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Synthesis and Characterization of Tetraalkylammonium Salts of Bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)cobaltate(III). Crystal Structure of $[(C_4H_9)_4N]_2[Co(DDDT)_2]_2$

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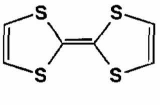
Abstract

The reaction between $CoCl_2 \cdot 6H_2O$ and K_2DDDT (the potassium salt of 1,2-dithiolene 5,6-dihydro-1,4-dithiin-2,3-dithiolate) under an argon atmosphere yields a dimeric dianion which can be isolated as a tetraalkylammonium salt. Constant potential electrolysis of the formally Co(III) product yields a Co(II) species. Both complexes are extremely sensitive to air in solution. The solid Co(III) product, however, is sufficiently air stable to allow a structural analysis of the tetrabutylammonium salt. The crystal belongs to the monoclinic space group *C*2/*c* with unit cell dimensions of $a = 23.626(3)$, $b = 16.915(3)$, $c = 16.294(2)$ Å, $\beta = 101.62(1)°$, $Z = 8$. The coordination around the cobalt atom is best described as square pyramid with an average basal Co–S bond length of 2.197(1) Å and an apical Co–S distance of 2.328(1) Å. The dimeric structure allows for S···S contacts in the crystal lattice as short as 3.22 Å. The structure refined to $R = 0.037$ and $R_w = 0.053$. The frozen glass ESR spectrum of the Co(II) complex exhibits three sets of eight lines with $g_1 = 1.933$, $g_2 = 2.067$ and $g_3 = 2.860$. A cyclic voltammogram contains a two-electron reversible wave, a quasi-reversible one-electron wave and a reversible one-electron wave indicating a four-member electrochemical series: $[Co(DDDT)_2]_2^0 \rightleftarrows [Co(DDDT)_2]_2^- \rightleftarrows [Co(DDDT)_2]_2^{2-} \rightleftarrows 2Co(DDDT)_2^{2-}$. The solid-state ^{13}C NMR spectrum shows different resonances for carbons in the double bonds of the ligand, consistent with splitting of the C=C stretch in the IR spectrum.

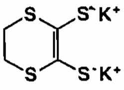
Introduction

The coordination chemistry of transition metal dithiolenes has been an area of great interest for a number of years. The abundance of research concerning these compounds has resulted in a number of detailed reviews [1–5]. The study of these complexes has largely been concentrated in several areas: (i) the difficulty in assigning formal oxidation states to the coordinated metal; (ii) the observation of trigonal prismatic coordination, a rare structural form found in tris complexes of dithiolenes; and (iii) the potential electrical conductivity in donor–acceptor complexes of these ligands. The discovery of the first totally sulfur-based organic superconductor, bis(ethylenedithiolo)tetrathiafulvalenium rhenate, $(BEDT–TTF)_2ReO_4$, fueled excitement in this latter area [6]. The tetrathiafulvalene (TTF) framework and more specifically, the tetrathioethylene subunit is believed to be the key structural feature required for superconductivity [7, 8].



TTF

Recently, a scheme was designed to combine the tetrathioethylene structural unit with inorganic systems which have also shown high conductivity such as the partially oxidized tetracyanoplatinates [9]. One objective of this investigation was the synthesis of the ligand 5,6-dihydro-1,4-dithiin-2,3-dithiolate and the characterization of transition metal square planar complexes containing this unit.



K_2DDDT

The nickel group and copper complexes synthesized in the presence of air are monoanions containing metals in the formally +3 oxidation state. They have been isolated as a wide variety of tetraalkylammonium salts. A structural analysis of $[(C_2H_5)_4N]$-

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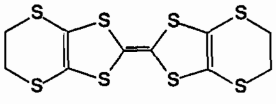
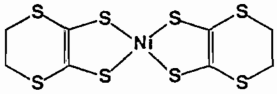


BEDT-TTF



Ni(DDDT)$_2^-$

[Ni(DDDT)$_2$] showed the anion to have structural features quite similar to BEDT–TTF [10].

In a continuation of this work and the search for compounds with close sulfur–sulfur and metal–sulfur contacts in the solid state, a prerequisite property for superconductivity, the cobalt complex of DDDT^{2-} has been synthesized. The simplest formula of the tetraethylammonium salt, [$(C_2H_5)_4$N] [Co(DDDT)$_2$], suggests Co(III) as the formal metal oxidation state. In addition, the complex as determined by an X-ray structural analysis is dimeric in the solid state, a feature not unexpected since two of the four cobalt dithiolene structures reported to date are dimeric [11, 12]. However, this structure offers new information on the theory concerning the cause of dimerization. We report the synthesis, structure, and physical properties of this new cobalt dithiolene complex.

Experimental

Reagents

Potassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate, (K_2DDDT), was prepared by literature methods [10] and analyzed by IR and NMR. Cobaltous chloride hexahydrate was purchased from Fisher Scientific Company. Acetonitrile, dimethylformamide, tetraethylammonium bromide and tetrabutylammonium bromide were purchased from the Aldrich Chemical Company. Tetraethylammonium perchlorate was purchased from Southwestern Analytical Chemicals. Ethyl alcohol was purchased from the Aaper Alcohol and Chemical Company. Argon was purchased from Air Products Inc. All chemicals were used without further purification.

Procedures

Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. All solvents used in synthesis and recrystallization were degassed with bubbling argon for 45 min prior to their use. All solutions were made and sealed inside an anhydrous atmosphere glove box.

