changed from amber to dark purple immediately. The solution was stirred for 1 h at room temperature and then filtered to remove by-product. A solution of 0.25 g (1.1×10^{-3} mol) of tetraethylammonium bromide in 5 mL of water was added, and stirred 20 min. A dark purple precipitate was formed and collected by filtration. The yield was 0.13 g (21%). Single crystals were obtained by careful recrystallization from acetonitrile/isopropanol: mp. 196-197°C; ^{1}H NMR (DMSO-d^6) δ 3.20 (q, 8H), 2.68 (br. s, 8H), 1.70 (br. s, 8H), 1.15(dt, 12H); IR (KBr pellet) 2980(m), 2920(m), 2840(m), 1480(s), 1450(s), 1428(s), 1410(s), 1390(s), 1170(s), 1005(s), 955(s), 890(s), 870(s), 805(s), 780(s), 430(m), 380(m) cm^{-1}; *Anal.* calcd. for $CuC_{20}H_{36}NS_8$: C, 39.35; H, 5.94; N, 2.29. Found: C, 39.46; H, 6.08; N, 2.30.

Physical Measurements: Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer over the range 4000–200 cm^{-1}. Electrochemical data were obtained with a BAS CV-27 potentiostat. A platinum wire was used for both the working and auxiliary electrode and a 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. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Nuclear magnetic resonance spectra were obtained with a G.E. GN 300 (300MHz) spectrometer. Chemical shifts are in δ units (ppm) with TMS (0.0ppm) used as an internal standard for ^{1}H NMR.

Single-crystal X-ray Analysis: Unit cell dimensions were determined by rotation photographs and obtained from 15 reflections. A data set was collected on a Nicolet R3m/μ diffractometer equipped with a graphite monochrometer 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. Table 1 contains all relevant crystallographic parameters for both structures reported.

$[(C_2H_5)_4N][Ni(C_6H_8S_4)_2]$: Reddish brown crystals suitable for X-ray analysis were grown by the slow evaporation of a saturated anhydrous acetonitrile solution. Axial photographs and unit cell constants demonstrated that the crystal possessed orthorhombic symmetry. Systematic absences were consistent with the nonstandard space group Pbca, which was confirmed by successful refinement of the structure. Two check 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.[20] Relevant crystallographic information is given in Table 1. The nickel and sulfur atoms were located by the direct methods program SOLV of the crystallographic software package SHELXTL.[21] The remaining non-hydrogen atoms were found by the subsequent difference Fourier techniques to give the appropriate trial structure. This trial structure was further refined by the block-diagonal least squares technique using SHELXTL on a Data

Table 1 X-ray crystallographic parameters of $[(C_2H_5)_4N][M(BDDT)_2]$

	Crystal Parameters	
Formula	$NiC_{20}H_{36}NS_8$	$CuC_{20}H_{36}NS_8$
Formular weight	605.69	610.54
Crystal size, mm	0.2 × 0.3 × 0.5	0.2 × 0.2 × 0.6
Crystal color	red-brown	dark green
Crystal habit	orthorhombic	monoclinic
Cell dimensions	$a = 9.762(9)$ Å $b = 12.53(2)$ Å $c = 23.166(3)$ Å	$a = 25.567(6)$ Å $b = 8.011(3)$ Å $c = 14.504(3)$ Å $\beta = 106.17(2)^0$
Volume	2833.6 Å^3	2853.1 Å^3
Space group	Pbca	C2/c
Molecules/unit cell	4	4
Density calc., g/cm^3	1.42	1.42
F(000)	1276	1280
	Data Collection Parameters	
Radiation (MoKα)	$\lambda = 0.71069$ Å	$\lambda = 0.71069$ Å
Temperature	ambient	ambient
2Θ range	3° - 36°	3° - °60°
Scan type	Θ - 2Θ	Θ - 2Θ
No. of reflections	6568	4173
No. of reflections used (I3$\sigma_{(I)}$)	1233	2119
Linear absorption coefficient	12.65 cm^{-1}	13.40 cm^{-1}
	Refinement Parameters	
Final *R* index	$R = 0.0901$ $R_w = 0.0895$	$R = 0.042$ $R_w = 0.043$
Goodness of fit	4.515	1.08
Largest Δ/σ	0.06	<0.01
Data/parameter ratio	8.7	14.6

