Inorg. Chem. **1985**, *24*, 2905–2910 **2905**

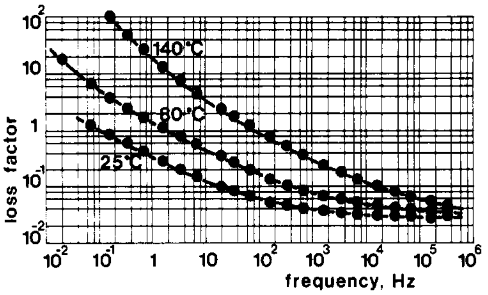

Figure 9. Loss factor vs. frequency from isothermal dc data.

compound. On the contrary, the loss factor increases to very high values with decreasing frequency and increasing temperature, as can be seen in Figure 8. The tendency of the slope to unity for the highest temperature (140 °C) and frequencies below 10 Hz is noteworthy. The low value of the apparent activation energy of conduction and the dielectric absorption increasing with increasing temperature and decreasing frequency, with the slope approaching unity at 140 °C, point out an ionic mechanism of conduction.[11,30-33] The same is supported by the relaxation phenomenon found below $\sim 10^{-2}$ Hz by the Hamon treatment of the isothermal dc data,[9-11] as can be seen in Figure 9. This relaxation process is temperature activated and may be ascribed to polarization effects of the Maxwell–Wagner–Sillars type due to crystal interfaces in these polycrystalline samples.[31-33]

Charge carriers might be identified in protons coming from hydrogen bonding of molecules in the material, according to the stacking of molecular units in the crystals. The conduction transiton near 60 °C could arise from molecular phenomena associated with proton dissociation and hopping in crystal lattice.

Conclusions. Our dimeric copper(II) chloride salt exhibits a new stacking pattern previously not observed in copper oligomers. The direction of displacements alternates as one progresses along the stack, leading to a net displacement always parallel to the Cu–Cu direction. The coordination geometry of the Cu(II) ions in the noncentrosymmetric $Cu_2Cl_6^{2-}$ dimers is probably best described as distorted square pyramidal (4 Cu–Cl = 2.3 Å; 1 Cu–Cl = 2.7 Å).

Magnetically, the system behaves as a chain of ferromagnetically coupled antiferromagnetic ($S = 0$ ground state) dimers. The intradimer interaction of $\Delta E/k = 54$ K is consistent with the results of other $Cu_2Cl_6^{2-}$ dimers that are nearly planar and have net antiferromagnetical coupling between the copper ions. Detailed analysis of the magnetostructural correlations is not possible due to the complexity of the structure and to the approximate nature of the magnetic analysis. Finally, the material behaves as an electrical insulator whose small dc conductivity is explainable[6] on the basis of an ionic mechanism of conduction while dipolar relaxation processes do not appear to be meaningful. The principal charge carriers seem to be the protons associated with the hydrogen network in the crystal, which arises from molecular stacking in the crystals.

Acknowledgment. This work was supported in part by NSF Grants DMR-8219430 and INT-8219425 and in part by a contribution of the Ministero della Pubblica Istruzione of Italy. The assistance of Professor C. P. Landee with the magnetic data collection is gratefully acknowledged.

Registry No. $(melH_2)Cu_2Cl_6$, 94007-98-4.

Supplementary Material Available: Listings of the thermal parameters for the atoms of the title complex, observed and calculated structure factors, torsion angles for the $Cu_2Cl_6^{2-}$ anion chain, and deviations of atoms from least-squares planes and TG and DSC figures (26 pages). Ordering information is given on any current masthead page.

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Synthesis and Coordination Chemistry of a New 1,2-Dithiolene Containing the Tetrathioethylene Unit[†]

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and JEFFERY H. HELMS[§]

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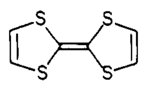
The synthesis and characterization of a new 1,2-dithiolene ligand, the dipotassium salt of 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT), are reported. This salt reacts with Ni(II) in methanol to yield the apparent Ni(III) product, $Ni(DDDT)_2^-$, which was isolated as the tetraethylammonium salt. A single-crystal structural study on this complex was carried out. Crystals belong to the monoclinic space group $C2/c$ with $a = 22.297$ (4) Å, $b = 8.152$ (1) Å, $c = 17.103$ (3) Å, $\beta = 129.31$ (1)°, $R = 5.1\%$ for 1168 reflections, and ρ(calcd) = 1.518 ρ(obsd) = 1.52, for $Z = 4$. The structure was solved by a combination of Patterson, Multan, Fourier, and least-squares techniques. The Ni atoms are located on crystallographic centers of symmetry. The average Ni–S distance of 2.148 (2) Å is very close to those of other monoanionic nickel dithiolenes. Single-crystal ESR data gave the principal g value assignments of $g_{zz} = 2.022$ (1), $g_{xx} = 2.057$ (1), and $g_{yy} = 2.119$ (1). A solution and frozen-glass ESR study of the ^{61}Ni-enriched complex yielded the hyperfine splitting values (in gauss) of $\langle A\rangle_0 = 4.5$, $A_{zz} < |0.2|$, $A_{yy} = |2.4\ (3)|$, and $A_{xx} = |14.2\ (3)|$. A variable-temperature magnetic study showed antiferromagnetic behavior ($J = -8.5$ cm^{-1}) with long-range magnetic ordering below 15 K. The structural data, ESR data, and magnetic data when taken together support a highly delocalized π HOMO.