Syntheses

$[(C_2H_5)_4N]_2[Co(S_4C_4H_4)_2]_2$

Under an argon atmosphere and with use of standard Schlenk techniques, 0.6 g of $CoCl_2 \cdot 6H_2O$ (2.5×10^{-3} mol) in 10 ml EtOH was added dropwise to 1.4 g of K_2DDDT (5.5×10^{-3} mol) in a mixture of 25 ml H_2O and 40 ml EtOH. The solution was stirred for 1 h from the beginning of dropwise addition during which time the reaction color changed from orange to purple. After filtration to remove any residue, 1.5 g (7.1×10^{-3} mol) of tetraethylammonium bromide was added to the filtrate. The solvent was removed by rotoevaporation to leave a solid residue which was then recrystallized in acetonitrile to yield 0.5 g (36%) of a crystalline material. The solid was stored under an argon atmosphere. Solutions of this complex are extremely unstable in air. Melting point (m.p.) = 195 °C. ^{1}H NMR (Me_2SO-d_6) 2.92 ppm (q, CH_2), 0.92 ppm (t, CH_3); IR (KBr): 1450(m), 1410(s), 1385(s), 1335(m), 1245(s), 1175(w), 1160(s), 1020(s), 995(m), 910(w), 860(s), 850(s), 775(m), 430(m), 360(w), 330(w) cm^{-1}. *Anal.* Calc. for $Co_2C_{32}H_{56}N_2S_{16}$: C, 34.95; H, 5.13; N, 2.55; S, 46.65. Found: C, 35.06; H, 5.14; N, 2.53; S, 46.46%.

$[(C_4H_9)_4N]_2[Co(S_4C_4H_4)_2]_2$

The above procedure was followed with the substitution of tetrabutylammonium bromide for tetraethylammonium bromide. The yield was 0.8 g (42%) of cubic crystals; m.p. = 210 °C. IR (KBr): 2950(w), 2860(w), 1470(s), 1415(s), 1375(s), 1335(m), 1250(s), 1175(w), 1160(s), 1015(s), 910(w), 860(s), 850(s), 730(m), 605(m), 430(m), 360(w), 330(w) cm^{-1}. *Anal.* Calc. for $Co_2C_{48}H_{88}N_2S_{16}$: C, 43.54; H, 6.70; N, 2.12; S. 38.74. Found: C, 43.37; H, 6.60; N, 2.09; S, 38.73%.

Physical Measurements

IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer over the range 4000–300 cm^{-1}. Vis/near-IR spectra were recorded on a Cary 2300 spectrophotometer over the range 10 500–33 300 cm^{-1} in DMF. ESR spectra were recorded with a Varian E-3 spectrometer at 100 K in DMF. The magnetic field was calibrated with VO(acac)$_2$ and DPPH. All electrochemical experiments were carried out with the use of a BAS CV-27 potentiostat. A platinum wire was employed for both the working and auxiliary electrodes and a Ag/AgCl electrode was employed as the reference electrode. The solutions contained 0.1 M tetraethylammonium perchlorate as the supporting electrolyte in DMF with metal complex concentrations of 10^{-3} M.

Single-crystal X-ray Analysis

A representative crystal was surveyed, and cell dimensions were obtained by a least-squares fit of setting angles of 25 high-angle reflections ($2\theta > 20°$). A data set was collected on a Nicolet R3m/μ diffractometer equipped with a graphite monochromator and molybdenum radiation ($\lambda = 0.71069$). Systematic absences indicated that the crystal belonged to the monoclinic space group *Cc* or *C*2/*c* (hkl, $h + k = 2n + 1$; $h0l$, $h, l = 2n + 1$). The latter was confirmed as the correct space group by the successful refinement of the structure. Two check reflections collected after every 98 reflections revealed no unexpected variation in intensity. Of the four thousand six hundred and ten unique reflections recorded in the range $3° < \theta < 45°$, three thousand eight hundred and twenty-one of these (having $I > 2\sigma(I)$) were used in the structure analysis. Data were corrected for Lorentz and polarization effects but not for absorption owing to the low absorption coefficient (10.7 cm^{-1}). An isotropic secondary extinction correction was made (secondary extinction coefficient = 1.2×10^{-7}). Atomic scattering factors for all atoms were taken from the International Tables for X-Ray Crystallography [13]. Pertinent crystal, data collection, and refinement parameters are summarized in Table 1.

The cobalt and several sulfur atoms were located by the direct methods program SOLV of the crystallographic program package SHELXTL [14]. The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. The structure was refined by the block-diagonal least-squares technique using SHELXTL on a Data General Microeclipse computer. The quantity minimized was $\Sigma w(\Delta F)^2$, where $w = 1/(\sigma_F^2 + 0.00029F^2)$. The non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions 0.96 Å away from the attached carbon atom and were not refined. The final *R* indices are given in Table 1. A final difference Fourier map revealed no missing or misplaced electron density. See also 'Supplementary Material'. The refined structure was plotted by using the SHELXTL graphics package.