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 $w = 1/\sigma^2_{(F)}$. Non-hydrogen atoms were refined with anisotropic temperature factors except for C4 and C5, which were refined with isotropic temperature factors. All hydrogen atoms were placed in calculated positions 0.96 Å away from the attached carbon nuclei and were not refined. A final difference Fourier map revealed no missing or misplaced electron density. Atomic coordinates, anisotropic temperature factors, calculated and observed structure factors are available in the supplementary material. The thermal ellipsoid drawing of the anion alone was plotted using the SHELXTL graphic package and is displayed in Figure 1. Packing diagrams were plotted using the program ORTEP and are available in the supplementary material[22]. Atomic coordinates are presented in Table 2. Bond lengths and bond angles are given in Tables 3 and 4.

$[(C_2H_5)_4N][Cu(C_6H_8S_4)_2]$: A representative crystal grown from isopropanol/acetonitrile was surveyed. Systematic absences indicated that the crystal belongs to the monoclinic space group C2/c. 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. Relevant crystallographic information is given in Table 1. The nickel and sulfur atoms were located by the direct method program SOLV of the crystallographic program package SHELXTL. The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. The 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 $w = 1/(\sigma^2_{(f)} + 0.00090F^2)$. Non-hydrogen atoms were refined with anisotropic temperature factors. Refinement with hydrogen atoms placed at calculated positions 0.96 Å away from the attached carbon atom gave a final R value of 0.042. A final difference Fourier map revealed no missing or misplaced electron density. Atomic coordinates, anisotropic temperature factors, calculated and observed structure factors are available in the supplementary material. The thermal ellipsoid drawing of the anion

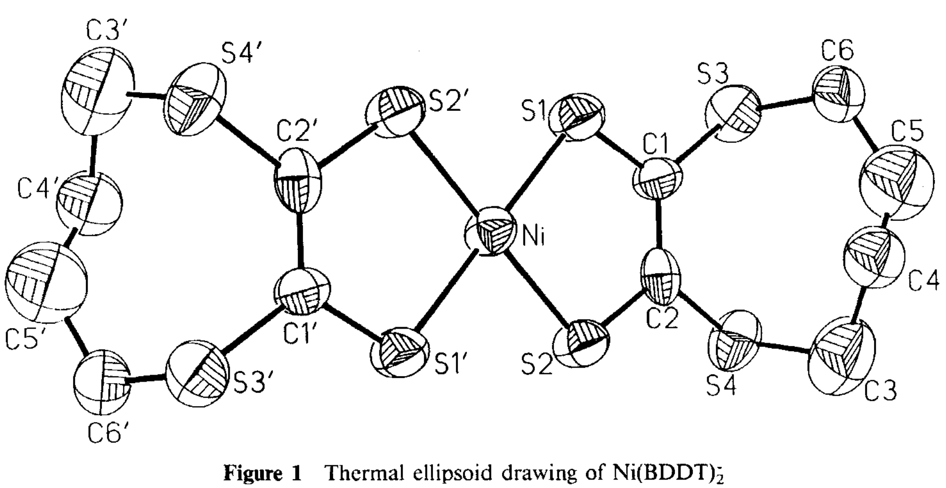


Figure 1 Thermal ellipsoid drawing of $Ni(BDDT)_2^-$

Table 2 Atomic coordinates (X10^4) and their standard deviations of the anion [Ni(BDDT)$_2^-$]*

	x	*y*	*z*
Ni	0	0	0
S(1)	- 1636 (4)	- 958 (3)	340 (1)
S(2)	141 (4)	894 (3)	793 (1)
S(3)	- 3222 (4)	- 1075 (4)	1436 (2)
S(4)	- 1374 (4)	932 (3)	1909 (2)
C(1)	- 1972 (13)	- 4477 (11)	1012 (5)
C(2)	- 1148 (13)	348 (10)	1226 (5)
C(3)	- 245 (21)	125 (18)	2349 (7)
C(4)	- 1180 (31)	- 886 (25)	2583 (14)
C(14)	- 167 (32)	- 1218 (24)	2160 (12)
C(5)	- 1281 (22)	- 1716 (17)	2249 (9)
C(6)	- 2290 (17)	- 2102 (11)	1813 (6)

* Atomic coordinates and their standard deviations of the cation ([$C_2H_5)_4N]^+$) are available in the supplementary data.