Introduction

Over the past 10 years, the organic chemistry of sulfur has been highly influenced by the unique physical properties of tetrathiafulvalene (TTF).[1-4] The early proposal by Wudl[5] and others that the TTF framework might yield the prerequisite properties necessary to yield an "organic metal", coupled with the recent findings that bis(tetramethyltetraselenafulvalenium) perchlorate is a superconductor at 1 K,[6] has further increased the interest in



TTF

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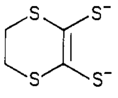
this area. At the same time, there has been a great deal of interest in inorganic complex based conducting species. Examples such as the partially oxidized tetracyanoplatinates have prompted many laboratories to explore new complexes in this area.[7] We have designed a scheme to combine the properties of the "TTF type" organosulfur molecules and the inorganic systems that have been recently studied. Since it is apparently the tetrathioethylene unit of TTF that is fundamentally important to that class of molecules, we have undertaken a synthetic program to investigate inorganic complexes of new ligands containing this subunit.

We report here the synthesis of the dianion 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT). This dianion also represents an



DDDT

unsaturated dithiolene, an area that has produced a great deal of interest in its own right.[8-10] The "Ni(III)" complex of this new ligand is reported along with a structural and magnetic study.

Experimental Section

Reagents. 2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-en-8-one (TTBEO) was prepared by literature methods[11] and characterized by NMR and melting point data. Tetraethylammonium hexafluorophosphate was prepared from the corresponding chloride by metathesis with KPF_6, recrystallized twice from water and once from methanol, and dried in vacuo at 140 °C. Tetraethylammonium bromide was purchased from Fisher Scientific Co., recrystallized from ethanol, and dried in vacuo at 140 °C prior to use. Nickel(II) chloride hexahydrate was purchased from Matheson Coleman and Bell was used without further purification. Ar was purchased from Air Products Inc. All solvents were dried by standard techniques prior to use. THF was dried over Na/benzophenone and was distilled prior to use. ^{61}Ni was obtained from Oak Ridge National Laboratory.

Procedures. All reactions were carried out under Ar with standard Schlenk techniques unless otherwise stated. Analyses were performed by Atlantic Microlabs, Atlanta, GA.

Syntheses. $K_2(C_4H_4S_4)$. TTBEO (5 g, 2.4×10^{-2} mol) was added to 200 mL of THF containing 9.6×10^{-2} mol of potassium ethoxide. A yellow-orange precipitate formed immediately; the mixture was stirred overnight, after which 100 mL of hexane was added and the precipitate collected, dried, and stored in a Schlenk tube until further use. Because of the extreme air sensitivity, an elemental analysis of K_2DDDT was not obtained: yield 90%; ^{1}H NMR (Me_2SO-d_6) 3.31 ppm (s, SCH_2CH_2S); ^{13}C NMR (Me_2SO-d_6) 116.1 (C=C), 34.7 ppm (SCH_2); IR (Nujol) 1665 (m), 1582 (w), 1510 (w), 1290 (s), 1135 (s), 1065 (m), 995 (s), 925 (s), 870 (m), 810 (s), 730 (s) cm^{-1}. The dianion is, however, fairly stable in alcohol solutions, and further reactions were carried out in methanol without the use of an Ar atmosphere.

$N(C_2H_5)_4Ni(C_4H_4S_4)_2$. A solution of 0.46 g ($1.9 \times 10^{-3}$ mol) of $NiCl_2 \cdot 6H_2O$ in 50 mL of methanol was added dropwise to 1.0 g (3.8×10^{-3} mol) of K_2DDDT in 100 mL of methanol. The solution color changed from amber to dark green as the reaction proceeded. The solution was stirred for 1 h, after which 1 equiv of tetraethylammonium bromide was added, and a dark green precipitate formed. The green solid was then collected by filtering and recrystallized from acetonitrile, yielding 0.5 g (50%) of pure product as dark green crystalline plates: mp 175–176 °C; IR (KBr) 1475 (m), 1415 (m), 1350 (s), 1290 (s), 1170 (s), 1130 (m), 1045 (m), 1008 (m), 920 (m), 885 (m), 855 (s), 775 (m), 475 (s), 410 (s) cm^{-1}. Anal. Calcd for $NiC_{16}H_{28}NS_8$: C, 34.97; H, 5.14; N, 2.55; S, 45.56. Found: C, 35.01; H, 5.12; N, 2.57; S, 46.77.

