much more stable in solution than the corresponding diphenylphosphine complexes,[7] and no evidences of tris-phosphine adducts have been obtained with dicyclohexylphosphine.[15] The same stability order is found in the case of the $[Ni(HPR_2)_4X]^+$ species, which are formed only with diethylphosphine.

Steric arguments could provide the most obvious interpretation of this trend. However, we believe that this fact alone cannot explain entirely the drastic collapse of the stability of the five-coordinate adducts, going from diethylphosphine to dicyclohexylphosphine.

Probably, as already suggested for the case of tertiary phosphine complexes,[2-5] the stabilization of five-coordinate species depends on a favorable balance of electronic as well steric factors.

Acknowledgments.—The authors are grateful to Professor A. Turco for stimulating discussion and to Mr. L. Turiaco and G. Gomiero for technical assistance.

(15) P. Rigo and M. Bressan, unpublished results.

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Dithiotropolonates. III.[1] Ring-Alkylation Reactions of Bis(dithiotropolonato)nickel(II) and -zinc(II) Complexes

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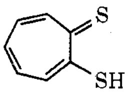
Bis(dithiotropolonato)nickel(II) and -zinc(II) have been found to undergo reactions consistent with electrophilicity of the seven-membered ring. Reaction of $M(SST)_2$ (**2**, **3**) with methyllithium in THF has been shown to yield the anionic methylated complexes $[Ni(H,Me\text{-}SST)_2]^{2-}$ (**6**), $[Zn(H,Me\text{-}SST)(SST)]^-$ (**9**), and $[Zn(H,Me\text{-}SST)_2]^{2-}$. Controlled oxidation of the nickel dianion gave the spin-doublet complex $[Ni(H,Me\text{-}SST)_2]^-$ (**7**). Pure salts of the anions **6**, **7**, and **9** were isolated. Exhaustive oxidation of the nickel mono- or dianion afforded the methyl-substituted dithiotropolonate complex $Ni(Me\text{-}SST)_2$ (**8**). Electrochemical, epr, and spectral studies of the nickel complexes have revealed the existence of the electron-transfer series $[Ni(H,Me\text{-}SST)_2]^z$, where z = 2−, 1−, 0, and other familiar electronic characteristics of nickel dithiolenes. These findings together with the results obtained from spin-decoupled pmr spectra of the zinc dianion establish that methylation has occurred at the α carbon of the seven-membered ring. Certain parallels are pointed out between the reactions of azulene and $M(SST)_2$ complexes with organolithium reagents. Methylation reactions of the complexes are considered to proceed by direct nucleophilic attack rather than by a free-radical process.

Introduction

In parts I[1a] and II[1b] of this series we have reported the synthesis of dithiotropolone (2-mercaptocycloheptatrienethione, **1**) and certain of its bis(chelate)-metal(II) complexes, $M(SST)_2$ (**2**, **3**). These complexes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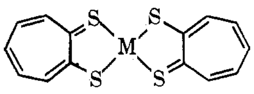
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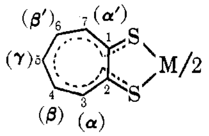

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are of particular interest because, like the thoroughly studied bis-dithiolene complexes,[3-5] they contain unsaturated five-membered chelate rings with sulfur donor atoms. However, the dithiotropolonates of the nickel group do not possess ground-state electronic structures equivalent or analogous to the corresponding neutral dithiolenes, a situation which is most simply expressed in VB terms. The dithiotropolonate chelate ring lacks the dithiolate–dithione resonance properties strictly analogous to those considered responsible for the relatively high electron affinities of the neutral dithiolenes.[3-5] The most nearly analogous resonance forms are obtainable only with invocation of presumably excited ligand structures which involve charge separation or unpairing of electrons[1b] and, therefore, would make only small contributions to the ground-state electronic structure. Consistent with this situation are the considerably more negative (0.75–1.0 V) half-wave potentials for the electrochemically irreversible reductions of the nickel group dithiotropolonates compared to the values for the reversible reductions of the dithiolenes of this group. The electronic structures of dithiotropolonate complexes are best described by **2** and its symmetry-related form, which lead to the delocalized structure **3**. Dithiotropolonates are therefore examples of complexes containing odd-atom monoanionic ligands with an even number of π electrons[4] and do not possess low-energy vacant orbitals. In contrast, the dithiolenes (*e.g.*, $M(S_2C_2R_2)_2{}^z$, $M(S_2C_6H_4)_2{}^z$) are of the even–odd types,[4] leading to dithiolate–dithione resonance contributions in the neutral species which impart partial α-dithione character to each coordinated ligand, thereby accounting for the relatively high electron affinities of these complexes.

This view of the electronic structure of $M(SST)_2$ complexes has been confirmed in substantial part by the recent X-ray structural determination of $Ni(SST)_2$.[6] The complex is planar (overall D_{2h} symmetry), consistent with its diamagnetism,[2] and has an average Ni–S distance of 2.147 Å, indicating some metal–ligand

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(1) (a) Part I: C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 6884 (1968); (b) part II: C. E. Forbes and R. H. Holm, *ibid.*, **92**, 2297 (1970).