Table 3 Bond lengths (Å) of the anion [Ni(BDDT)$_2^-$]*

Ni-S(1)	2.148(4)	Ni-S(2)	2.156(3)
Ni-S(1A)	2.148(4)	Ni-S(2A)	2.156(3)
S(1)-C(1)	1.690(13)	S(2)-C(2)	1.748(13)
S(3)-C(1)	1.778(13)	S(3)-C(6)	1.802(15)
S(4)-C(2)	1.758(12)	S(4)-C(3)	1.810(20)
C(1)-C(2)	1.368(18)	C(3)-C(4)	1.652(38)
C(3)-C(14)	1.740(37)	C(4)-C(14)	1.453(43)
C(4)-C(5)	1.300(38)	C(14)-C(5)	1.270(37)
C(5)-C(6)	1.491(26)		

* Bond lengths of the cation ([$(C_2H_5)_4N]^+$) are available in the supplementary data.

Table 4 Bond angles (°) of the anion [Ni(BDDT)$_2^-$]*

S(1)-Ni-S(2)	91.5(1)	S(1)-Ni-S(1A)	180.0(1)
S(1)-Ni-S(1A)	88.5(1)	S(1)-Ni-S(2A)	88.5(1)
S(2)-Ni-S(2A)	180.0(I)	S(1A)-Ni-S(2A)	91.5(1)
Ni-S(1)-C(1)	104.9(5)	Ni-S(2)-C(2)	103.9(4)
C(1)-S(3)-C(6)	101.9(7)	C(2)-S(4)-C(3)	101.4(7)
S(1)-C(1)-S(3)	118.2(8)	S(1)-C(1)-C(2)	121.1(10)
S(3)-C(1)-C(2)	120.7(9)	S(2)-C(2)-S(4)	116.4(7)
S(2)-C(2)-C(1)	118.7(9)	S(4)-C(2)-C(1)	124.9(10)
S(4)-C(3)-C(4)	106.1(15)	S(4)-C(3)-C(14)	115.1(14)
C(4)-C(3)-C(14)	50.6(16)	C(3)-C(4)-C(14)	67.8(19)
C(3)-C(4)-C(5)	117.4(24)	C(14)-C(4)-C(5)	54.6(19)
C(3)-C(14)-C(4)	61.5(18)	C(3)-C(14)-C(5)	113.4(23)
C(4)-C(14)-C(5)	56.6(20)	C(4)-C(5)-C(14)	68.8(22)
C(4)-C(5)-C(6)	135.4(22)	C(14)-C(5)-C(6)	127.9(21)
S(3)-C(6)-C(5)	115.5(12)		

* Bond angles of the cation ([$C_2H_5)_4N]^+$) are available in the supplementary data.

was plotted using the SHELXTL graphic package and is displayed in Figure 2. The packing diagram was plotted using the program ORTEP and is available in the supplementary material. Atomic coordinates are presented in Table 5. Bond lengths and bond angles are given in Tables 6 and 7.

RESULTS AND DISCUSSION

The formal Ni(III) and Cu(III) complexes of the new 1,2-dithiolene, BDDT^{2-}, represents the third ligand in the series, $n = 2,3,4$.[19,23-29] The observed spectral and structural differences between the complexes with $n = 2$ and $n = 3$ were modest but real and suggested that a longer -(CH$_2$)- chain would further induce stereoelectronic changes in metal complexes.[29]

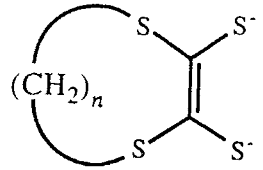


Table 8 shows key bond distances and angles in both the formal Ni(III) and Cu(III) series. The C = C bond distance in these dithiolenes has been used as a judge of the degree of delocalization in the five-membered chelate ring. Perhaps a better way, however, to judge the degree of delocalization in the chelate ring is to compare the C-S(coordinated S) distance and the C-S(non-coordinated) distance. Table 9 contains these values along with ΔD, their differences. As can be seen, the difference is small for the copper complex, as was also observed for the PDDT complex,[29] but is quite large for the nickel complex. In fact, the largest difference in all complexes studied to date is observed here. Relatively few other trends appear in the structural data. The average exocyclic bond angle, S-C-S, increases for the nickel series, DDDT, PDDT, BDDT, but the trend is not as obvious for the copper series. Taken