Table I. Single-Crystal X-ray Crystallographic Analysis

A. Crystal Parameters	
formula	$NiC_{16}H_{28}NS_8$ (M_r = 549.63)
crystallizn medium	acetonitrile
cryst size, mm	$0.06 \times 0.26 \times 0.27$
cell dimens	a = 22.297 (4) Å b = 8.152 (1) Å c = 17.103 (3) Å α = 90.0° β = 129.31 (1)° γ = 90.0° V = 2405.2 (6) Å^3
space group	$C2/c$
molecules/unit cell	4
density obsd, g/cm^3	1.52
density calcd, g/cm^3	1.518
linear abs coeff, cm^{-1}	73.2
μt_{min}	0.44
μt_{max}	2.78
B. Refinement Parameters	
no. of reflcns	1237
no. of nonzero reflcns ($I > 1.0\sigma$)	1168
R index = $\sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.051
$R_w = \sum(w^2\|F_o\|^2 - \|F_c\|^2)^2/\sum w^2\|F_o\|^4$	0.0107
GOF = $[\sum w(F^2 - F_c^2)^2/(m - s)]^{1/2}$	2.74
scale factor	0.930 (4)
secondary extinction coeff	1.8 (1) × 10^{-6}

Physical Measurements. The electrochemical instrumentation used and the procedures followed to obtain the voltammetric data have been described in detail elsewhere.[12] ESR spectra were recorded on a Varian E-3 spectrometer either at room temperature (single crystal) or at 100 K. IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer over the range 4000–300 cm^{-1}. Data were obtained from either KBr pellets or Nujol mulls.

Magnetic Measurements. Magnetic susceptibility data were collected with a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM) that was operated from zero field to 15 kOe by using procedures described earlier.[13] The VSM was calibrated with $HgCo(NCS)_4$,[14] and powdered samples of the calibrants and compound used in this study were contained in precision-milled Lucite sample holders. Approximately 150-mg amounts of each were used. Diamagnetic corrections for the constituent atoms were made by using Pascal's constants, and corrections for temperature-independent paramagnetism were estimated from tabulated data.[15-17]

Single-Crystal X-ray Analysis. A representative crystal was surveyed, and a 1-Å data set (maximum (sin θ)/λ = 0.5 Å^{-1}) was collected on a Syntex P$\bar{1}$ diffractometer. The diffractometer was equipped with a graphite monochromator and copper radiation (λ = 1.5418 Å). All diffractometer data were collected at room temperature. Atomic scattering factors for carbon, nitrogen, and sulfur were taken from ref 18; those for hydrogen, from Steward, Davidson, and Simpson;[19] and those for nickel, from Cromer and Mann.[20] Routine crystallographic calculations were facilitated by the CRYM computer library.[21] Pertinent crystal, data collection, and refinement parameters are summarized in Table I. Absorption corrections were made by the method of Gaussian quadrature.[22] A trial structure was obtained by the heavy-atom method.

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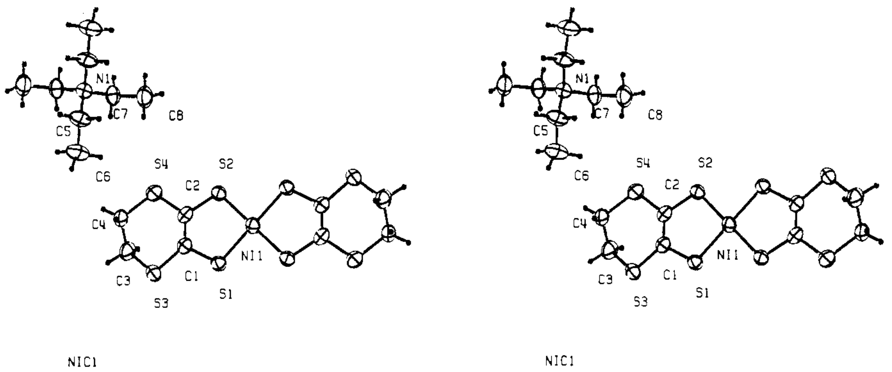

Figure 1. Stereo ORTEP diagram of the molecular structure of $N(C_2H_5)_4Ni(C_4H_4S_4)_2$.