(2) National Institutes of Health Predoctoral Fellow, 1968–1971.

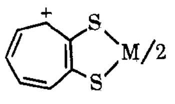
(3) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(4) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968); *Accounts Chem. Res.*, **2**, 72 (1969).

(5) E. Hoyer and W. Dietzsch, *Z. Chem.*, **11**, 41 (1971).

(6) G. P. Khare, A. J. Shultz, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 3597 (1971).

π bonding. The most salient structural feature is the C_1–C_2 bond distance of 1.448 Å, which is significantly longer than the other C–C distances (1.378–1.401 Å). This result is consistent with description **3**. However, as pointed out by Khare, *et al.*,[6] the C_1–C_2 distance is *ca.* 0.05 Å shorter than that estimated for a single bond between two trigonally hybridized carbons. They have proposed that resonance structures such as **4** and **5** contribute in minor part to the ground-state electronic description of Ni(SST)$_2$ and, presumably, to other dithiotropolonate complexes as well. These rather qualitative considerations, together with certain previously reported experimental results which are described below, imply that coordinated dithiotropolonate might be susceptible to attack by nucleophiles. This paper details our study of the reactions of Ni(SST)$_2$ and Zn(SST)$_2$ with alkyllithium reagents, principally methyllithium. Addition products were isolated and characterized, and the position of methylation was identified. In the case of nickel(II), the products were found to have the properties of dithiolene species and to undergo oxidative dehydrogenation affording the methyl-substituted dithiotropolonate complex.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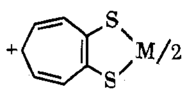
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Experimental Section

Preparation of Compounds.—Ni(SST)$_2$ and Zn(SST)$_2$ were prepared as previously described.[1b] Unless otherwise indicated all reactions and manipulations were carried out using degassed solvents under a rigorously oxygen-free nitrogen atmosphere. Reagent grade tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. The solution of methyllithium in diethyl ether (Foote Mineral Co.) employed in the reactions was found to be 1.82 *M* using Gilman's double-titration method.[7] Melting points are uncorrected.

(Me$_4$N)$_2$[Ni(H,Me-SST)$_2$] (6).—To a suspension of 0.30 g (0.82 mmol) of Ni(SST)$_2$ in 50 ml of THF at −78° was added 0.93 ml (1.7 mmol) of methyllithium solution. A deep red color developed immediately. The reaction mixture was stirred at −78° until all of the solid dissolved (*ca.* 7 hr). At this point the solution contained the lithium salt of [Ni(H,Me-SST)$_2$]$^{2-}$. The solvent was removed and the residue dissolved in 12 ml of 1-butanol. Addition of 0.20 g (1.9 mmol) of tetramethylammonium chloride dissolved in 10 ml of 1-butanol resulted in the separation of red-orange crystals. These were twice recrystallized from 25 ml of methanol to afford 273 mg (61%) of red-orange crystals, mp 177–178° dec (sealed tube). *Anal.* Calcd for $C_{24}H_{40}N_2S_4Ni$: C, 53.02; H, 7.43; N, 5.16; S, 23.59. Found: C, 52.75; H, 7.44; N, 5.09; S, 23.36. The compound is highly oxygen sensitive and must be protected from the atmosphere.

(Ph$_4$As)[Ni(H,Me-SST)$_2$] (7).—A sample of crude Li$_2$[Ni(H,Me-SST)$_2$] was obtained by the reaction of 0.20 g (0.55 mmol) of Ni(SST)$_2$ with 1.2 mmol of methyllithium. This material was dissolved in 10 ml of methanol and the solution was filtered. To the filtrate was added 0.46 g (1.1 mmol) of tetraphenylarsonium chloride dissolved in 10 ml of methanol followed by a solution of 70 mg (0.28 mmol) of iodine in 10 ml of methanol. The resultant dark violet solution deposited a black solid upon cooling, which was twice recrystallized from methanol. The pure product was obtained as fine purple-black crystals (168 mg, 46%), mp 161–162° dec (sealed tube). *Anal.* Calcd for $C_{40}H_{36}AsS_4Ni$: C, 61.70; H, 4.67; As, 9.62; S, 16.47. Found: C, 60.97; H, 4.89; As, 9.71; S, 16.62. The compound should be protected from the atmosphere.

Ni(Me-SST)$_2$ (8).—A THF solution of Li$_2$[Ni(H,Me-SST)$_2$] resulting from the reaction of 0.50 g (1.4 mmol) of Ni(SST)$_2$ with 3.5 mmol of methyllithium was filtered and 1.4 g (5.5 mmol) of iodine in 30 ml of THF was added. The resultant dark green solution was refluxed for 36 hr to ensure complete reaction. After exposure to air and addition of 200 ml of water, a black solid separated and was collected by filtration (0.49 g). It was twice recrystallized from pyridine and dried *in vacuo* at 140° for 72 hr to afford 0.31 g (58%) of fine black crystals which did not melt up to 360°. *Anal.* Calcd for $C_{16}H_{14}S_4Ni$: C, 48.87; H, 3.60; S, 32.61. Found: C, 48.97; H, 3.75; S, 32.40. (Analysis also revealed a trace amount of nitrogen which could not be removed by further heating.) The mass spectrum of the compound exhibited intense peaks for the molecular ion $C_{16}H_{14}S_4Ni^+$ and the fragments $C_8H_7S_2Ni^+$, $C_8H_7S_2^+$, $C_8H_7S^+$, and $C_7H_7^+$.