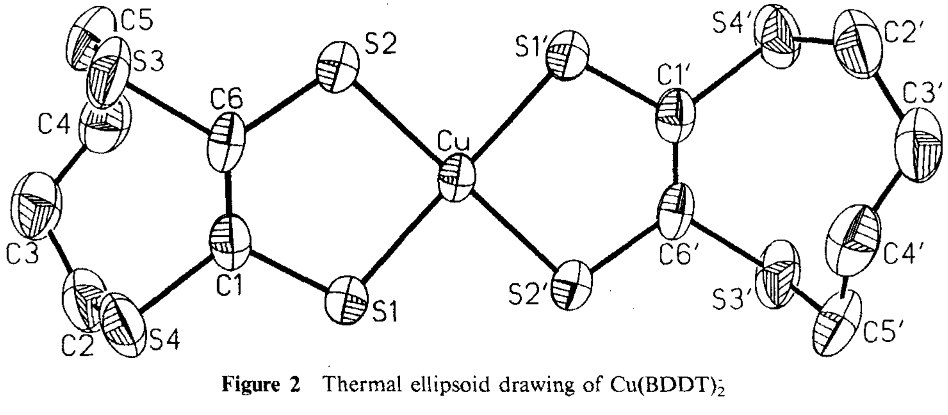


Figure 2 Thermal ellipsoid drawing of Cu(BDDT)$_2^-$

Table 5 Atomic coordinates (× 10^4) and their standard deviations of the anion [Cu(BDDT)$_2^-$]*

	x	*y*	*z*
Cu	5000	0	0
S(1)	5658(1)	925 (1)	- 558 (1)
S(2)	5547 (1)	- 116 (1)	1149 (1)
S(3)	6693 (1)	716 (2)	2385 (1)
S(4)	6810 (1)	1887 (2)	267 (1)
C(1)	6207 (1)	1111 (4)	474 (3)
C(2)	7174 (2)	- 22 (6)	173 (3)
C(3)	7420 (2)	- 972 (7)	1086 (3)
C(4)	7026 (2)	- 2014 (6)	1462 (3)
C(5)	6940 (2)	- 1412 (6)	2409 (3)
C(6)	6156 (1)	663 (5)	1328 (3)

Atomic coordinates and their standard deviations of the cation ([$(C_2H_5)_4N]^+$) are available in the supplementary data.

together, it *does not appear* that the extra carbon produces any extraordinary *structure* change in the copper *anion* or the nickel *anion.*

The packing diagrams for both complexes (available in the supplementary material) show stacks of anions with cations occupying the space between the stacks. Within the stacks, the anions are not parallel but alternate between a parallel and perpendicular orientation to the axis of the stack for Ni and between the alternating 45° orientation with the axis of the stack for Cu. In this latter case, a side view of the stack resembles an undulating ribbon like structure.

Table 10 gives the values for the oxidation and reduction potentials for these new nickel and copper complexes as well as comparative data for other 1,2-dithiolenes.

Table 6 Bond lengths (Å) of [Cu(BDDT)$_2^-$]*

Cu-S(1)	2.190(1)	Cu-S(2)	2.180(1)
Cu-S(1A)	2.190(1)	Cu-S(2A)	2.180(1)
S(1)-C(1)	1.751(3)	S(2)-C(6)	1.746(4)
S(3)-C(5)	1.851(5)	S(3)-C(6)	1.751(3)
S(4)-C(1)	1.763(4)	S(4)-C(2)	1.816(5)
C(1)-C(6)	1.330(6)	C(2)-C(3)	1.506(7)
C(3)-C(4)	1.522(7)	C(4)-C(5)	1.529(7)

* Bond lengths of the cation([$(C_2H_5)_4N]^+$) are available in the supplementary data.