TABLE 1. Single Crystal X-ray Crystallographic Analysis

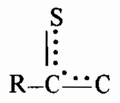
Crystal parameters	
Formula	$CoC_{24}H_{44}NS_8$
Molecular weight	662.07
Crystallization medium	acetonitrile
Crystal size (mm)	0.55 × 0.45 × 0.55
Crystal color	purple
Crystal habit	cube
Cell dimensions	$a = 23.626(3)$ Å $b = 16.915(3)$ Å $c = 16.294(2)$ Å $\beta = 101.62(1)°$
Volume	6379(1) $Å^3$
Space group	*C*2/*c*
Molecules/unit cell	8
Density calc. (g/cm^3)	1.38
$F(000)$	2800
Data collection parameters	
Temperature	298 K
2θ range	3–45°
Scan type	$\theta - 2\theta$
Scan speed	variable, 4–29.3°/min
Octants collected	hkl, $hk\bar{l}$
Background measurement	$\frac{1}{2}$ of total scan time at beginning and end of each scan
Linear absorption coefficient	10.7 cm^{-1}
Refinement parameters[a]	
Final *R* index	$R = 0.037$ $R_w = 0.053$
Goodness of fit	2.22
Largest Δ/σ	0.1
Data/parameter ratio	11.9

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

Results and Discussion

The first attempts to synthesize the cobalt complex of $DDDT^{2-}$ were conducted in air. The solutions which were purple at the point of addition of metal to ligand quickly yielded a blue precipitate which we were unable to identify. We had found earlier in the syntheses of Ni, Pt, Pd, and Cu complexes, where we started with M(II) salts, an oxidized product was obtained if the reaction were carried out in the presence of air and no oxidation if the reaction were carried out under argon [9]. However, in this case, we identified an oxidized product, $[(C_2H_5)_4N]_2[Co(DDDT)_2]_2$, isolated under argon. This is similar to the isolation of a vanadium(IV) species under argon when starting with vanadium(III) trichloride [15]. The $[Co(DDDT)_2]_2^{2-}$ anion was first isolated as the tetraethylammonium salt. However, several other tetraalkylammonium salts could be isolated. The tetrabutylammonium ion produced the highest quality crystals for X-ray crystallographic analysis. The solids are stable in air for several weeks although their solutions quickly decompose to yield the blue solid noted above.

The IR spectra of both tetraalkylammonium salts contain the characteristic absorptions of transition metal dithiolenes:

ν_1,	$C\overset{\cdots}{-}C$	at 1410 cm^{-1}
ν_2,	$C\overset{\cdots}{-}S$	at 1175 and 1160 cm^{-1}
ν_3,	 $R-C(\overset{\cdots}{-}S)\overset{\cdots}{-}C$	at 860 and 850 cm^{-1}
ν_4,	Co–S	at 430, 360 and 330 cm^{-1}

While the absorption due to the C=S stretch is usually quite intense in dithiolene complexes, the dimeric complexes typically exhibit a weaker signal that is split due to the inequality of the C=S groups [16]. This is true for $[Co(DDDT)_2]_2^{2-}$ which also shows splitting of the R–C(S)=C stretch and another band in the M–S region. This latter Co–S stretch, not seen in monomeric complexes, is assigned to the absorption of the axial Co–S bond.

A cyclic voltammogram of $[(C_2H_5)_4N]_2[Co(DDDT)_2]_2$ (Fig. 1) contains a reversible two-electron redox wave with $E_{1/2} = -0.70$ V. We suggest that this corresponds to the reduction of the dimeric dianion into two monomeric dianions. The quasi-reversible wave centered at –0.04 V followed by the reversible wave at $E_{1/2} = +0.18$ V are both one-electron waves indicating the existence of a monoanionic and neutral dimeric species. These species would constitute the following electrochemical series

$$[Co(DDDT)_2]_2^0 \rightleftarrows [Co(DDDT)_2]_2^- \rightleftarrows [Co(DDDT)_2]_2^{2-} \rightleftarrows 2Co(DDDT)_2^{2-}$$

A similar series has been reported for the cobalt complexes of $[S_2C_2(CF_3)_2]^{2-}$ and $[S_2C_2(CN)_2]^{2-}$, tfd^{2-} and mnt^{2-} respectively [17, 18]. More recently, the existence of the trianionic species, $Co[mnt]_2^{3-}$, has been detected with $E_{1/2} = -1.83$ V for the $-2 \rightleftarrows -3$ couple [19, 20]. The half-wave potential for the $-1 \rightleftarrows -2$ couple of the $DDDT^{2-}$ complex (–0.70 V) is more negative than those for the corresponding couples of tfd^{2-} and mnt^{2-} (–0.398 and –0.384 V respectively) and reflects the electron accepting ability of the ligand [21, 22]. Therefore, the trianionic species of the cobalt complex of $DDDT^{2-}$ cannot be detected since $E_{1/2}$ is estimated to be more negative than –2.00 V and this falls outside the solvent window.

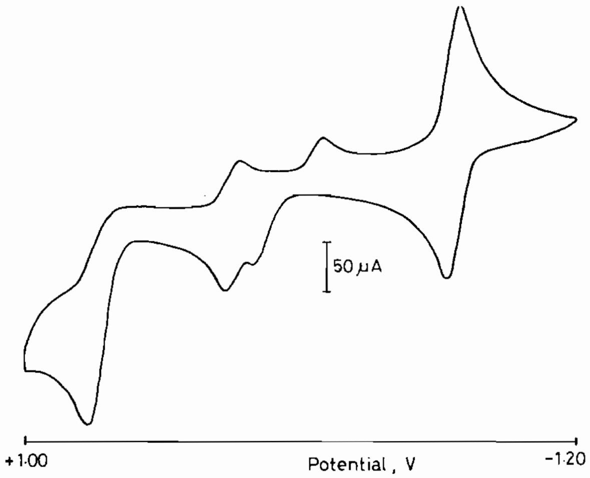


Fig. 1. Cyclic voltammogram of $[(C_2H_5)_4N]_2[Co(DDDT)_2]_2$. $E_i = -0.40$ V.