(Ph$_4$As)[Zn(H,Me-SST)(SST)] (9).—A suspension of 0.50 g (1.4 mmol) of Zn(SST)$_2$ in 100 ml of THF at −78° was treated with 2.0 equiv of methyllithium. The reaction was allowed to proceed at this temperature until all of the solid dissolved (*ca.* 7 hr). After removal of the solvent *in vacuo* the residue was dissolved in 30 ml of methanol, the solution was filtered, and 1.20 g (2.86 mmol) of tetraphenylarsonium chloride in methanol was added slowly, resulting in a red-brown crystalline precipitate. After recrystallization from 1-butanol and then acetonitrile, the pure product was obtained as red-brown crystals, mp 110–114° dec (sealed tube). *Anal.* Calcd for $C_{39}H_{33}AsS_4Zn$: C, 60.82; H, 4.32; As, 9.73; S, 16.65. Found: C, 61.12; H, 4.38; As, 9.46; S, 16.40. The compound should be protected from the atmosphere.

(Me$_4$N)$_2$[Zn(H,Me-SST)$_2$].—Zn(SST)$_2$ was treated with methyllithium as described in the preceding preparation except that the reaction was allowed to proceed for 2 days at −78° and then at −10° for 1 week. An additional 0.25 equiv of methyllithium was then added, the solution was allowed to stand at room temperature for several hours, and the solvent was removed *in vacuo*. The resultant orange solid was dissolved in the minimum amount of 1-butanol, the solution was filtered, and excess tetramethylammonium chloride in 1-butanol was added, producing a light yellow precipitate. This material was twice recrystallized from methanol to yield a yellow-orange powder which was sensitive to oxygen and could not be obtained in an analytically pure condition. As discussed in the text the pmr spectrum of the salt allowed identification of the anion as [Zn(H,Me-SST)$_2$]$^{2-}$.

In addition to the above experiments Ni(SST)$_2$ was treated with *tert*-butyllithium, isopropyllithium, and isopropylmagnesium bromide under similar conditions. Orange-red air-sensitive anions were produced in each case which upon partial oxidation gave an intense epr signal at $\langle g \rangle = 2.06$. Exhaustive oxidation afforded dark green substituted dithiotropolonate complexes which were identified by their electronic and mass spectra but were not fully purified.

Physical Measurements.—Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E spectrometer operating at 70 eV. Electrochemical measurements were carried out with a Princeton Applied Research Model 170 electrochemistry system using a rotating platinum electrode as the working electrode and an sce as the reference electrode. Solutions were *ca.* 10^{-3} *M* in complex and 0.05 *M* in tetra-*n*-propylammonium perchlorate as the supporting electrolyte. A Varian V-4502 spectrometer was used for epr measurements. The magnetic field was monitored with a Harvey Wells proton gaussmeter. Magnetic moments were measured by the Faraday method. Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Pmr spectra were obtained using Varian HR-100 and T-60 spectrometers. Proton decoupling experiments were performed with the latter instrument.

Results and Discussion

Reactions of Dithiotropolonates with Methyllithium.—Treatment of a suspension of Ni(SST)$_2$ in THF with 2 equiv of methyllithium resulted in smooth conversion to the dianion **6**, [Ni(H,Me-SST)$_2$]$^{2-}$, which was isolated in 61% yield as its diamagnetic, highly air-sensitive tetramethylammonium salt. Evidence supporting methylation at the α carbon in this species and in **7**, **8**, **9**, and [Zn(H,Me-SST)$_2$]$^{2-}$ is given below. Controlled oxidation of **6** with 1 equiv of iodine in methanol afforded the paramagnetic monoanion **7**, [Ni(H,Me-SST)$_2$]$^-$, isolated as its tetraphenylarsonium

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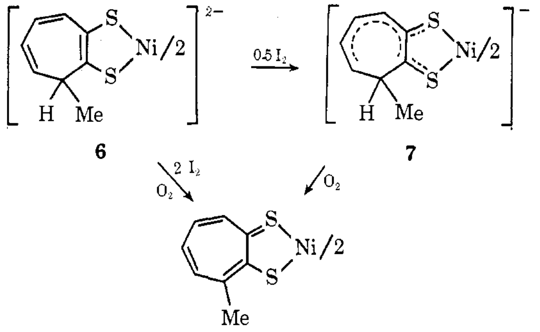
(7) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

TABLE I

EPR, POLAROGRAPHIC, AND SPECTRAL DATA FOR METHYLATED NICKEL DITHIOTROPOLONATES AND RELATED NICKEL DITHIOLENES[a]

