

It may be noted further that the presence in one molecule of an h^5 -C₅H₅ ring, an h^1 -C₅H₅ ring, and two with an intermediate relationship to the metal might reasonably be expected to lead to ready interchange of ring types, since the intermediate ones can, as demonstrated in (C₅H₅)₃MoNO, readily interchange with the h^1 -C₅H₅ type of ring and it seems obvious that they could, perhaps even more easily, exchange roles with the h^5 -C₅H₅ ring. Thus, our observation⁶ that site exchange of all 20 protons in (C₅H₅)₄Zr (and the hafnium

analog) persists down to low temperatures in solution is well accounted for by the structure we are proposing.

That (C₅H₅)₄Zr adopts a structure in which an effective 18-electron population is achieved at the metal atom, whereas (C₅H₅)₄Ti has only a 16-electron population, seems naturally attributable to the fact that the structure giving the higher population is sterically more demanding and only the larger metal atom can meet the requirements.

Crystal and Molecular Structure of Bis(dithiotropolonato)nickel(II)

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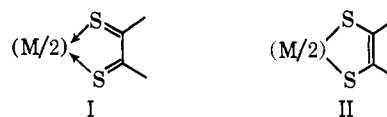
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Abstract: The crystal and molecular structure of bis(dithiotropolonato)nickel(II), Ni(S₂C₇H₅)₂, has been determined from three-dimensional single-crystal X-ray diffraction data collected by the θ - 2θ counter technique. The neutral complex crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^2 , no. 14) in a cell of dimensions $a = 7.845$ (10), $b = 13.638$ (20), $c = 6.913$ (10) Å, $\beta = 97^\circ 13' (2)'$, and $V = 733.9$ Å³. There are two molecules of the complex per unit cell ($\rho_{\text{exptl}} = 1.62 \pm 0.03$ g/cm³ and $\rho_{\text{calcd}} = 1.65$ g/cm³ for $Z = 2$). All atoms including hydrogens have been located, and their positional and thermal parameters have been refined by least-squares methods to a conventional R factor of 0.024 for 976 independent reflections. The complex is required to possess a center of symmetry and the coordination geometry is necessarily planar. The average Ni-S distance is 2.147 (3) Å with a S-Ni-S intrachelate ring bond angle of 90.11 (5)°. It is found that the C-C bond which is common to both the chelate ring and the tropolone ring is significantly longer (1.448 (4) Å) than the other carbon-carbon ring distances (1.378-1.401 (4) Å). This result is consistent with the previously reported chemical properties of Ni(S₂C₇H₅)₂ and underscores the lack of dithiolene character in this complex.

During the last several years, metal chelates containing the class of ligands known generically as the 1,2-dithiolenes or 1,2-dithienes have been extensively studied, and recently, several reviews of these systems have appeared.^{1,2} Complexes of the 1,2-dithiolenes have received this considerable attention principally because of the relatively facile and reversible electron-transfer reactions which they undergo, and because of the extended π systems and electron delocalization which are characteristic of their ground states.

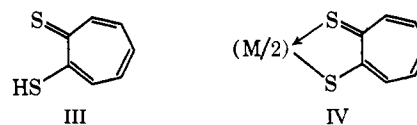
Particular attention in this area has been directed to the monomeric bis complexes which are found to possess the square-planar geometry for a wide variety of metal ions and d-electron configurations.^{3,4} The interesting and unusual properties of metal 1,2-dithiolenes have generally been attributed to the formation of unsaturated five-membered chelate rings and the effective overlap of the metal d functions with the π

molecular orbitals of the ligand. A valence-bond description of the electronic structures of the dithiolene complexes requires resonance structures of types I and II^{1,2} which may be weighted according to the overall



charge on the complex, the relative ligand and metal reduction potentials, the degree of delocalization, and various other factors.

Recently, Forbes and Holm synthesized and characterized dithiotropolone (III) and a number of bis complexes of the dithiotropolonate anion.⁵ Their study of complexes of type IV was based in simplest terms



on the notion that the dithione and dithiolate resonance structures I and II, which are of fundamental importance for the dithiolene complexes, play only a minor role in describing the electronic structures of the correspond-

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

(2) (a) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968); (b) *Accounts Chem. Res.*, **2**, 79 (1969).

