Another column was prepared using 20.0 g of ion-retardation resin (Bio Rad AG11A8 50–100 mesh) and was thoroughly washed with distilled water until free of chloride. The combined MTL fractions (pH 6.0) were passed through this column and eluted with H_2O. Twenty fractions of 4 mL each were collected and examined on TLC. The fractions having MTL were combined and lyophilized to obtain MTL as a white powder (9–11 mg).

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Registry No. 1, 154-21-2; **2**, 14810-93-6; G-3-P, 142-10-9; glucose, 50-99-7; pyruvic acid, 127-17-3; glycerol, 56-81-5.

Hieber and Bruck Revisited. The X-ray Molecular Structure and Properties of the Anionic Precursor to Hieber's Nickel(IV) Dithiolate, $[K(2,2,2\text{-crypt})][Ni(S_2CC_6H_5)_3]$

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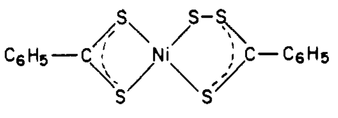
Contribution from the Laboratory of Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, Texas 77840. Received June 7, 1984

Abstract: The olive-green precursor to the sulfur-rich $Ni(S_2CC_6H_5)(S_3CC_6H_5)$, originally thought to be $[Ni^{IV}S(S_2CC_6H_5)_2]_2$, has been identified as $[Ni(S_2CC_6H_5)_3]^-$. This paramagnetic, six-coordinate anion, suggested by Hieber to be $[NiS_2(S_2CC_6H_5)_2]^{4-}$, readily reacts with acid to produce the sulfur-rich product. With use of $[K(2,2,2\text{-crypt})]^+$ as a cation it has been possible to obtain the structure of the anion. For $[K(2,2,2\text{-crypt})][Ni(S_2CC_6H_5)_3]$, a = 15.319 (4) Å, b = 18.277 (6) Å, c = 16.450 (6) Å, β = 106.00 (2)°, Z = 4. With use of 4659 Cu $K\alpha$ data, the structure of the anion has been deduced to contain a distorted NiS_6 octahedron with Ni–S ≈ 2.4 Å.

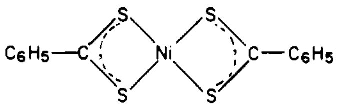
While studying synthetic methods for $Ni(CO)_4$, Hieber and Bruck published[1] evidence for the formation of a nickel complex containing only sulfur–metal coordination. This species, originally thought to contain Ni(IV), is known[2] to be I, the "sulfur-rich" $Ni(S_3CC_6H_5)(S_2CC_6H_5)$. However, the olive-green anionic precursor to this complex has defied formulation to date, although Hieber[1] thought it to be $[NiS_2(S_2CC_6H_5)_2]^{4-}$.



I

Since $[Ni(S_2CNR_2)_3]^+$, R = alkyl, contains $Ni^{IV}S_6$ coordination[3] and, with R = CH_3 or C_2H_5, this cation rapidly decomposes in solution to oxidized ligand species and Ni(II) complexes, we decided to reexamine the related Hieber chemistry. In particular we wanted to determine whether a $Ni^{IV}S_6$ species might indeed be present, at least as an intermediate, preceding the formation of the sulfur-rich product. Our interest was further picqued by the recent observation[4] of Ni(III) species containing sulfur coordination in a CO fixing bacterial system.

Although the purple (violet) species Hieber thought to contain Ni(IV), $[SNi^{IV}(S_2CC_6H_5)_2]_2$, has been shown[2] to be I, its blue, "sulfur-poor" precursor, II, is known[1] to react with CO in benzene containing NaSH and C_2H_5OH to give $Ni(CO)_4$. Early attempts to isolate and characterize the olive-green species that lead to I failed although evidence could be obtained in solution that a species of this color was formed. Attempts to prepare crystalline products with tetraalkylammonium salts, R = methyl (Me) or n-butyl (Bu), also were unsuccessful, although powders were isolated. With use of 2,2,2-Crypt to encapsulate the potassium ion, a green, crystalline product was obtained. The structure of this product is reported here along with the properties of the anion.