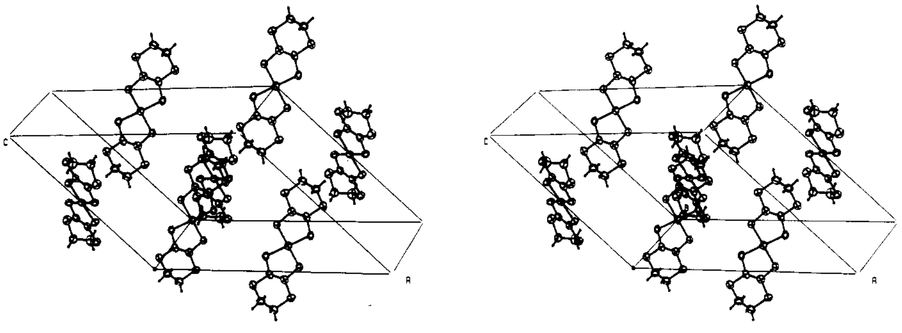

Figure 2. Stereo packing diagram for $N(C_2H_5)_4Ni(C_4H_4S_4)_2$ with tetraethylammonium ions removed.

The Ni and S atoms were located with use of the MULTAN program.[23] The nickel atoms occupied special positions. MULTAN was unable to conveniently locate any additional atoms. The remaining non-hydrogen atoms were located by conventional Fourier techniques to give a trial structure. This trial structure refined routinely. Hydrogen positions were calculated wherever possible. The methyl hydrogens were located by difference Fourier techniques. The hydrogen parameters were added to the structure factor calculations but were not refined. The final cycles of least-squares refinement contained the scale factor, secondary extinction coefficient, coordinates, and anisotropic temperature factors in a single matrix. The shifts calculated in the final cycle were all less than 0.0 of their corresponding standard deviation. The full-matrix routine minimized $\sum w(F_o^2 - F_c^2)^2$ where $w = 1/\sigma^2(F_o^2)$ on the basis of $\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (ds)^2$. The final R index was 0.051. A final difference Fourier revealed no missing or misplaced electron density. The refined structure was plotted with use of the ORTEP computer program of Johnson.[24] Hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material (Tables SI–III).

Interatomic distances and their standard deviations and bond angles and eds's are given in Table II. A stereoview with labeling of atoms within $[(C_2H_5)_4N][Ni(DDDT)_2]$ is shown in Figure 1. A stereoview of the molecular packing (with counterions removed for clarity) is shown in Figure 2, and a list of intermolecular contacts is shown in Table III. A comparison of the structural features of $Ni(DDDT)_2^-$ to other selected monoanionic nickel dithiolenes is shown in Table IV. Non-hydrogen coordinates are shown in Table V.

Results and Discussion

The synthesis of a new 1,2-dithiolene, dipotassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate, containing the tetrathioethylene unit has been achieved. This yellow salt as a *solid* is extremely air sensitive, even though we have found it to be stable for short periods of time *in solution* exposed to air. The formally nickel(III) complex of this ligand was prepared in methanol solution and isolated as the tetraethylammonium salt. If care is taken to exclude oxygen, the nickel(II) complex can easily be prepared. As might be expected, this brown nickel(II) complex is rapidly oxidized in solution to the green nickel(III) species by exposure to O_2.

Table II. Bond Distances (Å) and Angles (deg)

	Distances		
Ni1–S1	2.146 (2)	S4–C4	1.791 (6)
Ni1–S2	2.149 (2)	C1–C2	1.339 (11)
S1–C1	1.745 (8)	C3–C4	1.509 (13)
S2–C2	1.725 (6)	N1–C5	1.512 (9)
S3–C1	1.766 (6)	N1–C7	1.521 (8)
S3–C3	1.805 (9)	C5–C6	1.504 (12)
S4–C2	1.769 (8)	C7–C8	1.513 (10)
	Angles		
S2–N1–S1	91.2 (1)	C1–C2–S2	120.7 (5)
C1–S1–Ni1	104.6 (2)	C1–C2–S4	126.8 (5)
C2–S2–Ni1	104.4 (3)	C4–C3–S3	112.3 (5)
C3–S3–C1	101.8 (3)	C3–C4–S4	113.2 (5)
C1–S4–C2	102.2 (4)	C7–N1–C5	111.4 (4)
S3–C1–S1	112.4 (4)	C5[a]–N1–C5	105.6 (4)
C2–C1–S1	119.1 (4)	C7[a]–N1–C5	111.8 (4)
C2–C1–S3	128.5 (5)	C7[a]–N1–C7	105.0 (4)
S4–C2–S2	112.5 (4)		

[a] Atom generated by symmetry operation $\bar{x}, y, \bar{z} + {}^1/_2$.