Table 7 Bond angles (°) of [Cu(BDDT)$_2$]$^-$*

S(1)-Cu-S(2)	91.4(1)	S(1)-Cu-S(1A)	180.0(1)
S(1)-Cu-S(1A)	88.6(1)	S(1)-Cu-S(2A)	88.6(1)
S(2)-Cu-S(2A)	180.0(1)	S(1A)Cu-S(2A)	91.4(1)
Cu-S(1)-C91)	103.2(1)	Cu-S(2)-C(6)	103.3(1)
C(5)-S(3)-C(6)	100.3(2)	C(1)-S(4)-C(2)	102.0(2)
S(1)-C(1)-S(4)	114.5(2)	S(1)-C(1)-C(6)	120.6(3)
S(4)-C(1)-C(6)	124.9(2)	S(4)-C(2)-C(3)	117.2(4)
C(2)-C(3)-C(4)	115.8(3)	C(3)-C(4)-C(5)	115.1(4)
S(3)-C(5)-C(4)	114.6(3)	S(2)-C(6)-S(3)	115.1(2)
S(2)-C(6)-C(1)	121.2(2)	S(3)-C(60)-C(1)	123.5(3)

* Bond angles of the cation([$(C_2H_5N]^+$) are available in the supplementary data.

Table 8 Key bond angles and distances in $[(C_2H_5)_4N][Ni(DDDT)_2]$, $[(C_2H_5)_4N][Ni(PDDT)_2]$ and $[(C_2H_5)_4N]N_1(BDDT)_2$

	DDDT	PDDT	BDDT
average endocyclic angle			
C = C-S	127.7°(5)	124.2°(2)	122.8°(10)
average exocyclic angle			
S-C-S	112.5°(4)	116.1°(2)	117.3°(8)
C = C-S	119.9°(5)	119.5°(3)	119.9°(10)
bond distances			
C = C	1.339Å(11)	1.363Å(4)	1.355Å(35)
C-S (coordinated S)	1.735Å(8)	1.726Å(3)	1.719Å(13)

Key bond angles and distances in $[(C_2H_5)_4N][Cu(DDDT)_2]$, $[(C_2H_5)_4N][Cu(PDDT)_2]$ and $[(C_2H_5)_4N][Cu(BDDT)_2]$

	DDDT	PDDT	BDDT
average endocyclic angle			
C = C-S	121.3°(7)	120.9°(2)	120.9°(3)
average exocyclic angle			
S-C-S	111.9°(5)	114.8°(2)	114.8°(2)
C = C-S	126.8°(7)	124.4°(2)	124.2°(3)
bond distances			
C = C	1.342Å(12)	1.336Å(4)	1.350Å(6)
C-S (coordinated S)	1.745Å(9)	1.750Å(3)	1.749Å(4)

Both complexes of BDDT show redox behavior which is significantly different from the MNT complexes especially in the reduction wave. The redox behavior is also different from that of complexes with PDDT and DDDT. Since the structures of the anions are somewhat similar, this is surprising.

The observation that the copper(III) complex of the BDDT ligand shows redox behavior which is the most different from that of MNT complexes is interesting. We have previously noted[29] that the relative ability of dithiolenes to accept electron density in copper complexes was

MNT>DDDT>PDDT

Table 9 Bond distances (Å) for selected $[CuL_2]$-ditholene complexes

Ligand(L)	M-S	S-C[a]	C = C	C-S[b]	ΔD[c]	ref.
BDDT	2.185(1)	1.749(4)	1.330(6)	1.757(4)	0.008	
PDDT	2.182(1)	1.749(4)	1.337(5)	1.754(4)	0.005	29
DDDT	2.185(3)	1.745(9)	1.320(13)	1.772(3)	0.031	19

Bond distances (Å) for selected $[NiL_2]^-$ dithiolene complexes

Ligand(L)	M-S	S-C[a]	C = C	C-S[b]	ΔD[c]	ref.
BDDT	2.152(4)	1.719(13)	1.355(35)	1.768(13)	0.049	
PDDT	2.148(1)	1.726(3)	1.357(4)	1.758(3)	0.032	29
DDDT	2.148(2)	1.735(8)	1.339(11)	1.768(8)	0.033	19

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

Table 10 Cyclic voltammetry parameters for selected $[ML_2]^{n-}$ dithiolene complexes