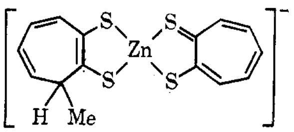
Complex	$\langle g \rangle$	g_1	g_2	g_3	$E_{1/2}$,[b] V $-2 \rightleftharpoons -1$	$-1 \rightleftharpoons 0$	λ_{max}, cm^{-1} (ϵ)
$[Ni(H,Me\text{-}SST)_2]^{2-}$	. . .	. . .	. . .	. . .	$-0.85^{c,d}$	$+0.01^{c,d}$	. . .
$[Ni(H,Me\text{-}SST)_2]^-$	2.055^f	1.995^f	2.040^f	2.117^f	$-0.83^{c,d}$	$+0.03^{c,d}$	10,550 (13,000)[c]
$[Ni(S_2C_2H_2)_2]^-$	2.056	1.996	2.039	2.126	-0.84^e	$+0.16^a$	11,500 (2400)[h]
$[Ni(S_2C_2Me_2)_2]^{-\,i}$	2.053	2.001	2.040	2.119	-1.14	-0.14	g
$[Ni(S_2C_2Ph_2)_2]^{-\,i}$	2.057	1.999^i	2.041^i	2.122^i	-0.82	$+0.12$	11,100 (8000)[h]
$Ni(Me\text{-}SST)_2$	. . .	. . .	. . .	. . .	$-0.99^{d,j}$	$-1.38^{d,j}$	13,700 (14,400)[k]
$Ni(SST)_2$	. . .	. . .	. . .	. . .	$-0.86^{d,j}$	$-1.25^{d,j}$	13,500 (14,600)[l]

[a] Data for dithiolenes from ref 3 unless otherwise indicated [b] At 25°, *vs.* sce. [c] Acetonitrile. [d] One-electron transfers as deduced from comparison of i_d/mM values with those for $[Ni(tdt)_2]^{2-} \rightleftharpoons [Ni(tdt)_2]^- + e^-$ ($E_{1/2} = -0.58$ V (MeCN), -0.50 V (DMSO)). [e] E. Hoyer, W. Dietzsch, H. Hennig, and W. Schroth, *Chem. Ber.*, **102**, 603 (1969). [f] 3:1 v/v DMF–acetone. [g] Data not reported. [h] Pyridine. [i] Epr data from ref 9b. [j] DMSO. [k] $CHCl_3$. [l] DMF.



6 **7** **8**

salt. Oxidation of the dianion with 4 equiv of iodine in THF yielded the neutral dimethyl complex **8**, $Ni(Me\text{-}SST)_2$. Both anions could also be oxidized to this complex with oxygen, but reaction with iodine was found to be the cleaner preparative method. The reactions of $Zn(SST)_2$ with methyllithium were also investigated but in less detail. Initial experiments indicated that with 2 equiv or more of methyllithium the reaction in THF proceeded through two stages, indicated by the appearance of a red-brown solution followed by very slow conversion to a yellow-orange solution. The red-brown color was fully developed after *ca.* 7 hr at −78° while conversion to a yellow-orange color required a reaction time of about 1 week at −10°. Subsequent preparative experiments led to isolation of the monoanion **9**, $[Zn(H,Me\text{-}SST)(SST)]^-$, as its pure



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tetraphenylarsonium salt from the red-brown solution. Isolated from the yellow-orange solution was a somewhat impure sample of the air-sensitive salt $(Me_4N)_2[Zn(H,Me\text{-}SST)_2]$, whose anion was identified by pmr. That $(Ph_4As)[Zn(H,Me\text{-}SST)(SST)]$ is not an equimolar mixture of $Zn(SST)_2$ and $(Ph_4As)_2[Zn(H,Me\text{-}SST)_2]$ was demonstrated by its solubility in polar solvents such as methanol (in which $Zn(SST)_2$ is insoluble) and the absence of the polarographic reduction wave at −0.89 V *vs.* sce in DMF found for $Zn(SST)_2$.[1b] In contrast to the behavior of $Zn(SST)_2$, $Ni(SST)_2$ when treated with 2 equiv of methyllithium gave no visual indication of two reaction stages, and formation of $[Ni(H,Me\text{-}SST)_2]^{2-}$ was found to be completed within 7 hr at −78°.

Properties and Structures of Methyl-Substituted Complexes.—The reactions described above are, in effect, additions of methide to coordinated dithiotropolonate and could occur at any of the four distinct carbon atoms of the C_7 ring. In the case of monoaddition four positional isomers are possible. For diaddition involving different rings many cis- and trans-planar (nickel) or tetrahedral (zinc) diastereoisomers could result, with the number of distinguishable species primarily dependent upon whether or not addition takes place at symmetrically related sites of the initial $M(SST)_2$ complex. The physical studies described below suffice to establish the position of addition in each ring of a given complex but provide no further structural information. Electrochemical, spectral, and pmr data relevant to the establishment of positional isomers are presented in Tables I and II and Figures 1–3.