(3) For a review of the structural work in this area, see R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970).

(4) Representative chemical and physical studies of the bis complexes are: (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964); (b) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 3585 (1965); (c) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966); (d) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *ibid.*, **88**, 4870 (1966); (e) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

(5) C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 6884 (1968); **92**, 2297 (1970).

ing dithiotropolonate systems. In fact, the results of the study by Forbes and Holm⁵ demonstrated that complexes of type IV do not undergo the facile and reversible electron-transfer reactions characteristic of the analogous bis(dithiolene) systems.

We undertook an X-ray structural investigation of the bis(dithiotropolonate) complex of Ni(II) in order to determine if there exist significant differences in the molecular structural parameters between this complex and the structurally known Ni-dithiolene complexes which might be indicative of the differences in their electronic structures and their electron-transfer properties. It also appeared to be of interest to determine the structure of the Ni(II)-bis(dithiotropolonate) complex for comparison with those of the numerous Ni(II) complexes which contain the planar NiS₄ chromophore but which do not possess the electron-transfer properties of the dithiolenes.³ Included in this category are the Ni(II) complexes of dithiocarbamates, dithiophosphinates, xanthate, dithiophosphate, and trithiocarbonate, among others.

The present paper presents the complete description of the structure determination of bis(dithiotropolonato)-nickel(II), Ni(S₂C₇H₅)₂.

Collection and Reduction of the X-Ray Data

A generous sample of the Ni(S₂C₇H₅)₂ complex was kindly supplied to us by Professor R. H. Holm of MIT. Apparently suitable crystals of the complex in the form of parallelepiped-shaped plates were grown from dimethyl sulfoxide-methanol solutions. However, optical and photographic examinations of the crystals revealed an overwhelming majority of them to exist as twinned crystals. The twinning mechanism was of the normal type with {100} as the composition plane. A lengthy search of the available crystals finally uncovered an approximately single crystal which was subsequently used for the intensity data collection. Weissenberg and precession photographs of this crystal revealed that its twinned components were in the approximate ratio of 20:1 and that the problem of overlap in the gathering of intensity data would not be a significant one. Numerous other attempts which were made to grow single crystals of the Ni(S₂C₇H₅)₂ complex proved unsuccessful.

The single-crystal photographs and optical measurements of the crystals examined indicated the Ni(S₂C₇H₅)₂ complex to crystallize in the monoclinic system in a cell of refined (*vide infra*) dimensions $a = 7.845$ (10), $b = 13.638$ (20), $c = 6.913$ (10) Å, $\beta = 97^\circ 13$ (2)' and $V = 733.9$ Å³. The observed extinctions, $h0l$ for l odd and $0k0$ for k odd, uniquely determine the space group as $P2_1/c$ (C_{2h}^5 , no. 14).⁶ The observed density of 1.62 ± 0.03 g/cm³ obtained by the flotation method in methylene iodide-carbon tetrachloride solution agrees with the value of 1.65 g/cm³ calculated for two molecules per unit cell. Hence the Ni(S₂C₇H₅)₂ complex is crystallographically required to possess a center of symmetry.

The crystal used for the collection of intensity data was of approximate dimensions $0.20 \times 0.20 \times 0.11$ mm (the shortest dimension being in the a^* direction) with the {100} and {011} faces showing development.

(6) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1960, p 99.

The crystal was mounted on a glass fiber parallel to the b axis and aligned accurately by photographic methods. After being transferred to a Picker four-circle automated diffractometer, the crystal was offset by 4° in order to minimize the possibility of multiple reflections.⁷ Approximately 20 reflections of both general and special classes were then centered in the counter aperture by varying 2θ , χ , and ϕ in conjunction with the left-right and top-bottom balancing features of the variable receiving aperture. The settings for these reflections formed the basis for a least-squares refinement of the unit cell parameters and orientation angles using our PICKLST program.⁸ The mosaic spread of the crystal was estimated from open-counter-narrow-source ω scans⁹ through several strong reflections and found to have an average value of 0.2° .