An extensive investigation of the electrochemistry of complexes of tdt^{2-}, $[S_2C_6H_3CH_3]^{2-}$ has recently been published and includes a cobalt complex [23]. The authors report evidence for the formation of a bond between a radical thiolate ligand and a d electron of the metal atom in the monoanionic species containing metals with unpaired electrons. This formulation gives a Co(II) metal center. The half-wave potential for the $-1 \rightleftarrows -2$ couple is –1.41 V, more negative than that observed for the $DDDT^{2-}$ complex [21]. This is different behavior from that observed for vanadium where the tdt^{2-} complex is more easily reduced than the $DDDT^{2-}$ complex [15].

The quasi-reversible behavior of the $[Co(DDDT)_2]_2^{2-} \rightleftarrows [Co(DDDT)_2]_2^-$ couple is not unusual as a similar redox wave has been reported for $[Co(tdt)_2]_2^{2-}$ [23]. A report by Vlcek and Vlcek showed that the oxidation product of $Co(mnt)_2^{2-}$ was the monomer, $Co(mnt)_2^-$, which underwent a slow dimerization to yield $[Co(mnt)_2]_2^{2-}$ [20]. Initially, it was thought that the quasi-reversible behavior of the $[Co(DDDT)_2]_2^{2-} \rightleftarrows [Co(DDDT)_2]_2^-$ couple was the result of a similar preceeding equilibrium. However, upon scanning in the positive direction from –0.40 V, the voltammogram was identical to the original one. Thus a monomer–dimer equilibrium is not responsible for the quasi-reversible behavior.

The cyclic voltammogram also exhibits an irreversible oxidation at +0.76 V. We cannot state with certainty the nature of this process. However, it is believed to be an oxidation of the ligand possibly creating the disulfide. The copper and manganese complexes of $DDDT^{2-}$ also show an irreversible oxidation in this area [9, 24]. Further investigation of these oxidations is warranted along with the electrochemical characterization of the uncoordinated ligand.

Constant potential electrolysis of $[(C_2H_5)_4N]_2[Co(DDDT)_2]_2$ at –1.00 V resulted in a peach colored solution of the $Co(DDDT)_2^{2-}$ complex. Even though a good solution ESR signal could not be obtained, a frozen-glass spectrum characteristic of Co(II) was obtained (Fig. 2). Two sets of eight lines corresponding to g_2 and g_3 are apparent. The third set of eight lines are collapsed into a single line due to the small metal hyperfine coupling constant. The values are

$g_1 = 1.933$ A_1 = small

$g_2 = 2.067$ $A_2 = 5.3 \times 10^{-3}\ cm^{-1}$

$g_3 = 2.860$ $A_3 = 6.7 \times 10^{-3}\ cm^{-1}$

These are similar to those reported for $Co[mnt]_2^{2-}$ and $Co[tfd]_2^{2-}$ which also exhibited rhombic symmetry [22, 25]. The small hyperfine splittings are

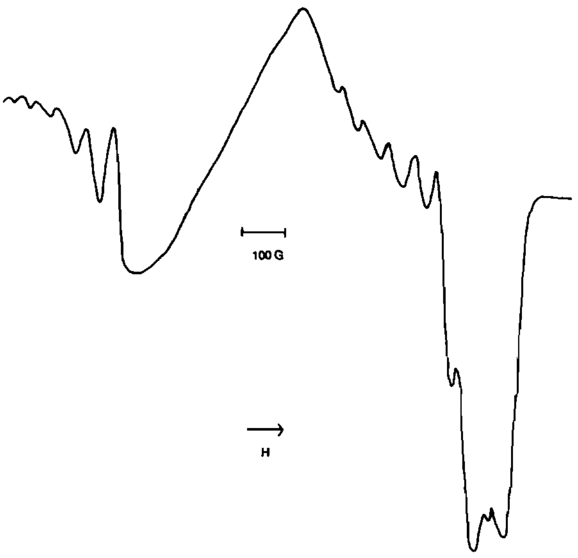


Fig. 2. Frozen-glass ESR spectrum of $[(C_2H_5)_4N]_2[Co(DDDT)_2]$.

TABLE 2. Vis/near-IR Bands (cm^{-1}) for $[(C_2H_5)_4N]_2[Co(DDDT)_2]_2$ and $[(C_2H_5)_4N]_2[Co(DDDT)_2]$

$[Co(DDDT)_2]_2^{2-}$	$Co(DDDT)_2^{2-}$
32000 (13000)	32900 (3300)
28700 (9500)	24800 (3100)
19500 (1800)	21000 (1200)
17000 (6900)	19800 (1400)
15400 (1400)	17600 (530)
10600 (5300)	

consistent with a significantly delocalized π* HOMO as was proposed for $Co[mnt]_2^{2-}$ [22].

The Vis/near-IR bands obtained for solutions of $[(C_2H_5)_4N]_2[Co(DDDT)_2]_2$ and $[(C_2H_5)_4N]_2[Co(DDDT)_2]$ are shown in Table 2 for the range 33 000 to 10 500 cm^{-1}. The molar absorptivities suggest bands with significant charge transfer character for all absorptions except the band at 17 600 cm^{-1} of the Co(II) complex.