TABLE II

PMR DATA FOR METHYLATED NICKEL AND ZINC DITHIOTROPOLONATES

Compound	Solvent	Chem shift[a]	Assignment
$Li_2[Ni(H, Me\text{-}SST)_2]$	THF	1.15 d[b]	$CH(CH_3)$
		4.89 "t" (∼1)	Olefinic
		5.64 m (2)	
		6.26 "d" (1)	
$(Me_4N)_2[Zn(H,Me\text{-}SST)_2]$[c]	DMSO-d_6	1.30 d (3)[d]	$CH(CH_3)$
		2.33 q (1)[d]	$CH(CH_3)$
		3.04 s (1)	NMe_4^+
		4.89 "t" (1)	Olefinic
		5.74 m (2)	
		6.70 "d" (1)	
$(Ph_4As)[Zn(H,Me\text{-}SST)(SST)]$	DMSO-d_6	1.27 d (3)[d]	$CH(CH_3)$
		2.30 q (1)[d]	$CH(CH_3)$
		4.92 "t" (1)	Olefinic
		5.82 m (2)	
		6.70 "d" (1)	
		7.22 m (∼3)	SST-$H_{\beta,\gamma}$
		7.80 s (20)	Ph_4As^+
		8.67 "d" (2)	SST-H_α

[a] Ppm downfield from TMS at ∼30°. Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; relative intensities given in parentheses. [b] Intensity could not be established due to overlap with solvent side bands. [c] Impurity peaks of low intensity at 1.83 and 4.23 ppm. [d] $J_{HMe} \approx$ 6–7 Hz.

A partial definition of the position of methylation in the nickel complexes can be obtained from their electrochemical, spectral, and epr properties. Polarographic studies of $[Ni(H,Me\text{-}SST)_2]^{2-}$ and $[Ni(H,Me\text{-}SST)_2]^-$ reveal that the former can be oxidized in two steps and the latter oxidized and reduced, with all processes involving one-electron transfers. The data in Table I and the cyclic current–voltage curves shown in Figure 1 demonstrate that each process is reversible. As described above, oxidation of the dianion to the mono-

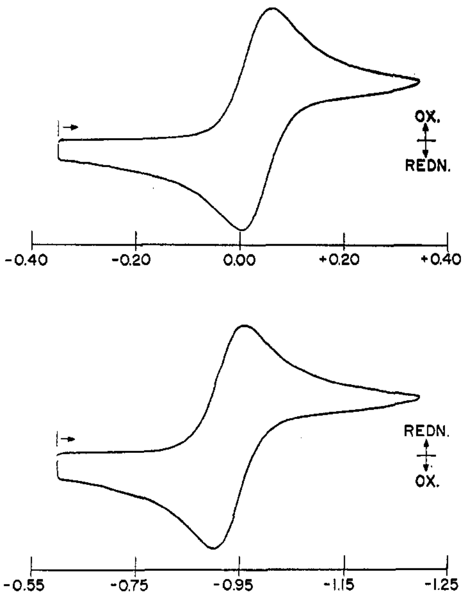


Figure 1.—Cyclic voltammograms for the one-electron oxidation (top) and reduction (bottom) of $[Ni(H,Me\text{-}SST)_2]^-$ in acetonitrile recorded at a scan rate of 0.020 V/sec.

anion has also been effected chemically. These results establish the three-membered electron-transfer series $[Ni(H,Me\text{-}SST)_2]^z$, where $z = 2-, 1-, 0$. The monoanion has a spin-doublet ground state as indicated by the magnetic moment of 1.70 BM obtained for the crystalline tetraphenylarsonium salt at ambient temperature. In 3:1 v/v DMF–acetone solution the monoanion displays an intense epr signal with $\langle g \rangle = 2.055$. In a glass of this composition at $-196°$ three principal g values (Table I) were observed for the monoanion. The electronic spectrum of this species (Figure 2) contains an intense band in the near-infrared region at 10,550 cm^{-1} (ϵ 13,000) which is absent in the spectrum of the dianion. Exhaustive chemical oxidation of either the dianion or monoanion afforded a green-black slightly soluble compound whose properties are unmistakably those of a methyl-substituted nickel dithiotropolonate complex. $Ni(Me\text{-}SST)_2$ shows two irreversible polarographic reductions (Table I) at potentials slightly more negative than the corresponding processes of $Ni(SST)_2$ and an electronic spectrum (Figure 2) which is virtually identical with that of $Ni(SST)_2$ in DMF.[1b,8]

The foregoing results place certain restrictions upon the positions of methylation. Barring the unlikely event of methyl migration during the oxidations **6**, **7** → **8**, the close similarities of $Ni(Me\text{-}SST)_2$ and $Ni(SST)_2$ require location of the methyl group at the α, β, or γ carbons. Further, the convincing resemblance of epr, polarographic, and near-infrared spectral features of **6** and **7** to those of the nickel dithiolenes **10**[3-5,9] (R = H, Me, Ph; *cf.* Table I) indicates that β addition has not occurred in either ring. The reversibility of the electrochemical processes allows formulation of the terminal oxidized members of the electron-transfer series as $[Ni(H,Me\text{-}SST)_2]^0$. This species clearly resembles the neutral nickel dithiolenes in its ability to be reversibly reduced, a feature which is associated with the dithiolate–dithione resonance property. Consequently, *each* of its rings must be methylated at the α or γ positions, inasmuch as β-methylated species lack this resonance property. One of the appropriate resonance forms for the α-methylated species is shown by **11**. The close correspondence of redox