The intensity data were collected by the θ - 2θ scan technique using Zr-filtered Mo K α radiation. A take-off angle of 1.5° was used for the data collection with a counter opening of 5×5 mm. Each reflection was scanned from -0.60 to $+0.80^\circ$ of the calculated 2θ value of the reflection with a scan rate of $1^\circ/\text{min}$. Allowance was made in the scan range for the separation of the Mo K α doublet at higher 2θ angles. Stationary-counter-stationary-crystal background counts of 10-sec duration were collected at both ends of the 2θ scan range for each reflection. The maximum 2θ value for reflections which were measured was 50° . Pulse-height analysis designed to accept 90% of the diffracted Mo K α radiation was employed, and no attenuation was found to be necessary. The intensities of four standard reflections were measured after every 100 reflections and showed no significant change during the data collection. The greatest single deviation of any of the standard reflections from its respective mean was 1%.

The intensities of 1349 independent reflections were measured, and these were then corrected for the usual Lorentz and polarization factors to yield a set of F_o values, where F_o is the observed structure factor amplitude. Of the 1349 independent reflections measured, 976 were assumed to be statistically reliable, having intensities greater than twice their estimated standard deviations (*vide infra*). The data were then corrected for absorption using W. C. Hamilton's GONO9 absorption program. The linear absorption coefficient for Ni(S₂C₇H₅)₂ is 18.4 cm⁻¹ and for this crystal, the transmission coefficients range from 0.76 to 0.83.

Solution and Refinement of the Structure

With two molecules per unit cell, the position of the nickel atom is fixed at a center of symmetry which was chosen as the origin. A difference Fourier map based on phases obtained solely from the Ni atom contribution revealed the positions of the two independent sulfur atoms. This difference Fourier synthesis is actually similar to a Patterson function, since all phases based

(7) W. H. Zachariasen, *Acta Crystallogr.*, **18**, 705 (1965).

(8) In addition to the PICKLST setting program, the main programs used in this work were local versions of the Hamilton GONO9 absorption program, the Busing-Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, the Busing-Martin-Levy ORFFE function and error program, and the Johnson ORTEP plotting program. Various other local programs were also used. All computing was performed on Brown's IBM 360/67 computer.

(9) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

Table I. Final Parameters for Ni(S₂C₇H₆)₂^a

Atom	<i>x</i> ^b	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Ni	0.0	0.0	0.0	<i>c</i>
S(1)	0.0544 (1)	0.1546 (1)	0.0074 (1)	<i>c</i>
S(2)	-0.2694 (1)	0.0305 (1)	-0.0628 (1)	<i>c</i>
C(1)	-0.1394 (4)	0.2151 (2)	-0.0342 (4)	<i>c</i>
C(2)	-0.2933 (4)	0.1558 (2)	-0.0679 (4)	<i>c</i>
C(3)	-0.4625 (4)	0.1901 (3)	-0.1059 (5)	<i>c</i>
C(4)	-0.5257 (5)	0.2853 (3)	-0.1230 (5)	<i>c</i>
C(5)	-0.4362 (5)	0.3731 (3)	-0.1047 (5)	<i>c</i>
C(6)	-0.2614 (5)	0.3872 (3)	-0.0637 (5)	<i>c</i>
C(7)	-0.1324 (5)	0.3172 (2)	-0.0326 (5)	<i>c</i>
H(3)	-0.547 (4)	0.136 (2)	-0.124 (4)	1.9 (8)
H(4)	-0.647 (4)	0.290 (2)	-0.147 (4)	1.7 (7)
H(5)	-0.503 (5)	0.432 (2)	-0.130 (5)	2.2 (9)
H(6)	-0.221 (4)	0.456 (2)	-0.054 (4)	1.3 (7)
H(7)	-0.028 (4)	0.342 (2)	-0.005 (4)	0.9 (7)