Table III. Closest S–S Contacts (Å)

interlayer		interlayer	
$S3^B$–$S3^D$	4.49	$S4^B$–$S3^C$	3.98
$S2^C$–$S3^D$	4.99	$S3^A$–$S4^D$	3.98
$S3^B$–$S4^C$	5.38	$S4^B$–$S4^C$	4.25

Symmetry Operations

A: $-x + 1, -y + 1, -z + 1$

B: $x + 1, y, -z + {}^1/_2$

C: $x + {}^1/_2, y + {}^1/_2, z$

D: $x + {}^1/_2, -y + 1{}^1/_2, z + {}^1/_2$

$Ni(DDDT)_2^-$ displays a very rich IR spectrum with all five characteristic absorptions of monoanionic nickel dithiolenes present:[25] ν_1, C⩦C at 1415 cm^{-1}; ν_2, C⩦S at 1170 cm^{-1}; ν_3,

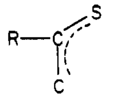

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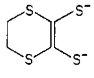
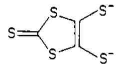
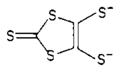
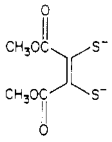
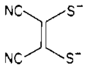
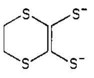
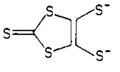
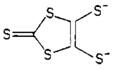
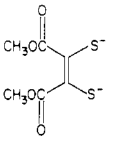
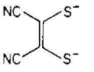
Table IV. $[NiL_2]^{n-}$ Distances (Å)

ligand L	M-S	S-S (intra)	S-S (inter)	S-C	C-C (chelate ring)	ref
 n=1	2.148 (2)	3.068 (3)	3.004 (3)	1.735 (8)	1.339 (11)	*a*
 n=1	2.156 (3)	3.137^f	2.962^f	1.72 (1)	1.35 (1)	*b*
 n=2	2.216 (6)	3.1935^f	3.085^f	1.75^f	1.39^f	*c*
 n=1	2.129 (6)	3.060 (9)	2.965 (8)	1.711 (8)	1.327 (8)	*d*
 n=1	2.147 (4)	3.095 (3)	2.967 (3)	1.714 (4)	1.356 (7)	*e*

ligand L	S-M-S (intra-ring)	M-S-C	S-C-C
 n=1	91.2 (1)	104.5 (2)	119.9 (5)
 n=1	93.2 (1)	102.1 (4)	121.4 (8)
 n=2	92.2^f	103.5^f	120.5^f
 n=1	92.15^f	104.9 (2)	120.2 (4)
 n=1	92.4 (1)	103.3 (3)	120.6 (5)

[a] This work. [b] Lindquist, O.; Andersen, L.; Sieler, J.; Steimecke, G.; Hoyer, E. *Acta Chem. Scand., Ser. A A36* **1982,** *10,* 855. [c] Lindquist, O.; Sjölin, L.; Sieler, J.; Steimecke, G.; Hoyer, E. *Acta Chem. Scand., Ser. A A33* 1979, *6,* 445. [d] Brown, R. K.; Bergendahl, T. J.; Wood, J. S.; Waters, J. H. *Inorg. Chim. Acta* **1983,** *68,* 79. [e] See ref 8, pp 77–78. [f] Standard deviations not reported.

Table V. Coordinates ($\times 10^4$) and Their Standard Deviations

	x/a	*y/b*	*z/c*
Ni1	5000 (0)	5000 (0)	5000 (0)
S1	4545 (1)	5137 (2)	3459 (1)
S2	3961 (1)	6073 (2)	4611 (1)
S3	3142 (1)	6254 (2)	1509 (1)
S4	2468 (1)	7239 (2)	2823 (1)
C1	3626 (3)	6001 (7)	2811 (4)
C2	3376 (3)	6381 (7)	3323 (4)
C3	2348 (4)	7580 (9)	1124 (5)
C4	1925 (3)	6977 (8)	1491 (5)
N1	0 (0)	5453 (8)	2500 (0)
C5	168 (4)	4332 (8)	1955 (5)
C6	364 (4)	5158 (9)	1357 (5)
C7	680 (3)	6588 (7)	3228 (4)
C8	1434 (4)	5768 (9)	4075 (5)

at 855 cm^{-1}; ν_4 and ν_5, Ni–S at 410 and 475 cm^{-1}, respectively.

As expected, a cyclic voltammogram of $Ni(DDDT)_2^-$ revealed two well-defined reversible waves (Table VI). The first is at +0.014 V vs. Ag/AgCl and represents the neutral to monoanion reduction, and the second, at −0.81 V, represents the monoanion to dianion reduction.