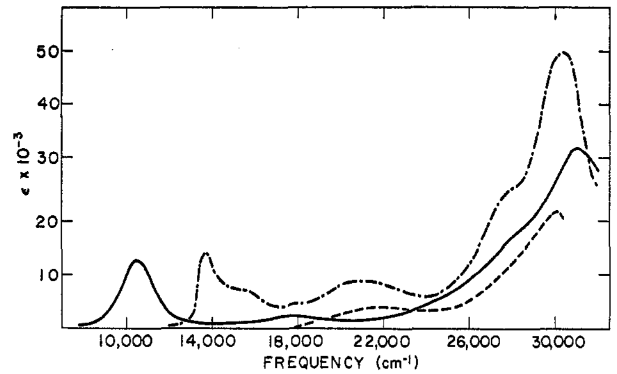


Figure 2.—Electronic absorption spectra of methylated nickel complexes: —, $(Ph_4As)[Ni(H,Me\text{-}SST)_2]$ in acetonitrile; - - -, $[Ni(H,Me\text{-}SST)_2]^{2-}$ in acetonitrile (obtained by reduction of the monoanion with hydrazine); —·—·, $Ni(Me\text{-}SST)_2$ in chloroform.

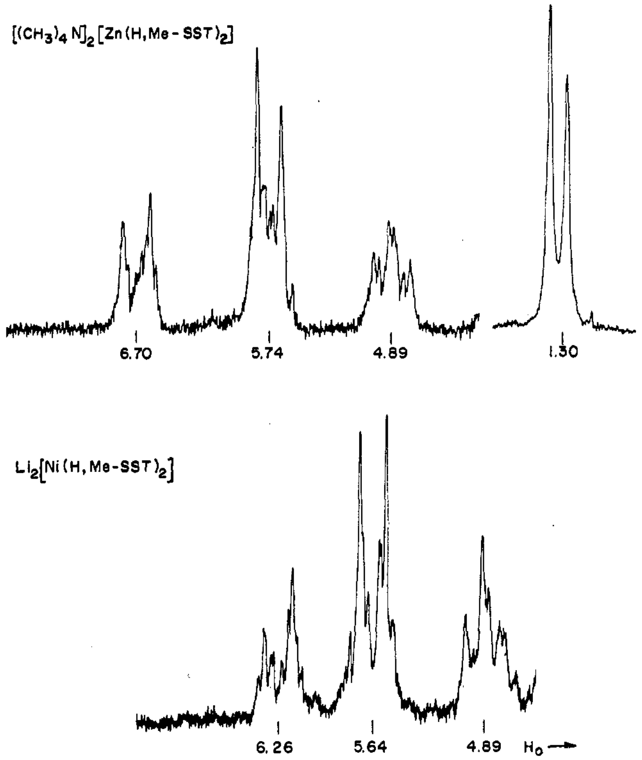
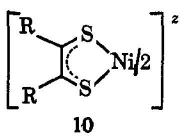


Figure 3.—Pmr spectra of $(Me_4N)_2[Zn(H,Me\text{-}SST)_2]$ in DMSO-d_6 and $Li_2[Ni(H,Me\text{-}SST)_2]$ in THF. Shifts are in ppm downfield of TMS reference. Regions obscured by solvent and water resonances are omitted.



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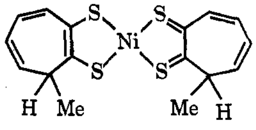

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potentials and g anisotropy of the monoanion with those of the dithiolenes, together with the appearance

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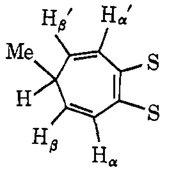
[8] Spectral data (λ_{max}, cm^{-1} (ϵ)) for $Ni(SST)_2$ in DMF: 13,500 (14,600); 15,200 (sh) (7300); 20,200 (sh) (8000); 21,600 (9200); 27,600 (sh) (25,800); 30,500 (61,700). Tabulation of the lowest energy bands for the two dithiotropolonates in Table I is not meant to imply that they result from transitions similar to those in the monoanionic nickel dithiolenes.

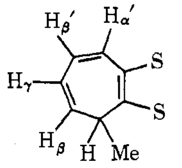
of a near-infrared band in the spectrum of the monoanion, further indicates that $[Ni(H,Me\text{-}SST)_2]^{0,-,2-}$ are in fact complexes of the dithiolene type. The monoanion **7** doubtless has a ground state analogous to that ($^2B_{3g}$) established for $[Ni(mnt)_2]^-$,[9] in which the odd electron is extensively delocalized over the ligands in an out-of-plane π MO.

Establishment of the α carbon as the position of methylation in the nickel and zinc complexes has been accomplished by pmr experiments. Spectra of the dimethylated zinc and nickel dianions are shown in Figure 3; chemical shift data are collected in Table II. The spectra of the two dianions in different solvents are quite similar, with only small chemical shift variations, and reveal in the olefinic region approximate triplet, multiplet, and approximate doublet features of relative intensities 1:2:1 from high to low field. In addition, these two complexes and $[Zn(H,Me\text{-}SST)(SST)]^-$ show *one* methyl doublet ($J \approx$ 6–7 Hz) in the interval 1.15–1.30 ppm. Irradiation of the methine quartet of $[Zn(H,Me\text{-}SST)_2]^{2-}$ at 2.33 ppm causes collapse of the methyl doublet to a singlet with no changes in the olefinic region. These observations rule out methylation at C_1. The spectral similarities of the two dianions and the absence of additional resonances at lower field (*ca.* 7–9 ppm) found in the spectra of H-(SST)[1b] and $[Zn(H,Me\text{-}SST)(SST)]^-$ indicate that both rings have been methylated at the same position.