Atom	Anisotropic Thermal Parameters					
	β_{11} ^d	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0125 (1)	0.0037 (0)	0.0181 (1)	0.00002 (5)	0.0018 (1)	-0.0003 (1)
S(1)	0.0141 (1)	0.0041 (1)	0.0298 (2)	-0.0004 (1)	0.0017 (1)	-0.0004 (1)
S(2)	0.0131 (1)	0.0042 (1)	0.0260 (2)	-0.0001 (1)	0.0010 (1)	-0.0003 (1)
C(1)	0.0165 (6)	0.0042 (2)	0.0153 (7)	0.0008 (3)	0.0027 (5)	0.0002 (3)
C(2)	0.0142 (6)	0.0044 (2)	0.0155 (7)	0.0011 (3)	0.0020 (5)	0.0003 (3)
C(3)	0.0164 (6)	0.0059 (2)	0.0198 (8)	0.0013 (3)	0.0018 (6)	0.0006 (3)
C(4)	0.0185 (8)	0.0074 (3)	0.0074 (3)	0.0020 (9)	0.0045 (4)	0.0015 (4)
C(5)	0.0273 (10)	0.0058 (2)	0.0205 (9)	0.0053 (4)	0.0020 (7)	0.0013 (4)
C(6)	0.0275 (9)	0.0042 (2)	0.0210 (9)	0.0020 (4)	0.0036 (7)	0.0000 (4)
C(7)	0.0202 (7)	0.0044 (2)	0.0217 (8)	-0.0002 (3)	0.0027 (6)	0.0001 (3)

^a Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. ^b *x*, *y*, *z* are in fractional coordinates. ^c Atoms refined anisotropically. ^d Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

on the Ni atom are positive. The positional parameters of the two sulfur atoms along with individual isotropic temperature factors for the three atoms were refined through several cycles of least-squares refinement. A second difference Fourier map, based on the contributions of the Ni and S atoms, revealed the positions of the carbon atoms of the seven-membered ring.

The trial structure was refined using a least-squares procedure. The function minimized was $\sum w(F_o - F_c)^2$, where the weights *w* were assigned as $4F_o^2/\sigma^2(F_o^2)$ and the standard deviations were estimated from counting statistics according to the formula

$$\sigma(F^2) = \frac{1}{TLp} \left(C + \left(\frac{t_c}{2t_b} \right)^2 (B_1 + B_2) + (0.03I)^2 \right)^{1/2}$$

where *Lp* is the Lorentz-polarization, *T* is the transmission coefficient, *C* is the total integrated count obtained in time *t_c*, *B₁* and *B₂* are the background counts, each obtained in time *t_b*, and *I* is the net integrated count.¹⁰ The nickel, sulfur, and carbon atom scattering factors used were those tabulated by Cromer and Waber^{11a} and the hydrogen atom scattering factor was that of Stewart, *et al.*^{11b} The effects of anomalous scattering were included in the calculated structure factors with values of $\Delta f'$ and $\Delta f''$ for Ni and S taken from Cromer's tabulation.¹² Only those reflections with F_o^2 greater than $2\sigma(F_o^2)$ were included in the refinement and in the calculation of the discrepancy indices *R* ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) and *R'* ($R' = (\sum w(F_o - F_c)^2 / \sum wF_o^2)^{1/2}$).

(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(11) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(12) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

In the initial round of calculations, all atoms were assigned individual isotropic temperature factors. This refinement of 37 positional and thermal parameters and one variable scale factor converged after four cycles to values of *R* and *R'* of 0.086 and 0.093, respectively. Refinement was continued assuming the ellipsoidal anisotropic thermal model for all of the nonhydrogen atoms. Another two cycles of least-squares refinement converged to discrepancy indices of 0.037 for *R* and 0.048 for *R'*. A difference Fourier synthesis at this stage led to the location of the five hydrogen atoms. Finally, four cycles of refinement of the positional and thermal parameters of all atoms in the structure including individual isotropic thermal parameters assigned to the hydrogen atoms resulted in convergence at *R* = 0.024 and *R'* = 0.026 for the 976 reflections above 2σ . In the final cycle, the largest parameter shifts, which were approximately one-third of their estimated standard deviations, were observed for some of the positional parameters of the hydrogen atoms. None of the parameters of any other atoms changed by more than one-tenth of its corresponding estimated standard deviation.