On the basis of a single-crystal ESR study of $Ni(mnt)_2^-$,[26] the principal *g* values have been assigned. The lowest *g* value, near 2, was shown to be g_z which led to an assignment of a $^2B_{2g}$ ($(XY)^2(YZ)^1$) ground state. Since there is a rather large intermolecular distance between the Ni(III) atoms (8.152 (1) Å in this structure, we aligned a pure single crystal in an ESR cavity to see if it was possible to determine the assignment of the three *g* values observed in a frozen glass. Even though a slight line broadening was observed, g_z was also clearly the lowest *g* value.

In order to obtain more information from spin-Hamiltonian parameters, we synthesized the ^{61}Ni derivative of $Ni(DDDT)_2^-$. A frozen-glass ESR study of the ^{61}Ni-enriched complex revealed a rhombic **g** tensor with $g_x = 2.119$, $g_y = 2.057$, and $g_z = 2.022$. $|A|$ values in gauss are as follows: $A_x = |14.2|$, $A_z < |0.2|$. Isotropic values are $\langle g \rangle_0 = 2.057$ and $\langle A \rangle_0 = |4.5|$.

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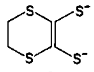
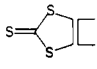
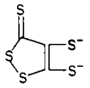
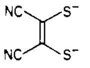
(26) Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580.

Table VI. Cyclic Voltammetry Parameters for Selected $[NiL_2]^{n-}$ Dithiolene Compounds

	$E_{1/2}$, V		
ligand L	n: $1 \rightleftharpoons 2$	n: $0 \rightleftharpoons 1$	ref
	−0.81	+0.014	*a*
	−0.19		*b*
	−0.07		*c*
	+0.259	+1.05	*d*

[a] This work (DMF, vs. Ag/AgCl, 100 mV/s). [b] Steimecke, G.; Sieler, H. J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49 (CH_3CN, vs. SCE) (n: $0 \rightleftharpoons 1$ not reported). [c] Steimecke, G.; Sieler, H. J.; Kirmse, R.; Dietzsch, W.; Hoyer, E. *Phosphorus Sulfur* **1982**, *12*, 237 (CH_3CN, vs. SCE) (n: $0 \rightleftharpoons 1$ not reported). [d] See ref 8, pp 84–86 (DMF, vs. Ag/AgCl).

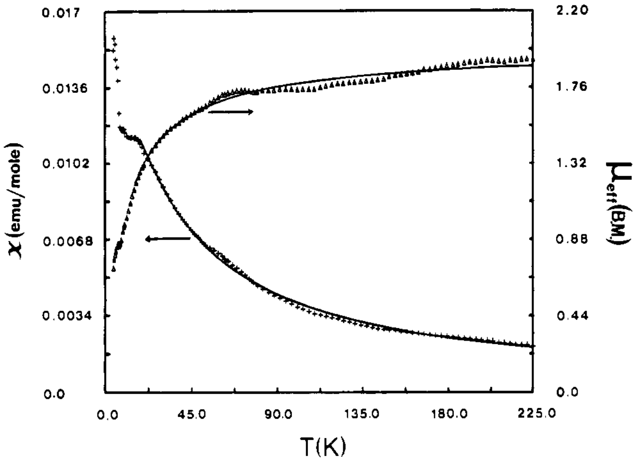


Figure 3. Magnetic susceptibility and magnetic moment of $[(C_2H_5)_4N][Ni(DDDT)_2]$ collected at 10 kOe. The data were dependent on the applied magnetic field below 15 kOe. The solid line through the data was calculated with quadratic-layer theory as described in the text.

Magnetic susceptibility and magnetization measurements were made on several samples of the compound. All measurements were in good agreement. Magnetic moments and magnetic susceptibility data, displayed in Figure 3, show three interesting features. First, the high-temperature magnetic moment is 1.9 μ_B, as expected for a doublet state arising from nickel(III). Next, there is a decrease in the magnetic moment with temperature, indicative of antiferromagnetic intermolecular interactions. At approximately 15 K, there is an abrupt change in the magnetic susceptibility, and below this temperature, the magnetic susceptibility becomes markedly dependent on the applied magnetic field. The abrupt change in magnetic susceptibility and the field dependence of the data below the temperature suggest long-range magnetic ordering.

Inspection of the stereoview (Figure 2) of molecular packing reveals a layered structure. As shown in Table III, there are short intermolecular contacts, and these apparently must transmit superexchange interactions within the plane.