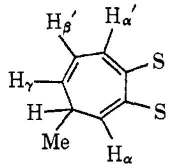
The γ-methyl ligand structure **12** can be eliminated. An AA′BB′ pattern should be observed in the olefinic region and is not consistent with three sets of resonances having the observed intensity ratio. The α-methyl structure **13** is compatible with the results of proton–proton decoupling experiments. A full analysis of the pmr spectrum of tropolone[10] has shown that coupling constants for adjacent protons are 10–11 Hz whereas those for nonadjacent protons are less than *ca.* 1 Hz. On this basis it is assumed that the approximate (first-order) multiplet structures evident in Figure 3 and noted in Table II arise from coupling of adjacent ring protons, with the additional fine structure due to coupling of protons separated by more than three bonds. Multiplet structures of the upfield and low-field olefinic resonances of the nickel and zinc dianions did not differ at 60 and 100 MHz. In the spectrum of $[Zn(H,Me\text{-}SST)_2]^{2-}$ either H_α' or H_β of **13** is assigned to the low-field doublet (6.70 ppm) and either H_β' or H_γ to the high-field triplet (4.89 ppm). Irradiation at slightly lower field than that at 5.74 ppm causes collapse of the doublet to a singlet. If the H_α' signal is this doublet, the signal of H_β' must be included in the 5.74-ppm feature, requiring that H_β is also in this feature and that H_γ gives rise to the triplet. Irradiation at fields slightly above 5.74 ppm effects collapse of the triplet to a doublet, a result also consistent with this assignment because H_β is adjacent to H_γ. The alternate assignment of signals—H_β, 6.70 ppm; H_α', H_γ, 5.74 ppm; H_β', 4.89 ppm—is, for similar reasons, also concordant with the decoupling experiments. It is noted that the chemical shift of the low-field doublet is the most metal dependent (Figure 1), which may imply that the first assignment is correct. The decoupling results are also inconsistent with the β-methyl structure **14**, which has not yet been specifically discounted for the zinc complexes. For this structure the triplet must be assigned to H_β'. (H_γ is eliminated since irradiation of the methine resonance has no effect on this signal.) The low-field doublet is then due to either H_γ or H_α' and the 5.74-ppm multiplet arises from H_α and either H_α' or H_γ. Collapse of the doublet to a singlet is inconsistent with the assignment of either H_γ or H_α' as the doublet since H_γ, H_α', and H_α are not adjacent in structure **14**. Regardless of the absolute assignment of the pmr spectra, the available evidence strongly favors α methylation of coordinated dithiotropolonate to generate 1,2-dithiolato-3-methyl-1,4,6-cycloheptatriene complexes.



12



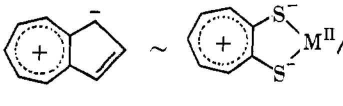
13



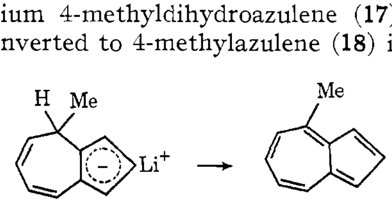
14

Related Results.—Prior to the inception of this investigation there existed several reports of the reactions of coordinated 1,2-disubstituted cycloheptatriene ligands. Reaction of bis(tropolonato)copper(II) and its β-methyl derivative with organolithium compounds or Grignard reagents resulted in breakdown of the complex and afforded 2-alkyl- or 2-aryltropones.[11–13] A reaction whose course is more closely related to those studied here is that between lithium aluminum hydride and bis(*N*,*N*′-dimethylaminotroponiminato)boron cation, $[B(Me_2ati)_2]^+$, which results in hydride addition.[14] The position of added hydrogen in the product, $[B(H,\text{-}H\text{-}Me_2ati)(Me_2ati)]^0$, was not established, however.

The facile alkylation of $M(SST)_2$ complexes can also be likened to similar reactions of azulene if the analogy between limiting dipolar forms such as **15** and **16** is accepted. The former is frequently invoked as a minor contributing structure to account for the electrophilic character of the seven-membered ring.[15] Azulene has been shown to react with methyllithium yielding initially lithium 4-methyldihydroazulene (**17**), which is readily converted to 4-methylazulene (**18**) in the pres-



15 **16**



17 **18**

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[9] (a) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964); (b) R. D. Schmitt and A. H. Maki, *ibid.*, **90**, 2288 (1968). The epr spectrum of $[Ni(H,Me\text{-}SST)_2]^-$ yielded no resolvable proton hfs, as is the case for all monoanionic nickel dithiolenes.

[10] D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *ibid.*, **91**, 5286 (1969).