The parameters obtained in the last cycle of refinement are taken as the final parameters for the structure and are given in Table I along with their estimated standard deviations as obtained from the inverse matrix. A table of the *F_o* and $|F_c|$ values (in electrons $\times 10$) for the 976 reflections included in the refinement has been deposited with the ASIS National Auxiliary Publication Service.¹³ In Table II, the root-

(13) For this table, order Document No. NAPS-01294 from the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022, remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to CCMIC-NAPS.

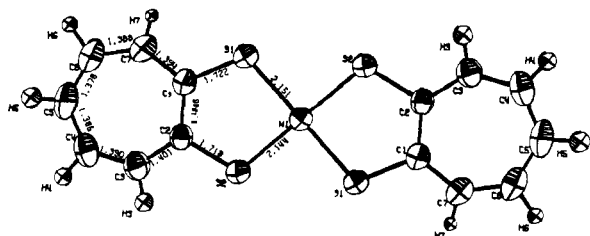


Figure 1. A perspective drawing of the $[\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2]$ molecule. The thermal ellipsoids have been scaled to 30% probability distribution.

Table II. Root-Mean-Square Amplitudes of Vibration (\AA)

Atom	Minimum	Intermediate	Maximum
Ni	0.185 (2)	0.196 (3)	0.209 (1)
S(1)	0.195 (1)	0.210 (2)	0.268 (1)
S(2)	0.198 (1)	0.202 (2)	0.252 (1)
C(1)	0.190 (6)	0.195 (8)	0.229 (4)
C(2)	0.190 (9)	0.193 (9)	0.220 (4)
C(3)	0.210 (5)	0.222 (6)	0.246 (5)
C(4)	0.192 (5)	0.234 (5)	0.297 (5)
C(5)	0.187 (5)	0.226 (5)	0.318 (5)
C(6)	0.194 (5)	0.223 (5)	0.295 (5)
C(7)	0.204 (5)	0.227 (5)	0.249 (4)

mean-square amplitudes of vibration of the atoms refined using the anisotropic thermal model are presented.

Description of the Structure

The $\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2$ complex is crystallographically required to be centrosymmetric, and its coordination geometry is necessarily planar. A drawing of the complex is presented in Figure 1, and important bond distances and angles are tabulated in Table III. The two inde-

Table III. Principal Intramolecular Distances and Angles in $\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2$

Distances, \AA		Angles, deg	
Ni-S(1)	2.151 (3)	S(1)-Ni-S(2)	90.11 (5)
Ni-S(2)	2.144 (3)	Ni-S(1)-C(1)	107.3 (1)
S(1)-S(2)	3.040 (3)	Ni-S(2)-C(2)	107.4 (1)
S(1)-S(2)'	3.034 (3)	S(1)-C(1)-C(2)	117.4 (2)
S(1)-C(1)	1.722 (4)	S(2)-C(2)-C(1)	117.8 (2)
S(2)-C(2)	1.718 (4)	C(1)-C(2)-C(3)	126.5 (3)
C(1)-C(2)	1.448 (4)	C(2)-C(3)-C(4)	130.4 (3)
C(2)-C(3)	1.401 (4)	C(3)-C(4)-C(5)	128.9 (4)
C(3)-C(4)	1.390 (5)	C(4)-C(5)-C(6)	128.2 (3)
C(4)-C(5)	1.386 (5)	C(5)-C(6)-C(7)	128.6 (4)
C(5)-C(6)	1.378 (5)	C(6)-C(7)-C(1)	131.2 (4)
C(6)-C(7)	1.388 (5)	C(7)-C(1)-C(2)	126.2 (3)
C(7)-C(1)	1.394 (4)		
C(3)-H(3)	0.98 (3)		
C(4)-H(4)	0.95 (3)		
C(5)-H(5)	0.96 (3)		
C(6)-H(6)	0.99 (3)		
C(7)-H(7)	0.88 (3)		

pendent Ni-S distances average 2.147 (3) \AA , which can be compared with values of 2.166 (6), 2.146 (1), 2.135 (4), 2.122 (3), and 2.101 (2) \AA found in the nickel-dithiolene complexes $[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{2-}$,¹⁴ $[\text{Ni}(\text{S}_2\text{C}_2-$

(14) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965); R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 113 (1964).