In view of the structural results, the theory developed by Lines[27] for the quadratic-layer antiferromagnet was adopted for the description of the magnetic susceptibility data above 20 K. Using the Hamiltonian

$$\mathcal{H}_{ex} = -\sum_{nn} J\hat{S}_i \cdot \hat{S}_j \qquad (1)$$

in which the summation runs over pairs of nearest neighbors of spins i and j, Lines has shown that the reduced magnetic susceptibility for the quadratic layer is given by

$$\chi_0 J = (1/3\theta)[1 - \sum_{i=1}^{\infty} B_i/\theta^i] \qquad (2)$$

where $\chi_0 = \chi_m/Ng^2\mu_B$, $\theta = kT/JS(S+1)$, and coefficients B_i are available for $i \leq 10$. Here, to adhere with current convention, $-J$ designates an antiferromagnetic interaction. Since interplanar interactions were evident from the abrupt change in magnetic susceptibility near 15 K, a molecular field term was added to eq 2, yielding for the magnetic susceptibility

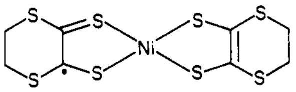
$$\chi = \chi_M/(1 - [2ZJ'\chi/Ng^2\mu_B^2]) \qquad (3)$$

Equation 3 was fit to the magnetic susceptibility data with the use of Simplex nonlinear fitting routine. The function that was minimized in curve fitting was

$$R = \sum_i (\chi_i^{obsd} - \chi_i^{calcd})^2/(\chi_i^{obsd})^2$$

The solid lines in Figure 3 were generated with the best-fit parameters $J = -8.5$ cm^{-1}, $J' = -3.4$ cm^{-1} (assuming, on the basis of the structural data, that $Z = 4$), and $g = 2.27$.

The structural results show that the gross geometry of $[(C_2H_5)_4N][Ni(DDDT)_2]$ is similar to that of other monoanionic nickel dithiolenes. That is, the local NiS_4 D_{2h} symmetry, the average Ni–S bond distance 2.148 (2) Å, the C–C chelate ring distance 1.339 (11) Å, and all other bond distances and angles are fairly typical (Table II). There are, however, several structural features of note. The Ni atom sits on an inversion center; therefore, the NiS_4 core is planar. As it turns out the entire anion unit is planar with the exception of the outer ethylene units. Unlike the case for $Ni(mnt)_2^-$, there is no stacking of molecules in the solid state (the nearest Ni–Ni distance is 8.152 Å) even though the layered structure is present. The existence of this layered structure and close S–S contacts (<4 Å) has profound effects on the magnetic properties of this compound. Finally, it can be seen that the C2–S2 and C1–S1 distances are shorter than the C2–S4 and C1–S3 distances, respectively. This is not surprising since resonance structures with the ligand in the radical form allow for a partial C1–S1 and C2–S2 double bond.



By analogy with the results of Maki et al.[26] on the ^{61}Ni-enriched $Ni(mnt)_2^-$, it is predicted that $Ni(DDDT)_2^-$ has a $^2B_{2g}$ ground state composed of metal d_{yz} orbital contribution and out-of-plane sulfur $2p_z$ orbitals. We confirmed this using equations from Maki's treatment for a d_{yz} ground state that relate g and A values to the bonding parameters P and K through configurational excitation energies C_i:

$$g_{xx} = 2 - 6C_1 = 2C_3 \qquad g_{yy} = 2 - 2C_4 \qquad g_{zz} = 2 - 2C_2$$

$$A_{xx} = P[-6C_1 - 2C_3 - K - 4/7 - 3/7(C_2 + C_4)]$$
$$A_{yy} = P[-2C_4 - K + 2/7 + 3/7(C_1 + C_2 - C_3)]$$
$$A_{zz} = P[-2C_2 - K + 2/7 + 3/7(C_3 - C_1 - C_4)]$$

Here P is defined as $g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$ and K as $-2/3\chi(g_e g_N \beta_e \beta_N/hca_0^3)/P$, the Fermi contact term, A values are in cm^{-1}, and C_1–C_4 are equal to the effective spin–orbit coupling constant divided by the energy difference between the ground state and the appropriate excited state.

Using this treatment for various ground-state possibilities, we found $d_{yz}^1 d_{xy}^0$ most reasonable. Using the reduction of P from its free-ion value as measure of covalency, we calculated the ratio P/P_0, a measure of the metal spin density. A summary of these data is shown in Table VII. The value of P/P_0 for $Ni(DDDT)_2^-$ of 0.21 is very similar to those of other monoanionic nickel dithiolenes. That is, they all have highly delocalized ground states.

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(27) Lines, M. E. *J. Phys. Chem. Solids* **1970**, *31*, 101–116.

Table VII. ESR Results for Nickel Dithiolenes[a]

	g_1	g_2	g_3	A_1	A_2	A_3	A_{iso}	P/P_0	K	ref
Ni(DDDT)_2^-	2.119	2.057	2.022	(−)14.2	(+)2.4	<2	(−)4.5	0.21	0.25	*b*
Ni(mnt)_2^-	2.160	2.042	1.988	(−)15	(+)2.9	<2	(−)4.6	0.24	0.21	*c*
Ni(dmit)_2^-	2.105	2.041	2.001	(+)13	(−)5.3	4.5		0.22	0.13	*d*

[a] *A* values in gauss. [b] This work. [c] Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580. [d] Kirmse, R.; Stach, J.; Dietsch, W.; Steimecke, G.; Hoyer, E. *Inorg. Chem.* **1980**, *19*, 2679.