II

Experimental Section

Materials. The reagents and solvents used in this work were purchased from commercial sources and used without further purification. The 2,2,2-Crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane), $N(C_2H_4OC_2H_4OC_2H_4)_3N$, was obtained from Fluka. All liquid reagents were of research grade and were dried over 4 Å molecular sieves.

Sodium and potassium hydrogen sulfides were prepared by reacting either sodium or potassium ethoxide with H_2S gas according to procedures described in the literature.[5]

Synthesis of 1,1-Dithiolato Nickel(II) complexes. The perthiobenzoato(dithiobenzoato)nickel(II), $Ni(dtb)_2S$, and bis(dithiobenzoato)nickel(II), $Ni(dtb)_2$, were prepared and purified according to procedures previously reported.[2]

The following reactions were carried out under an atmosphere of dry nitrogen. The solvents were carefully degassed and standard Schlenk ware was used. The reactions involving 2,2,2-Crypt were carried out by using a modified procedure described by Darensbourg and co-workers[6]

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‡ Nicolet Instruments, Madison, Wisconsin.

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for the synthesis of $[M(CO)_5SH]^-$ anions (M = Cr, Mo, W).

Preparation of $[K(2,2,2\text{-Crypt})]^+SH^-$. Under a dry nitrogen atmosphere 0.0190 g (0.263 mmol) of KSH and 0.099 g (0.263 mmol) of 2,2,2-Crypt were added to 20 mL of degassed CH_3CN. The mixture was stirred vigorously at room temperature for 24 h and then allowed to sit at room temperature for 3 h. The colorless solution was filtered and the filtrate containing $[K(2,2,2\text{-Crypt})]^+SH^-$ in CH_3CN was stored under nitrogen.

Synthesis of the Complex $[K(2,2,2\text{-crypt})][Ni(dtb)_3]$. Under an inert N_2 atmosphere, 5 mL of the $[K(2,2,2\text{-Crypt})]^+SH^-$ solution was added to a suspension of 0.120 g (0.033 mmol) of $Ni(dtb)_2$ in 20 mL of CH_3CN. The resulting green solution was stirred for 12 h at room temperature and filtered. The volume of the filtrate was reduced to ~10 mL with a N_2 gas stream. Dark green crystals suitable for X-ray analysis were grown from the concentrated CH_3CN solution maintained at <0 °C for several days. Anal. Calcd for $C_{39}H_{51}N_2O_6S_6NiK$: C, 50.18; H, 3.86; S, 20.60. Found: C, 51.03; H, 4.05; S, 21.15. The compound decomposes in air at ~160 °C.

Synthesis of the Complexes $[R_4N][Ni(dtb)_3]$ (R = *n*-Butyl, Methyl). Derivatives of $[Ni(dtb)_3]^-$ containing the $[R_4N]^+$ counterion were synthesized under inert atmosphere in carefully degassed ethanol (absolute) with use of standard Schlenk techniques. In a typical experiment a mixture of 0.5026 g (1.377 mmol) of $Ni(dtb)_2$ and 0.2046 g (2.835 mmol) of KSH in 50 mL of ethanol was vigorously stirred at room temperature for 6 h. During this period, the solution slowly turns dark green. The reaction mixture was filtered, and a solution of 0.443 g (1.37 mmol) of $[Bu_4N]Br$ in 10 mL of ethanol was added to the filtrate. A dark-green precipitate forms immediately. The solid product was collected by filtration, washed with ethanol (3 × 5 mL), and dried under vacuum. This procedure gave 0.401 g of a green crystalline material. The tetraalkylammonium salts of $[Ni(dtb)_3]^-$ are air stable in the solid state. These complexes are soluble in solvents such as acetone and acetonitrile, and the solutions are air stable for long periods of time. However, in solvents such as ether or chloroform the complexes decompose rather quickly. Due to the high solubility in certain solvents and low air stability in others, an effective method of purification by crystallization was not found.