$(\text{CN})_2)_2]^-$,¹⁵ $[\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2]^-$,¹⁶ $[\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2]^0$,¹⁷ and $[\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2]^0$,¹⁸ respectively. The value of 2.147 (3) \AA is considerably shorter than the 2.22–2.24- \AA sum of the covalent radii for sulfur¹⁹ and low-spin Ni(II),²⁰ and is significantly less than the 2.19–2.24- \AA range of Ni-S distances reported for monomeric bis(dithiolato) complexes³ which include complexes of *N,N*-dialkyl-dithiocarbamates, *O*-ethyl xanthate, *N*-cyanodithiocarbamate, *O,O'*-diethyl dithiophosphate, dithiobenzoate, trithiocarbonate, and dialkyl dithiophosphinates. The relative shortness of the Ni-S distance in the present case thus appears to indicate that the dithiotropolonate ligand does possess some π -acid character.

The Si-Ni-S bond angle is 90.11 (5) $^\circ$, with inter- and intraligand S-S distances of 3.034 (4) and 3.040 (3) \AA , respectively. Hence, the coordination geometry is perfectly square to within experimental limits. The complex as a whole does not deviate significantly from planarity. Least-squares planes through different sections of the complex and the deviations of the atoms from their respective planes are presented in Table IV.

Table IV. Weighted Least-Squares Planes and the Distances of the Atoms from Their Respective Planes^a

Atom	Distance, \AA
Tropolone Ring: $-1.58X + 0.11Y + 6.89Z - 0.01 = 0$	
C(1)	-0.006 (3)
C(2)	-0.002 (3)
C(3)	0.007 (3)
C(4)	-0.001 (3)
C(5)	-0.006 (3)
C(6)	0.003 (3)
C(7)	0.005 (3)
H(3)	0.01 (3)
H(4)	0.02 (3)
H(5)	-0.07 (3)
H(6)	0.01 (3)
H(7)	0.03 (3)
All Ligand Atoms: $-1.52X + 0.06Y + 6.90Z + 0.02 = 0$	
S(1)	-0.002 (1)
S(2)	0.000 (1)
C(1)	0.011 (3)
C(2)	0.009 (3)
C(3)	0.007 (3)
C(4)	-0.010 (3)
C(5)	-0.014 (3)
C(6)	0.003 (3)
C(7)	0.016 (3)
H(3)	0.01 (3)
H(4)	0.01 (3)
H(5)	-0.08 (3)
H(6)	0.01 (3)
H(7)	0.05 (3)
Chelate Ring: $-1.49X - 0.01Y + 6.90Z + 0.03 = 0$	
S(1)	-0.0001 (9)
S(2)	0.0001 (8)
C(1)	0.001 (3)
C(2)	-0.001 (3)
Ni	0.032

^a Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, **14**, 185 (1961).

(15) C. J. Fritchie, Jr., *Acta Crystallogr.*, **20**, 107 (1966).
 (16) R. M. Wing and R. L. Schlupp, *Inorg. Chem.*, **9**, 471 (1970).
 (17) R. D. Schmitt, R. M. Wing, and A. H. Maki, *J. Amer. Chem. Soc.*, **91**, 4394 (1969).
 (18) D. Sartain and M. R. Truter, *Chem. Commun.*, 382 (1966); *J. Chem. Soc. A*, 1264 (1967).
 (19) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., Chapter 7.
 (20) B. T. Kilbourn and H. M. Powell are quoted as giving 1.16 \AA as the correct Ni(II) radius in square complexes in G. R. Davies, R. H. B. Mais, and D. G. Owston, *J. Chem. Soc. A*, 1750 (1967).