The high-temperature magnetic moment of 1.9 μ_B confirms the assignment of the formal oxidation state III to nickel in $[(C_2H_5)_4N][Ni(S_4C_4H_4)_2]$ as implied by the chemical formula. There is marked decreased in magnetic moment at low temperatures as a result of intermolecular magnetic interactions. These interactions are transmitted by a superexchange network provided by short sulfur–sulfur contacts at 3.98 Å in the layer structure and lead to a two-dimensional magnetic system.

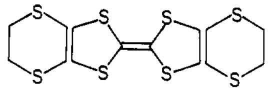
The magnetic data may be described by Line's theory for a two-dimensional magnetic system (eq 2) modified with a mean-field corrosion to account for interplanar interactions. The *g* value is expected to be greater than the free-electron *g* value since the electronic configuration has a greater than half-filled shell. There is a significant deviation of the *g* value deduced from the magnetic measurements and that obtained from the ESR studies at room temperature. It is conjectured that the difference arises from intermolecular interactions, which become increasingly important in determining the bulk magnetic properties at lower temperatures.

There are no precedents to guide the interpretation of the exchange coupling constant of -8.5 cm^{-1} (antiferromagnetic interaction), but the value for this constant deduced from eq 3 permits a reasonable description of the data as shown by the best-fit line in Figure 3. The transition to the ordered state occurs at a rather high temperature especially when viewed in sight of the interlayer nickel–nickel separation of 8.152 Å. We consider the shortest interlayer separation of 4.5 Å (see Table III) to be large and conclude that the magnetic data suggest that there is significant delocalization of electron density onto the ligand. This delocalization decreases the electronic $\langle r_{ij} \rangle$ and leads to an enhancement of magnetic interactions. The chemical consequences of the electronic delocalization are discussed elsewhere in this paper.

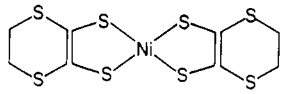
Conclusions

K_2DDDT represents only the second ligand system to date containing the tetrathioethylene unit. A comparison of the spin-Hamiltonian parameters of Ni(DDDT)_2^- and Ni(dmit)_2^-[28] (Table VII), which also contains the tetrathioethylene unit, reveals that both complexes have the same type of highly delocalized π MO as the HOMO. The molecular structures of the compounds are also very similar. One interesting difference between the two is their redox behavior. Ni(dmit)_2^- is as much more easily reduced to the dianion than is Ni(DDDT)_2^-. A simple explanation for this lies in the greater electron-accepting ability of the thioketone function in dmit^{2-} as compared to the ethylene unit in DDDT^{2-}.

Finally, the recent discovery of the first S-based organic superconductor,[29] $(\text{BEDT-TTF})_2\text{ReO}_4$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene), has further stimulated our interest in this ligand system. We believe our DDDT^{2-} compounds have many of the same physical characteristics that allow $(\text{BEDT-TTF})_2\text{ReO}_4$ to be superconducting. For example, both molecules are planar and are approximately the same size; also, both molecules have a two-dimensional layered type structure with close sulfur–sulfur contacts. Finally, BEDT-TTF exists as a partially oxidized radial cation while Ni(DDDT)_2^- is a fully oxidized radical anion. Ultimately, we hope to take advantage of these properties in our search for new highly conducting materials.



BEDT-TTF



Ni(DDDT)_2^-

Acknowledgment. We wish to express gratitude to David E. Morris of this department for collecting the voltammetric data on Ni(DDDT)_2^-. This work was supported by the donors of the Petroleum Research Fund, administed by the American Chemical Society (R.D.B.).

Registry No. TTBEO, 74962-29-1; $N(C_2H_5)_4Ni(DDDT)_2$, 97337-12-7; Ni(DDDT)_2^{2-}, 97337-13-8; Ni(DDDT)_2, 97337-14-9; K_2(DDDT), 97337-15-0.

Supplementary Material Available: Listings of hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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(28) Kirmse, R.; Stach, J.; Dietzch, W.; Steimecke, G.; Hoyer, E. *Inorg. Chem.* **1980**, *19*, 2679.

(29) Parkin, S. R.; Engler, E. M.; Schumaker, R. R.; Lagier, R.; Lee, V. Y.; Scott, J. C.; Greene, R. L. *Phys. Rev. Lett.* **1983**, *50*, 270.