The compound $[Me_4N][Ni(dtcu)_3]$ (dtcu = $S_2CC_6H_4$-*p*-iso-C_3H_7) was synthesized following the procedure described above. The high solubility of this material in ethanol precluded the formation of crystals. A solid product was obtained after evaporation of the solvent. The stability of this complex in the solid state as well as in solution is similar to that of the tetraalkylammonium salts.

Physical Measurements. The KBr (Fisher), $CHCl_3$, and CH_3CN (Aldrich) used for the physical measurements were of spectrophotometric grade. The Me_4Si (Aldrich, 99.9%), chloroform-d_1, and acetone-d_6 (SIC, 99.8%) were of NMR grade.

Spectra. The Raman spectrum of $[Bu_4N][Ni(dtb)_3]$ was recorded in the solid state. Samples were prepared by pressing the material into potassium bromide. Spectra were obtained with use of a Coherent Radiation Model CR-8 Ar^+ laser and a Spex 14018 double monochromator employing a RCA C31034 photomultiplier tube as the detector. A Spex 1445A sample rotator was used to rotate the solid sample. This technique was used to minimize thermal decomposition of the sample.[7] Infrared spectra were obtained by using solid samples pressed in KBr pellets and recorded with a Perkin-Elmer 598 spectrometer. The electronic absorption spectra were obtained on a Cary Model 14 spectrophotometer. The ^1H NMR spectra were obtained on a Varian XL-200 FT NMR spectrometer.

Magnetic Susceptibility and Conductivity Measurements. Magnetic susceptibility measurements were performed on solid polycrystalline samples with use of a Faraday apparatus.[8] The conductivity data were obtained with use of a Beckman conductivity bridge Model RC-19. The cell constant was determined by using a standard aqueous solution of potassium chloride.

Reaction of the $[Ni(dtb)_3]^-$ Anion with HCl. When anhydrous gaseous HCl is bubbled through a solution containing $[Ni(dtb)_3]^-$ in acetone, the mixture turns purple and $Ni(dtb)_2S$ (I) precipitates out. In a typical experiment anhydrous HCl is bubbled through a solution of 0.100 g (0.132 mmol) of $[Bu_4N][Ni(dtb)_3]$ in 15 mL of acetone. The solution turns purple, and after a few minutes a purple precipitate forms. To the reaction mixture 50 mL of water was added. The resulting mixture was filtered, and the solid product was washed with water and 1:1 water/ethanol and vacuum dried. A total of 0.0425 g (0.117 mmol) of purple solid is obtained. The electronic absorption spectrum of this product in $CHCl_3$ which shows an absorption peak at 530 nm and its IR spectrum are characteristic[2] of the $Ni(dtb)_2S$ complex. This reaction produced the crude $Ni(dtb)_2S$ complex in approximately 90% yield.