[11] W. von E. Doering and C. F. Hiskey, *ibid.*, **74**, 5688 (1952).

[12] W. von E. Doering and J. R. Mayer, *ibid.*, **75**, 2387 (1953).

[13] R. D. Haworth and P. B. Tinker, *J. Chem. Soc.*, 911 (1955).

[14] E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, **86**, 5132 (1964).

[15] D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier, Amsterdam, 1966, Chapter VIII.

ence of air and alcohol or by thermolysis.[16] Nucleophilic attack at the 4 position is consistent with calculated π-electron charge densities for azulene.[17] MO calculations for dithiotropolone and its anion[18] indicate positive π-charge density at each carbon but do not indicate preferential electrophilicity at the α position. Calculations for $M(SST)_2$ complexes have not been carried out.

Finally, it is observed that, although the formation of the anions **6**, **9**, and $[Zn(H,Me\text{-}SST)_2]^{2-}$ is consistent with direct nucleophilic addition, a process involving reduction of $M(SST)_2$ to $M(SST)_2\cdot^-$ followed by reaction with methyl radicals cannot be completely discounted. However, this process is regarded as less probable for at least two reasons. First, only one positional isomer was detected in appreciable quantity; it is not clear why a radical process would not give appreciable amounts of more than one isomer. Second, numerous extremely careful attempts[19] to generate radical anions by electrochemical and chemical reductions have never resulted in the formation of any epr-detectable species, even under conditions where relatively short-lived species would have been observable. In this connection it is noted that the failure to detect the epr signal of the naphthalenide ion during the reaction of naphthalene with *tert*-butyllithium has been taken as sound evidence for direct addition of RLi to the hydrocarbon.[20]

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant GP-18978X) for support of this research.

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(17) L. Salem, "Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, p 130.

(18) J. Fabian, private communication.

(19) A. Gold and R. H. Holm, unpublished observations.

(20) R. L. Eppley and J. A. Dixon, *J. Amer. Chem. Soc.*, **90**, 1606 (1968).

CONTRIBUTION FROM THE LABORATORIO C.N.R. AND ISTITUTO DI CHIMICA GENERALE ED INORGANICA,
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Synthesis, Characterization, and Proton Magnetic Resonance Spectra of Nickel(II) and Cobalt(II) Complexes with *o*-Mercaptobenzaldiminates

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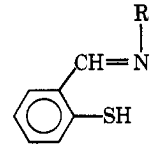
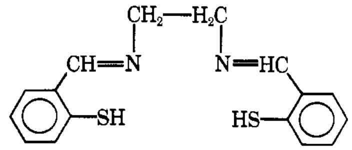
Nickel(II) and cobalt(II) complexes with Schiff base ligands formed from *o*-mercaptobenzaldehyde and mono- or polyamines having donor sets SN, S_2N_2, and S_2N_3, have been prepared and characterized. Planar, tetrahedral, and pentacoordinate complexes have been obtained. The stereochemistry and the solution behavior of these complexes have been compared with those of the analogous salicylaldiminate complexes. Among the bis-bidentate complexes the sulfur atoms favor the low-spin planar stereochemistry in comparison with the oxygen atoms. Pmr spectra of the pentacoordinate nickel complexes indicate the occurrence of an intramolecular interconversion involving the aromatic fragments and the Ni–S bonds. With this in mind the origin of the signal splitting observed for the analogous salicylaldiminate complexes is reconsidered.

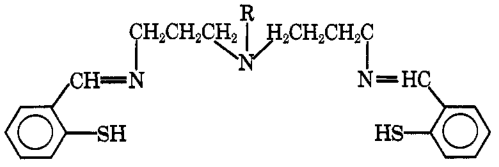
Introduction

It is well known that Schiff base ligands obtained from salicylaldehyde and mono- or polyamines (having donor sets ON, O_2N_2, O_2N_3, and O_2N_4) give rise to nickel(II) and cobalt(II) complexes with coordination numbers 4, 5, and 6.[1,2] Such complexes have been defined labile[2] in the sense that they may interconvert into complexes with different stereochemistries depending on the substituent group of the aromatic ring and on the synthesis conditions, *e.g.*, solvent, temperature, and presence of a different metal ion whose complex lattice may host the nickel or cobalt complex.[3] In solution many conformational equilibria have been described and, for some of them, the thermodynamic functions have been determined.[1,2]

The present paper deals with nickel(II) and cobalt(II) complexes with Schiff base ligands analogous to the above ligands but with the sulfur atoms substituting the oxygen atoms. Such ligands having donor sets SN, S_2N_2, and S_2N_3 have been obtained from *o*-mercaptobenzaldehyde (TIB) and various amines as shown below


TIB-R, R = Me
R = Et
R = *i*-Pr
R = *sec*-Bu
R = *tert*-Bu


TIB-en


TIB-DPT, R = H
TIB-MeDPT, R = Me

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(1) R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966); R. H. Holm and M. J. O'Connor, *ibid.*, **14**, 241 (1971).

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(3) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Amer. Chem. Soc.*, **87**, 3102 (1965); A. Chakravorty, *Inorg. Chem.*, **4**, 127 (1965).