A study of $Co[mnt]_2^{2-}$ reports a band at 15 000 cm^{-1} (200) that could correspond to the 17 600 cm^{-1} band seen for the $DDDT^{2-}$ complex. This band was assigned as the $xz, yz \rightarrow xy$ transition [26]. Spectra for other monoanions contain bands at 9300 (58) and 11 300 (100) for $Co[tdt]_2^-$ and 14 000 (1200) and 12 800 (3700) for $Co[mnt]_2^-$ [27, 28]. The latter two spectral bands more closely match those of $[Co(DDDT)_2]_2^{2-}$ suggesting similarities in electronic configuration. The tdt^{2-} complex is high spin ($S = 1$), whereas the mnt^{2-} complex is diamagnetic.

The ^1H NMR spectrum of the tetraethylammonium salt in DMSO-d_6 shows a quartet and a triplet at 2.92 and 0.92 ppm, respectively, that correspond to the protons of the counterion. No signals were observed for the ligand protons. The most likely explanations are that in DMSO the anion is paramagnetic and that there is lack of association between the anion and the tetraethylammonium cation. To further investigate the properties of this complex, solid-state and solution spectra were obtained by ^{13}C NMR for both the tetraethylammonium and tetrabutylammonium salts. The ^{13}C NMR chemical shifts in ppm from TMS are shown in Table 3. See also 'Supplementary Material'.

TABLE 3. ^{13}C NMR Results for $[(C_2H_5)_4N]_2[Co(DDDT)_2]_2$ and $[(C_4H_9)_4N]_2[Co(DDDT)_2]_2$ in ppm

Solid-state	Solution	Assignment
Tetraethylammonium		
9.28	6.69	CH_3
28.82		CH_2–S
32.33		CH_2–S
55.01	51.10	CH_2–N
127.37		C=C
130.43		C=C
156.73		C=C
Tetrabutylammonium		
15.60	13.55	CH_3
19.99	19.32	CH_2
22.23	22.44	CH_2
24.57		CH_2–S
28.16		CH_2–S
31.87		CH_2–S
57.80	57.51	CH_2–N
61.08		CH_2–N
124.94		C=C
127.58		C=C
130.06		C=C
157.07		C=C

As expected, the carbon signals for the anion are absent from the solution ^{13}C NMR spectra of both salts. However, they are present in the solid-state spectra. This result indicates that the solid is diamagnetic and that it becomes paramagnetic in solution. This varying magnetic property of cobalt dithiolenes is not unusual. For some complexes, the spin state changes from one solvent to another. This behavior is best exemplified by $Co[S_2C_6Cl_4]_2^-$ which is a diamagnetic solid, paramagnetic in cyclohexanone and tetrahydrofuran and diamagnetic in pyridine. In dimethylsulfoxide, the complex is paramagnetic yet has a lower moment than expected for an $S = 1$ system [29].

Some of the resonances in the solid-state ^{13}C NMR spectrum of the tetraethylammonium salt are broader than in the spectrum of the tetrabutylammonium salt. Thus, the discussion is limited to the latter. Four signals were present that correspond to the four carbons of the alkyl chains of the tetrabutylammonium ion. The signal from the carbon bonded to the nitrogen is an asymmetric doublet. The carbons bonded to sulfurs on the outer rings of the ligand give a three line pattern. Finally, the carbon–carbon double bonds are separated into two signals. A single resonance at 157 ppm is shifted substantially downfield from the three line pattern centered around 127.6 ppm. This 30 ppm difference indicates significant delocalization of electron density away from one of the carbons. A similar difference in chemical shifts attributed to electron delocalization has been reported for the olefinic carbons in substituted styrenes [30]. In our case, we propose that it is the carbon bonded to the sulfur involved in dimerization and that the electron density is delocalized into the four-membered Co–S–Co–S ring of the dimer. This observation of the different resonances in the solid-state ^{13}C NMR spectra is consistent with the splitting of IR stretches discussed previously.

The asymmetric unit for the tetrabutylammonium salt of the Co dithiolene contains one cation and half of the dianion. The dimer consists of two Co-$(DDDT)_2^-$ units approximately parallel but slightly displaced such that each cobalt exhibits an axial bond to a sulfur of the second anion. Thus the coordination about the cobalt atom is essentially square pyramid with the cobalt displaced 0.30 Å from the plane of the four basal sulfurs toward the apical sulfur. The average basal Co–S bond length is 2.197(1) Å and the apical Co–S distance is 2.328(1) Å. The Co••Co distance in the dimer is 3.200 Å. The structure and numbering scheme of the dimeric dianion is shown in Fig. 3. The large thermal ellipsoid for carbon 8 reflects its high anisotropic temperature factor and possibly a slight disorder. However, this type of motion has been observed previously and is not a major concern of this structure analysis [15]. Bond lengths and bond angles are given in Tables 4 and 5, respectively. Atomic coordinates are shown in Table 6.

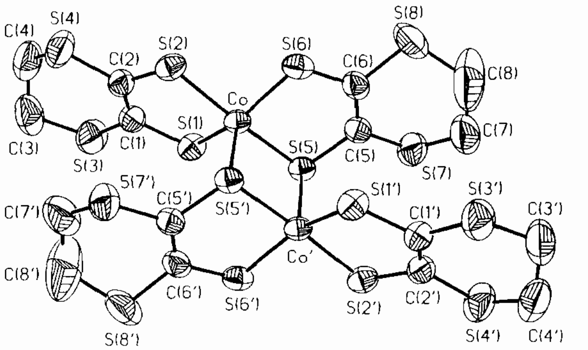


Fig. 3. Structure of $[Co(DDDT)_2]_2^{2-}$ showing the numbering scheme. Hydrogen atoms are not shown. Thermal ellipsoids are 50%.