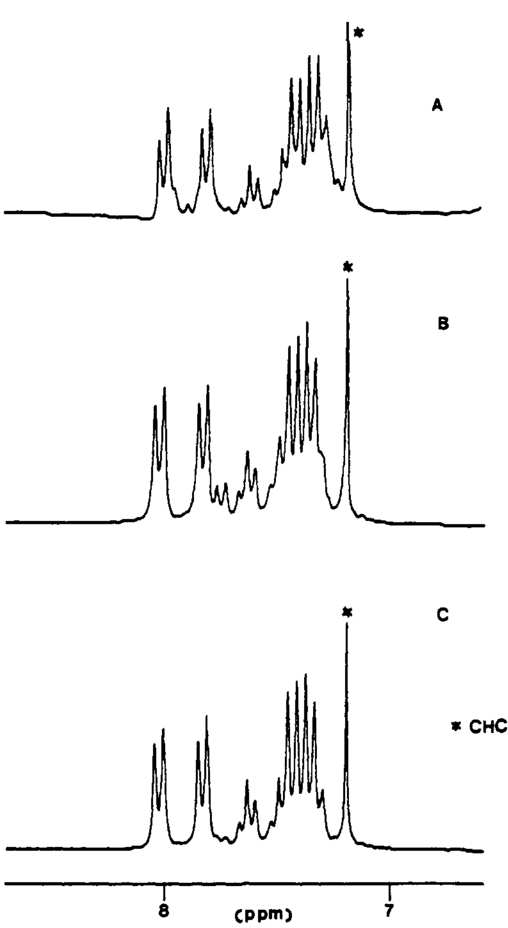

Figure 1. ^1H NMR spectra in $CDCl_3$: (A) $Bu_4N[Ni(dtb)_3]^-$ + HCl; (B) $Ni(dtb)_2S$ + HCl; (C) $Ni(dtb)_2S$.

The reaction of $[Ni(dtb)_3]^-$ with HCl also was monitored by UV-vis and NMR spectroscopy. HCl is bubbled through a solution of $[Bu_4N][Ni(dtb)_3]$ in acetone (6.6×10^{-5} M). The absorption peak at 690 nm ($A = 0.67$, $\epsilon = 10\,000$) due to the $[Ni(dtb)_3]^-$ anion disappears and an absorption band at 530 nm ($A = 0.39$, $\epsilon = 8000$) appears. This latter band is characteristic of the $Ni(dtb)_2S$ complex. In this reaction a 60% yield of $Ni(dtb)_2S$ based on the nickel content is obtained. Other products were not identified.

Anhydrous HCl is bubbled through a solution of $[Bu_4N][Ni(dtb)_3]$ in $CDCl_3$ in a 5-mm NMR tube. The ^1H NMR spectrum of this solution after 48 h and that of authentic $Ni(dtb)_2S$ in $CDCl_3$ are shown in Figure 1 in the 6–8 ppm region. The reaction of $[Ni(dtb)_3]^-$ with HCl leads to the formation of $Ni(dtb)_2S$ with a small amount of a species containing a phenyl group.

Crystallographic Studies. Crystallographic analyses were carried out at the Nicolet XRD Corp. (Fremont, CA). Crystallographic data for the complex $[K(2,2,2\text{-Crypt})][Ni(dtb)_3]$ have been tabulated in Table I. The intensity measurements were made with a Nicolet R3m-E diffractometer with graphite-monochromated Cu Kα radiation (λ 1.54178 Å) for a crystal of dimensions 0.20 × 0.15 × 0.15 mm. A total of 6748 reflections having $3.0 \le 2\theta \le 115$ were measured over two independent octants, *hkl* and hk-*l*. The 1.0° wide ω-scan technique was used with a variable scan speed of 3.91–29.30 deg/min in 2θ and a background-to-scan ratio equal to 1.0. During the data collection two standard reflections were monitored every 48 reflections.

The intensities were reduced by applying polarization and decay corrections. The unit cell parameters and the systematic absences are consistent with the monoclinic system, space group $P2_1/n$ (no. 14).[9] The number of reduced data with $I/\sigma(I) = 3.0$ is 3752.

The positions of the Ni, S, and K atoms were derived with use of the SHELXTL direct methods software. The remaining positions of the non-hydrogen atoms were obtained from a Fourier synthesis based on refined parameters for the nickel, sulfur, and potassium atoms. During the