Compound	$E_{1/2}$,V n:1⇌2	n:0⇌1	ref.
$[Cu(BDDT)_2]^-$	- 0.81	+ 0.54	
$[Cu(PDDT)_2]^-$	- 0.56		29
$[Cu(DDDT)_2]^-$	- 0.49	+ 0.38	19
[Cu(*dmit*)$_2$]	- 0.07		32
$[Cu(MNT)_2]^-$	+ 0.37		31
$[Ni(BDDT)_2]^-$	- 0.70	+ 0.29	
$[Ni(PDDT)_2]^-$	- 0.60	+ 0.30	29
$[Ni(DDDT)_2]^-$	- 0.81	+ 0.014	19
$[Ni(MTDT)_2]^-$	- 0.67	+ 0.10	33
[Ni(*dmit*)$_2$]$^-$	- 0.19		32
$[Ni(MNT)_2]^-$	+ 0.259	+ 1.049	31

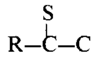
and it appears the BDDT ligand complex falls after $PDDT^{2-}$. This behavior is not the same as observed for the nickel complexes where the order was

MNT>PDDT>DDDT

The nickel complex of BDDT falls between PDDT and DDDT. Based on the results reported herein, the greatest *electronic* effect appears to be with the copper complexes, while the greatest *structural* effect is with the nickel complex.

Optical and infrared absorption maxima were obtained for each complex and are presented in Table 11. The infrared spectra contain all of the features of 1,2-dithiolenes. The C = C vibration near 1470 and 1480 cm^{-1} are both higher than the PDDT complexes of nickel and copper, respectively, which were both reported at 1445 cm^{-1}. Again, these data support the apparent increased delocalization in these complexes, perhaps more accurately than the crystallographic results. The optical transitions are essentially all charge transfer bands.

Table 11 Frequencies(cm^{-1}) and assignments of the bands observed in the infrared spectra of the complex $[(C_2H_5)_4N][M(BDDT)_2]$ as well as absorption maxima in the optical spectra

$[(C_2H_5)_4N][Ni(BDDT)_2]$	$[(C_2H_5)_4N][Cu(BDDT)_2]$	Assignments
1470(s)	1480(vs)	C=C
1286(s)	1302(s)	C=S
880(m)	890(s)	 $R{-}\overset{\overset{S}{|}}{C}{-}C$
860(m)	870(s)	
445(m)	430(m)	M-S
385(m)	380(m)	

UV/vis absorption maxima in DMF

Ni(BDDT)$_{2-}$ ε(M^{-1}cm^{-1})	ν(cm^{-1})	Cu(BDDT)$_{2-}$ ε(M^{-1}cm^{-1})	ν(cm^{-1})
1.49 × 10^4	(47600)	2.34 × 10^4	(37000)
2.62 × 10^4	(37000)	1.33 × 10^4	(33600)
2.14 × 10^4	(32500)	7.21 × 10^3	(28700)
2.10 × 10^4	(29100)	3.31 × 10^4	(20200)
1.78 × 10^4	(25000)		
1.54 × 10^3	(18400)		

SUMMARY

Taken together, the structural, optical and electrochemical data indicate the increased ring size in the backbone of the 1,2-dithiolene has a modest electronic effect. We are currently attempting to prepare partially oxidized complexes, similar to those reported for dmit, in order to characterize any possible conductive properties.

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Supplementary Material

Listing of structural parameters, hydrogen atom coordinates and isotropic thermal parameters, packing diagrams, atomic coordinates, bond distances and angles for the $[(C_2H_5)_4N]^+$ cation in both structures are available from the authors upon request.