Two other dimeric cobalt structures have similar structural parameters. The $Co_2(S_2C_2(CF_3)_2)_4$ complex has an average basal Co–S distance of 2.161 Å, an apical Co–S distance of 2.382 Å, and a Co••Co contact of 2.78 Å [12]. The values for the tetrabutylammonium salt of $[Co(S_2C_6Cl_4)_2]_2^{2-}$ are 2.185 Å, 2.404 Å and 3.10 Å, respectively [11]. The cobalt atoms are displaced from the plane of the basal sulfurs towards the apical sulfur by 0.37 Å for $Co_2(S_2C_2(CF_3)_2)_4$ and 0.26 Å for $[Co(S_2C_6Cl_4)_2]_2^{2-}$. The larger Co••Co distance in $[Co(S_2C_6Cl_4)_2]_2^{2-}$ was explained as resulting from a lesser displacement of the cobalt atom from the plane of the basal sulfurs [11]. The values of the present structure suggest this explanation is too simple and it is clear that there are many structural features contributing to this larger distance. For example, the S–Co–S angle forming the dimers are quite different. In the $DDDT^{2-}$ complex, the S5–Co–S5′ angle is 90.4°. In the other complexes the same angle is obtuse.

An inspection of anion dimensions for all cobalt dithiolene complexes reveals the similarities regardless of the existence of dimers (Table 7). Gray *et al.* conclude that the electron withdrawing substituents, Cl and CF_3, which should inhibit dimerization due to their bulky size, actually increase the tendency to dimerize by removing electron density from the vicinity of the cobalt atom [11]. They used a comparison of the molecular orbital results calculated for $Ni(S_2C_6H_4)_2^-$ and $Ni(S_2C_6Cl_4)_2^-$ to explain the dimerization in $[Co(S_2C_6Cl_4)_2]_2^{2-}$. More specifically, the highest filled b_{1u} π molecular orbital consists of 12% metal $4p_z$ character in $Ni(S_2C_6H_4)_2^-$ and only 8% metal character in $Ni(S_2C_6Cl_4)_2^-$, illustrating the withdrawal of electron density from the $4p_z$ orbital by the Cl substituents on the ring. The metal

TABLE 4. Bond Lengths (Å)

Co–S(1)	2.167(1)	Co–S(2)	2.193(1)
Co–S(5)	2.210(1)	Co–S(6)	2.218(1)
Co–S(5A)	2.328(1)	S(1)–C(1)	1.733(3)
S(2)–C(2)	1.728(4)	C(1)–C(2)	1.363(5)
C(1)–S(3)	1.766(4)	C(2)–S(4)	1.758(3)
S(3)–C(3)	1.803(4)	S(4)–C(4)	1.797(5)
C(3)–C(4)	1.497(6)	S(5)–C(5)	1.739(3)
S(5)–Co(A)	2.328(1)	S(6)–C(6)	1.730(3)
C(5)–C(6)	1.352(5)	C(5)–S(7)	1.754(3)
C(6)–S(8)	1.757(3)	S(7)–C(7)	1.808(6)
S(8)–C(8)	1.747(7)	C(7)–C(8)	1.446(9)
N(1)–C(9)	1.523(5)	N(1)–C(13)	1.516(4)
N(1)–C(17)	1.515(4)	N(1)–C(21)	1.519(4)
C(9)–C(10)	1.526(5)	C(10)–C(11)	1.528(6)
C(11)–C(12)	1.443(8)	C(13)–C(14)	1.512(5)
C(14)–C(15)	1.497(7)	C(15)–C(16)	1.305(12)
C(17)–C(18)	1.505(6)	C(18)–C(19)	1.499(6)
C(19)–C(20)	1.501(7)	C(21)–C(22)	1.510(5)
C(22)–C(23)	1.516(5)	C(23)–C(24)	1.510(6)

TABLE 5. Bond Angles (°)