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Table I. Crystallographic Data of Importance to the Structure Determination of $[K(2,2,2\text{-Crypt})][Ni(S_2CC_6H_5)_3]$

formula	$C_{39}H_{51}N_2O_6S_6NiK$
formula wt	934.08
space group	$P2_1/n$
systematic absences	$h0l$; $h + l = 2n$, $0k0$: $k = 2n$
a, Å	15.319 (4)
b, Å	18.277 (6)
c, Å	16.450 (6)
α, deg	90.00 (0)
β, deg	106.00 (2)
γ, deg	90.00 (0)
V, Å^3	4427.47
Z	4
d_{calcd}, g/cm^3	1.40
d_{obsd}, g/cm^3	1.45
crystal size, mm	0.2 × 0.15 × 0.15 mm
$F(000)$, e	195.75
μ(Mo Kα), cm^{-1}	44.28
radiation	monochromated in Cu Kα ($\lambda\alpha = 1.54178$ Å) incident beam
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3752
check reflections	2
R^a	9.62
R_w^b	9.53
goodness-of-fit indicator^c	2.211
largest shift/esd, final cycle	0.824 (in the cryptate part of the molecule)
largest peak, e/Å^3	0.70

$^a R = \sum||F_o| - |F_c||\sum|F_o|$. $^b R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_3|$; $w = [1 - \exp(-5.0(\sin\theta/\lambda)^2)]/[\sigma^2(|F_o|) + g|F_o|^2]$; $g = 0.0003$. ^{c}Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

consequent full-matrix least-squares refinement the bonding distances in the cryptate were constrained. Anomalous dispersion corrections and scattering factors were taken from the International Tables.[9]

The positions of the hydrogen atoms were calculated by using an idealized sp^3-hybridized geometry and a C–H bond length of 0.960 Å. The portion of the structure involving the cryptate suffers from disorder.

Due to the disorder in the 2,2,2-Crypt a high-angle least-squares refinement was chosen. This refinement gave more accurate information about the coordination sphere of nickel and at the same time down weighted the disordered part of the structure. Refinement with 494 parameters using isotropic thermal parameters for most of the cryptate atoms gave $R = 0.096$ and $R_w = 0.095$ with a goodness of fit of 2.2.

Figure 2 is an ORTEP diagram of the structure.

Results and Discussion

The reaction of SH^- in ethanol with $Ni(S_2CC_6H_5)_2$, $Ni(dtb)_2$, under conditions similar to those used by Hieber and Bruck[1], leads to the formation of the anion $Ni(dtb)_3^-$, which can be isolated as a green powder with Na^+, K^+, or tetraalkylammonium cations. When K(2,2,2-Crypt)SH is used, crystals suitable for X-ray analysis were obtained. Although the anionic product was formulated[1] by Hieber and Bruck as $[S_2Ni(dtb)_2]^{4-}$, it proves to be $Ni(dtb)_3^-$. A reasonable stoichiometric equation leading to the product is given in reaction 1. The sodium and potassium salts of $Ni(S_2CC_6H_5)_3^-$ in ethanol are very air sensitive and rapidly decompose to $Ni(S_3CC_6H_5)(dtb)$.

$$3Ni(dtb)_2 + 2NaSH = 2Na[Ni(dtb)_3] + NiS(s) + H_2S \quad (1)$$

The IR spectrum of $[Bu_4N][Ni(dtb)_3]$ shows carbon–sulfur s(C–S) and as(C–S) stretching frequencies at 940 and 980 cm^{-1}, respectively. These vibrational modes appear at 945 and 978 cm^{-1} in the $Ni(dtb)_2$. The as(Ni–S) stretching mode is observed at 372 cm^{-1} and the s(Ni–S) stretch appears as a weak Raman band at 318 cm^{-1}. These modes are observed at 345 and 335 cm^{-1}, respectively, in $Ni(dtb)_2$.

The UV–vis absorption spectra of the tetraalkylammonium salts of $[Ni(dtb)_3]^-$ in $CHCl_3$ solution exhibit absorption bands at ~690 nm (ϵ = 10000), ~375 nm (ϵ = 37000), and ~285 nm (ϵ = 39000).

Conductivity measurements at 25 °C of $M[Ni(dtb)_3]$, M = Na^+, K^+ or R_4N^+, in acetone and acetonitrile gave typical for a 1:1 electrolyte Λ_M(acetone) = 108.0 and Λ_M(acetonitrile) = 125.7.