References

1 G.N. Schrauzer and V.P. Mayweg, *J. Am. Chem. Soc.* **87**, 3585 (1965).
2. H.B. Gray, R. Williams, I. Bernal, and E. Billing, *J. Am. Chem. Soc.* **84**, 3596 (1962).
3. R. Williams, E. Billing, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.* **88**, 43 (1966).
4. P.I. Clemenson, *Coord. Chem. Rev.* **106**, 171 (1990).
5. M.R.A. Blomberg and U. Wahlgren, *Chem. Phys.* **49**, 117 (1980).
6. I. Fisher-Hjalmars and A. Henricksson-Enflo, *Adv. Quantum Chem.* **16**, 1 (1982).
7. J. Schultz, H.H. Wang, L.C, Soderholm, T.L. Sifter, J.M. Williams, K. Bechgaard, and M-H. Whangbo, *Inorg. Chem* **26**, 3757 (1987).
8. (a) R. Kirmse, J. Stach, W. Dietsch, G. Steimecke, and E. Hoyer, *Inorg. Chem.* **19**, 2679 (1980). (b) R. Bereman, K. Proctor, G. Chung and B. Knight, unpublished result.
9. P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark, and A.E. Underhill, *Coord. Chem. Rev.* **110**, 115 (1991).
10. V.E. Shklover, S.S. Nagapetyan, and Y.T. Struchkov, *Russ Chem. Rev.* **59**, 686 (1990).
11. R-M. Olk, B. Olk, W. Dietzsch, R. Kirmse, and E. Hoyer, *Coord. Chem. Rev.* **117**, 99 (1992).
12. A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, *Chem. Lett.* 1819 (1987).
13. H. Kim, A. Kobayashi, Y. Sasaki, R. Kato, and H. Kobayashi, *Chem. Lett.* 1799 (1987).
14. A. Kobayashi, H. Kobayashi, A. Miyamoto, R. Kato, R.A. Clark, and A.E. Underhill, *Chem. Lett.*, 2163 (1991).
15. H. Kobayashi, K. Bun, T. Naito, R. Kato, and A. Kobayashi, *Chem. Lett.*, 1909 (1992).
16. S. Alvarez, R. Vincente and R. Hoffmann, *J. Am. Chem. Soc.* **107**, 6253 (1985).
17. (a) W.F. Cooper, N.C. Kenny, J.W. Edmonds, A. Nagel, F. Wudl, and P. Coppens, *J. Chem. Soc. Chem. Commun.*, 889 (1971). (b) T.E. Phillips, T.J. Kistenmacher, J.P. Ferraris, and D.O. Cowan, *J. Chem. Soc., Chem. Commun.* 471 (1973).
18. U. Geiser, A.J. Schultz, H.H. Wang, M.A. Beno, and J.M. Williams, *Acta Cryst.* **C44**, 259 (1988).
19. C.T. Vance, R.D. Bereman, J. Bordner, W. Hatfield, and J. H. Helms, *Inorg. Chem.* **24**, 2905 (1985).
20. *International Table for X-ray Crystallography* (Kynoch: Birmingham, England, 1974) Vol. IV. pp 71-102.
21. *"SHELXTL"; X-Ray Instruments Group, Nicolet Instrument Corp.* (Madison, WI 53711, 1983).

22. C.K. Johnson, *ORTEP-II: A Fortran Thermal-Ellipsoid Plot Program For Crystal Structure Illustrations ORNL-5L38* (National Technical Information Service: Springfield, VA, 1876).
23. J.H. Welch, P. Singh, and R.D. Bereman, *Inorg. Chem.* **27**, 3680 (1988).
24. J.H. Welch, P. Singh, and R.D. Bereman, *Inorg. Chem.* **27**, 2682 (1988).
25. J.H. Welch, R.D. Bereman, P. Singh, and C. Moreland, *Inorg. Chim. Acta* **158**, 17 (1989).
26. J.H. Welch, R.D. Bereman, and P. Singh, *Inorg. Chim Acta* **163**, 93 (1989).
27. J.H. Welch, R.D. Bereman, P. Singh, D. Haase, W. Hatfield, and M. Kirk, *Inorg. Chim. Acta* **162**, 89 (1989).
28. J.H. Welch, R.D. Bereman, and P. Singh, *Inorg. Chem.* **29**, 68 (1990).
29. R.D. Bereman and H. Lu, *Inorg. Chim. Acta* **204**, 53 (1993).
30. O. Lindquist, L. Andersen, J. Sieler, G. Steimecke, and E. Hoyer, *Acta Chem. Scand. Ser A A36,* **10**, 855 (1982).
31. J.A. McCleverty, *Prog. Inorg. Chem.* **10**, 84 (1968).
32. G. Steimecke, H.-J. Sieler, R.Kirmse, and E. Hoyer, *Phosphorus and Sulfur 7* 49 (1979).
33. C.T. Vance and R.D. Bereman, *Inorg. Chim. Acta* **149**, 229 (1988).