S(1)–Co–S(2)	89.6(1)	S(1)–Co–S(5)	88.0(1)
S(2)–Co–S(5)	174.2(1)	S(1)–Co–S(6)	153.6(1)
S(2)–Co–S(6)	90.3(1)	S(5)–Co–S(6)	89.5(1)
S(1)–Co–S(5A)	112.2(1)	S(2)–Co–S(5A)	95.5(1)
S(5)–Co–S(5A)	90.4(1)	S(6)–Co–S(5A)	94.1(1)
Co–S(1)–C(1)	105.6(1)	Co–S(2)–C(2)	105.2(1)
S(1)–C(1)–C(2)	119.8(3)	S(1)–C(1)–S(3)	113.5(2)
C(2)–C(1)–S(3)	126.6(3)	S(2)–C(2)–C(1)	119.4(3)
S(2)–C(2)–S(4)	113.4(2)	C(1)–C(2)–S(4)	127.2(3)
C(1)–S(3)–C(3)	103.0(2)	C(2)–S(4)–C(4)	103.8(2)
S(3)–C(3)–C(4)	114.1(3)	S(4)–C(4)–C(3)	113.3(3)
Co–S(5)–C(5)	104.0(1)	Co–S(5)–Co(A)	89.6(1)
C(5)–S(5)–Co(A)	108.1(1)	Co–S(6)–C(6)	102.4(1)
S(5)–C(5)–C(6)	118.7(2)	S(5)–C(5)–S(7)	117.8(2)
C(6)–C(5)–S(7)	123.5(2)	S(6)–C(6)–C(5)	122.4(2)
S(6)–C(6)–S(8)	114.8(2)	C(5)–C(6)–S(8)	122.8(2)
C(5)–S(7)–C(7)	99.4(2)	C(6)–S(8)–C(8)	106.2(2)
S(7)–C(7)–C(8)	117.2(5)	S(8)–C(8)–C(7)	120.7(5)
C(9)–N(1)–C(13)	111.1(3)	C(9)–N(1)–C(17)	106.5(3)
C(13)–N(1)–C(17)	111.4(3)	C(9)–N(1)–C(21)	111.3(3)
C(13)–N(1)–C(21)	105.4(2)	C(17)–N(1)–C(21)	111.2(3)
N(1)–C(9)–C(10)	115.8(3)	C(9)–C(10)–C(11)	111.0(3)
C(10)–C(11)–C(12)	115.0(4)	N(1)–C(13)–C(14)	115.8(3)
C(13)–C(14)–C(15)	112.3(4)	C(14)–C(15)–C(16)	121.7(6)
N(1)–C(17)–C(18)	116.5(3)	C(17)–C(18)–C(19)	110.4(4)
C(18)–C(19)–C(20)	114.8(4)	N(1)–C(21)–C(22)	116.6(3)
C(21)–C(22)–C(23)	109.7(3)	C(22)–C(23)–C(24)	112.5(3)

TABLE 6. Atomic Coordinates (X 10^4) and Isotropic Thermal Parameters (Å^2 X 10^3)

	x	*y*	*z*	*U*[a]
Co	2665(1)	6811(1)	4418(1)	41(1)
S(1)	3294(1)	7343(1)	3786(1)	52(1)
S(2)	3161(1)	5706(1)	4540(1)	53(1)
C(1)	3841(1)	6650(2)	3843(2)	55(1)
C(2)	3780(1)	5921(2)	4172(2)	54(1)
S(3)	4425(1)	6979(1)	3404(1)	85(1)
S(4)	4281(1)	5141(1)	4301(1)	86(1)
C(3)	4980(2)	6260(3)	3778(3)	97(2)
C(4)	4782(2)	5420(3)	3654(3)	95(2)
S(5)	2148(1)	7903(1)	4156(1)	44(1)
S(6)	1864(1)	6141(1)	4455(1)	53(1)
C(5)	1440(1)	7566(2)	3876(2)	51(1)
C(6)	1329(1)	6795(2)	4001(2)	55(1)
S(7)	904(1)	8250(1)	3445(1)	81(1)
S(8)	636(1)	6380(1)	3709(1)	95(1)
C(7)	334(2)	7936(4)	3963(4)	125(3)
C(8)	150(3)	7121(4)	3856(5)	174(4)
N(1)	1878(1)	5116(2)	1962(2)	60(1)
C(9)	2420(2)	5081(2)	1591(2)	65(1)
C(10)	2968(2)	5411(3)	2141(2)	88(2)
C(11)	3454(2)	5479(3)	1651(3)	89(2)
C(12)	3383(2)	6106(4)	1039(4)	133(3)
C(13)	1975(2)	4717(2)	2811(2)	67(1)
C(14)	2153(2)	3858(2)	2828(2)	87(2)
C(15)	2159(3)	3481(3)	3661(4)	132(3)
C(16)	1712(4)	3514(5)	4018(5)	262(7)
C(17)	1404(2)	4710(2)	1340(2)	67(1)
C(18)	822(2)	4654(3)	1578(3)	85(2)
C(19)	403(2)	4223(3)	915(3)	101(2)
C(20)	– 182(2)	4087(3)	1117(4)	122(3)
C(21)	1716(2)	5964(2)	2116(2)	62(1)
C(22)	1591(2)	6500(2)	1361(2)	71(1)
C(23)	1453(2)	7325(2)	1628(3)	75(2)
C(24)	1286(2)	7881(3)	895(3)	99(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

orbital is thus more available for axial interactions such as solvent coordination or dimerization. This theory. does not explain the dimeric structure of $[Co(DDDT)_2]_2^{2-}$. The $-SCH_2CH_2S-$ group cannot be considered electron withdrawing especially when compared to the CN groups on the mnt^{2-} ligand which does not form a dimer as the cobalt complex.

The cell packing diagram for the dimer (Fig. 4) illustrates some of the geometrical features more clearly. The tetrathioethylene units of the ligands are essentially planar while each $Co(DDDT)_2^-$ unit bends at the cobalt atom to yield a butterfly-shaped dimer. A mean plane was calculated for each half of the

TABLE 7. Comparison of Distances for Cobalt Dithiolene Structures (Å)

	$[Co(DDDT)_2]_2^{2-}$ [a]	$[Co(S_2C_6Cl_4)_2]_2^{2-}$ [b]	$Co_2(S_2C_2(CF_3)_2)_4$ [c]	$[Co(S_2C_6H_3CH_3)_2]^-$ [d]	$[Co(S_2C_2(CN)_2)_2]^{2-}$ [e]
Co–S	2.20	2.18	2.16	2.17	2.16
Co–S′	2.33	2.40	2.38		
Co–Co′	3.20	3.10	2.78	10.21	9.81
S–C	1.73	1.76	1.69	1.77	1.72
C–C	1.36	1.38	1.39	1.40	1.34

[a] This work. [b] Ref. 11. [c] Ref. 10. [d] Ref. 31. [e] Ref. 32.