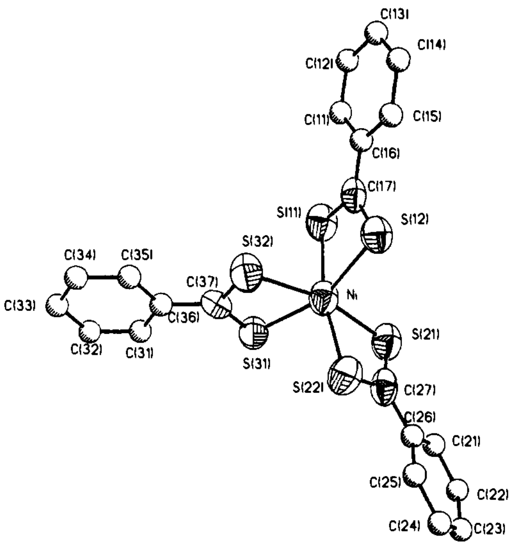

Figure 2. Molecular Structure of the $[Ni(S_2CC_6H_5)_3]^-$ anion (PLUTO plot at 50% probability).

The magnetic susceptibility at 20.7 °C of several salts indicated that the anion is paramagnetic with a $\mu_{eff} = \sim 3.0\ \mu B$.

UV-vis and ^1H NMR spectroscopic studies indicate that the anion reacts with HCl to form $Ni(dtb)_2S$. The ^1H NMR spectrum of the reaction of $[Bu_4N][Ni(dtb)_3]$ with HCl in CDC_3 is shown in Figure 1. The spectra of $Ni(dtb)_2$ in $CDCl_3$ and $Ni(dtb)_2S$ plus HCl in $CDCl_3$ are also given in this figure. Only small amounts of other products are formed. Although the organic products have not been identified conclusively, a reasonable description of the chemistry is given by reaction 2. The "$C_6H_5C(S)H$" is expected to oligimerize or be oxidized in air to other products.

$$KNi(dtb)_3 + HCl = KCl + Ni(S_3CC_6H_5)(dtb) + \text{“}C_6H_5C(S)H\text{”} \quad (2)$$

The crystallographic data for the complex $[K(2,2,2\text{-Crypt})][Ni(dtb)_3]$ are summarized in Table I. The positional parameters with their estimated standard deviations for the $[Ni(dtb)_3]^-$ anion are presented in Table II. The important bond distances and bond angles of the anion are tabulated in Table III. The X-ray structure of only one other $Ni^{II}S_6$ species has been reported, to our knowledge. It is the tris(ethylxanthato)nickel anion as found[11] in $[(CH_3)_3(C_6H_5)N][Ni(S_2COC_2H_5)_3]$. Both anions display a distorted octahedral geometry about the Ni^{II}. Both anions are paramagnetic with a susceptibility suggestive of two unpaired electrons. The Ni(II) configuration is $[Ar]3d^8$ with a $t_{2g}{}^6e_g{}^2$ configuration in the octahedral field.

The six sulfur atoms of three four-membered chelate rings in $Ni(dtb)_3^-$ are bonded to nickel with a Ni–S distance of 2.42 (2) Å. This distance is longer than the Ni–S distances found (~2.21 Å) for several[12] planar 1,1-dithiocarboxylato metal complexes. Considerable strain also exists within the 1,1-dithiolate chelate rings causing a significant deviation from the ideal octahedral coordination geometry. A measure of this distortion is shown by the 72.4 (3)° intraligand S–Ni–S angle. This angle is observed[13] to be 77.5° for $Ni(dtb)_2$, 77.0° for[14] $Ni(p\text{-dtc})_2S$, and 73.9° for[15] $Fe(p\text{-dtt})_3S$, dtt = dithiotoluate complexes, respectively. The intraligand S···S distance of 2.85 Å found in the $[Ni(dtb)_3]^-$ anion is longer than the average value of 2.76 Å observed for $Ni(dtb)_2$

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Table II. Atom Coordinates (×10) and Temperature Factors (A^2 × 10) for the $[Ni(S_2CC_6H_5)_3]^-$ Anion (Hydrogens are Listed in a Separate Table)

atom	*x*	*y*	*z*	U^a
Ni	6344 (1)	2711 (1)	9212 (1)	75 (1)
S(11)	6696 (2)	1723 (1)	8392 (2)	84 (1)
S(12)	5051 (1)	2552 (1)	7983 (2)	75 (1)
C(11)	5670 (8)	656 (6)	7018 (7)	98 (5)
C(12)	5313 (9)	140 (8)	6433 (8)	120 (6)
C(13)	4419 (10)	243 (7)	5926 (7)	120 (6)
C(14)	3946 (8)	840 (6)	6036 (7)	99 (5)
C(15)	4331 (6)	1346 (5)	6639 (5)	77 (3)
C(16)	5205 (5)	1265 (5)	7137 (5)	68 (3)
C(17)	5621 (5)	1817 (5)	7787 (5)	69 (3)
S(21)	7121 (2)	3705 (1)	8737 (2)	87 (1)
S(22)	5888 (2)	3827 (1)	9755 (2)	91 (1)
C(21)	7484 (8)	5341 (7)	9133 (13)	155 (9)
C(22)	7706 (11)	6079 (7)	9321 (15)	183 (11)
C(23)	7246 (11)	6500 (7)	9687 (10)	140 (7)
C(24)	6537 (13)	6232 (7)	9934 (7)	133 (7)
C(25)	6308 (10)	5499 (6)	9801 (6)	112 (6)
C(26)	6783 (7)	5046 (5)	9419 (6)	88 (4)
C(27)	6603 (6)	4251 (5)	9295 (5)	76 (3)
S(31)	7542 (2)	2404 (1)	10479 (1)	78 (1)
S(32)	5727 (2)	1864 (2)	10030 (2)	86 (1)
C(31)	7852 (7)	1381 (6)	12035 (5)	89 (4)
C(32)	8037 (10)	917 (9)	12729 (8)	133 (6)
C(33)	7363 (13)	476 (10)	12859 (10)	160 (9)
C(34)	6564 (12)	432 (9)	12302 (10)	149 (8)
C(35)	6346 (8)	885 (6)	11613 (6)	101 (5)
C(36)	6992 (6)	1360 (5)	11462 (5)	69 (3)
C(37)	6765 (5)	1844 (5)	10709 (5)	65 (3)

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

and $Ni(p\text{-}dtcu)_2S$ and longer than the 2.78 Å found for the complex $Fe(p\text{-}dtt)_3S$. The average C–S bond distance of 1.68 (2) Å in the chelate ring as well as the S–C–S angle of 85.6° are typical of the values found in compounds containing the dithiocarboxylate ligand.

The 2,2,2-Crypt portion of the [K(2,2,2-Crypt)]$^+$ counterion is disordered. The positional and isotropic thermal parameters for one structural solution of the [K(2,2,2-Crypt)]$^+$ are presented in Supplementary Table IV. The bond distances and bond angles for the anion in this solution are tabulated in Table III. The bond distances and bond angles in this table are comparable to those found[16,17] for [K(2,2,2-Crypt)]I and $[Na(2,2,2\text{-}Crypt)]_2[Fe_2(CO)_6(\mu_2\text{-}PPh_2)_2]$.