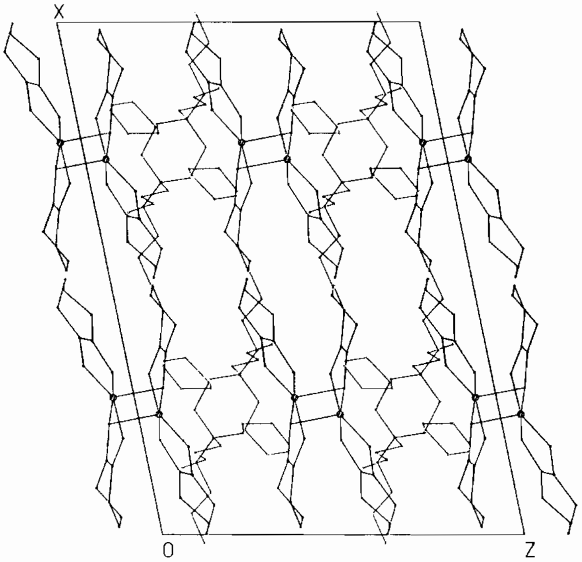


Fig. 4. Cell packing diagram for $[(C_4H_9)_4N]_2[Co(DDDT)_2]_2$.

monomer unit containing the Co and all atoms in the ligand excluding the outer $-CH_2CH_2-$ group. The dihedral angle between these planes is 34.4° indicating a significant deviation from planarity for the overall 'monomer' unit. The $-CH_2CH_2-$ groups on each ligand differ in orientation in that one group puckers with one carbon lying above and one carbon lying below the tetrathioethylene plane while in the other ligand, the $-CH_2CH_2-$ unit lies on one side of the plane. Structures on all square planar complexes of this ligand indicate no structural preference. There are two structures in which both ends are puckered, two that show both fragments lying to one side of the tetrathioethylene plane, and three including the present structure where the outer groups differ in orientation [9, 10, 33, 34]. Because the geometry of the fragments seem random in nature, steric interactions in the crystal lattice are most likely the determining factor.

One of the key interests in the crystallographic analysis of complexes of $DDDT^{2-}$ has been the S··S contact distances between anions with square planar coordination. This cobalt complex exhibits S··S contacts within a dimer as short as 3.22 Å for S5 to S5′. There are nine similar S··S distances less than 4.90 Å. The shortest S··S contact between two anions of different dimers is 3.72 Å for two S4 atoms. Four such S··S distances less than 4.80 Å exist in the crystal lattice. Table 8 lists these contacts and those of other metals with the $DDDT^{2-}$ ligand. The cobalt complex has the shortest S··S distances of these to date. A comparison of the important bond lengths in all complexes of this ligand discloses no significant structural changes. See also 'Supplementary Material'.

TABLE 8. S··S Contacts (Å)[a]

$[Co(DDDT)_2]_2^{2-}$

Intradimer				Interdimer	
S5–S5′	3.22	S2–S7′	3.98	S4–S4′	3.72
S5–S6′	3.33	S1–S7′	4.64	S3–S3′	4.39
S2–S5′	3.35	S4–S7′	4.66	S8–S8′	4.45
S1–S5′	3.73	S1–S8′	4.85	S7–S7′	4.74
S1–S6′	3.92				

$Au(DDDT)_2$ (≥3.70 Å)[b]

S1–S7′	3.59
S2–S3′	3.59
S3–S4′	3.61
S5–S6′	3.66
S7–S8′	3.67

$Ni(DDDT)_2^-$

$[(C_2H_5)_4N]^+$ [c]		$[(C_4H_9)_4N]^+$ [d]	
S4–S3′	3.98	S7–S7′	3.43
S3–S4′	3.98	S8–S1′	3.88
S4–S4′	4.25	S8–S4′	4.33
S3–S3′	4.49	S3–S4′	4.78
S2–S3′	4.99		

$Cu(DDDT)_2^-$

$[(C_4H_9)_4N]^+$ [e]	
S4–S3′	4.47

[a] ≤5.00 Å unless otherwise stated. [b] Ref. 34. [c] Ref. 10. [d] Ref. 33. [e] Ref. 9.

The tetrabutylammonium cation exhibits the tetrahedral structure expected with an average of 109.5(3)° for the six C–N–C angles. The individual values of all C–N and C–C bond lengths lie close to the averages of 1.518(5) and 1.488(7) Å respectively except for one C–C distance of 1.31(1) Å. This length corresponds to the bond between C15 and C16, two carbons ending one of the alkyl chains. Carbon 16 also has the highest temperature factor of all atoms in the tetrabutylammonium ion. The motion inherent in these long carbon chains is common resulting in high temperature factors and thus inaccurate bond lengths. Two tetrabutylammonium cations lie between each dimer in the unit cell disallowing any close S···S contacts between dimers in the *z* direction (Fig. 4).

Supplementary Material

Solid-state ^{13}C NMR spectrum of $[(C_4H_9)_4N]_2$-$[Co(DDDT)_2]_2$; a table of bond lengths in complexes of DDDT^{2-} and listings of anisotropic temperature factors, hydrogen coordinates and isotropic thermal parameters (4 pages); tables of calculated and observed structure factors (20 pages) are available from the authors on request.

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