Table III. Bond Lengths (Å) for the $[Ni(S_2CC_6H_5)_3]^-$ Anion

Ni–S(11)	2.402 (3)	Ni–S(12)	2.426 (2)
Ni–S(21)	2.418 (3)	Ni–S(22)	2.407 (3)
Ni–S(31)	2.433 (3)	Ni–S(32)	2.407 (3)
S(11)–C(17)	1.682 (7)	S(12)–C(17)	1.680 (9)
C(16)–C(17)	1.481 (11)		
S(21)–C(27)	1.695 (10)	S(22)–C(27)	1.683 (10)
C(26)–C(27)	1.482 (13)		
S(31)–C(37)	1.690 (9)	S(32)–C(37)	1.672 (7)
C(36)–C(37)	1.485 (11)		

C–C (average for the phenyl rings)	1.367
C–H (phenyl rings)	0.960

Nonbonded Distances

S(11)···S(12)	2.857
S(21)···S(22)	2.861
S(31)···S(32)	2.849

Bond Angles, deg

S(11)–Ni–S(12)	72.6 (1)	S(11)–Ni–S(21)	100.2 (1)
S(12)–Ni–S(21)	100.5 (1)	S(11)–Ni–S(22)	168.1 (1)
S(12)–Ni–S(22)	99.0 (1)	S(21)–Ni–S(22)	72.7 (1)
S(11)–Ni–S(31)	94.3 (1)	S(12)–Ni–S(31)	159.4 (1)
S(21)–Ni–S(31)	97.3 (1)	S(22)–Ni–S(31)	96.0 (1)
S(11)–Ni–S(32)	90.8 (1)	S(12)–Ni–S(32)	91.9 (1)
S(21)–Ni–S(32)	165.4 (1)	S(22)–Ni–S(32)	98.0 (1)
S(31)–Ni–S(32)	72.1 (1)	Ni–S(11)–C(17)	85.4 (3)
Ni–S(12)–C(17)	84.7 (3)	S(11)–C(17)–S(12)	116.4 (5)
S(11)–C(17)–C(16)	120.9 (6)	S(12)–C(17)–C(16)	122.7 (6)
Ni–S(21)–C(27)	85.5 (3)	Ni–S(22)–C(27)	86.1 (4)
S(21)–C(27)–S(22)	115.6 (6)	S(21)–C(27)–C(26)	123.6 (8)
S(22)–C(27)–C(26)	120.7 (8)	Ni–S(31)–C(37)	85.4 (3)
Ni–S(32)–C(37)	86.6 (3)	S(31)–C(37)–S(32)	115.8 (5)
S(31)–C(37)–C(36)	122.0 (6)	S(32)–C(37)–C(36)	122.1 (7)

Although the results of this study clarify the troubling question of the formation of the "sulfur-rich" Ni dithiolates from Hieber's reaction of the "sulfur-poor" $Ni(dtb)_2$ with basic solutions of H_2S, some interesting additional observations can be made. First, these six-coordinate paramagnetic anions are chemically labile, both with regard to Ni–S and C–S bonds. In the presence of acid, rapid decomposition occurs to form the S catenated product. Very likely these observations are related to the observations of McCleverty[18] that tris(dithiolato)zinc anions catalyze labilization of sulfur and the vulcanization of olefin rubber. Second, Hieber and Bruck[1] observed a brown intermediate upon oxidation which they thought to be the Ni(IV) anion $[NiS_2(S_2CC_6H_5)]^{2-}$. While no complex has been isolated, oxidation to the red $Ni(S_3CC_6H_5)(dtb)$ may involve the formation of $[Ni(S_2CC_6H_5)_3]^+$, a species expected to have a structure like that of the $[Ni(IV)(S_2CNR_2)_3]^+$. This latter cation is known to be unstable in the presence of acid to form coupled sulfur and Ni(II) products. When coupled sulfur products are formed with the dithiobenzoates, it is known[2] that they are sulfur atom labile.

It appears that anionic NiS_6 species generally are capable of being oxidized to Ni(III) or Ni(IV) products. Their stability is variable depending on the specific ligand. The relevance of this oxidation–reduction chemistry to the Ni containing enzyme[4] systems containing sulfur remains to be explored further.

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Supplementary Material Available: Packing arrangement for the $[Ni(S_2CC_6H_5)_3]^-$ anion and tables of H coordinates, temperature factors, and observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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