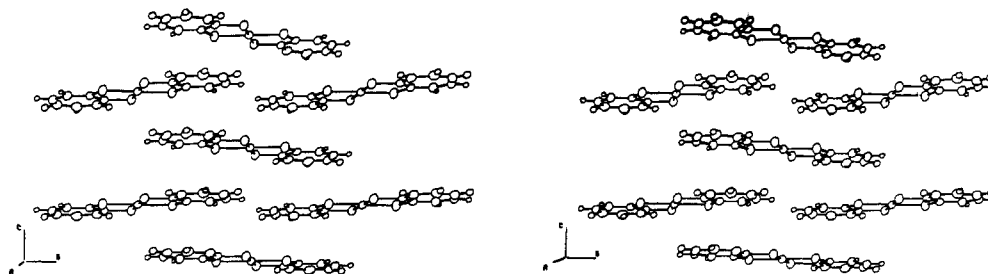


Figure 2. These drawings present a view of the packing of the $[\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2]$ molecules down the a axis of the crystal. The drawings constitute a stereopair and may be viewed with a hand viewer.

Among the other important distances in this structure is the average C–S distance of 1.720 (4) Å. This value is in the middle of the 1.70–1.75-Å range of C–S distances found in the bis(1,2-dithiolene) complexes^{14–18} and is also in agreement with the C–S distances of 1.69–1.72 Å observed in the appropriate 1,1-dithiolato systems.³ In addition, it should be noted that the C–S distance of 1.720 (4) Å agrees closely with the C–S distance of 1.720 (9) Å reported for thiourea^{21a} and the corresponding C–S distances in metal complexes of thiourea.^{21b} The value is significantly shorter than the 1.81-Å sum of covalent radii for a C–S single bond.¹⁹

The seven-membered ring of the dithiotropolonate ligand is rigorously planar, and the ligand possesses essentially C_{2v} symmetry. We find the bond distance between the two carbon atoms common to both the five-membered chelate ring and the seven-membered carbon ring is significantly longer at 1.448 (4) Å than the other C–C endo ring distances which range from 1.378 (5) to 1.401 (4) Å and average 1.389 (8) Å. This result is similar to those reported for sodium tropolonate²² and tris(tropolonato)iron(III)²³ in which the C(1)–C(2) distances are found to be 1.487 (6) and 1.463 (7) Å, respectively. The C(1)–C(2) bond length in the present structure, however, is significantly shorter than the 1.504-Å value suggested for a C_{sp^2} – C_{sp^2} single bond on the basis of covalent radii,¹⁹ indicating that there is a small amount of π -bond character in the bond. Although the rest of the C–C distances do not differ significantly in a statistical sense, there does appear to be a systematic ordering of the observed values if one assumes C_{2v} symmetry. The averaged values corresponding to the C(2)–C(3), C(3)–C(4), and C(4)–C(5) bonds are 1.398 (5), 1.389 (5), and 1.382 (5) Å, respectively, which compare favorably with the related sets of values of 1.426 (6), 1.390 (6), and 1.388 (6) Å for sodium tropolonate²² and 1.387 (7), 1.385 (7), and 1.379 (7) Å for $\text{Fe}(\text{O}_2\text{C}_7\text{H}_5)_3$.²³ The implications of these results will be discussed below. It is worthwhile noting that these results are in contrast with the structure of bis(tropolonato)copper(II)²⁴ in which the tropolonate ligands are viewed as *not* possessing C_{2v} symmetry, because of the dominance of one of the two major resonance forms (*vide infra*) over the other.

(21) (a) M. R. Truter, *Acta Crystallogr.*, **22**, 556 (1967); (b) A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963); W. T. Robinson, S. L. Holt, Jr., and G. B. Carpenter, *Inorg. Chem.*, **6**, 605 (1967); M. S. Weininger, J. E. O'Connor, and E. L. Amma, *ibid.*, **8**, 424 (1969), and references therein.

(22) R. Shiono, *Acta Crystallogr.*, **14**, 42 (1961), and references therein.

(23) T. A. Hamor and D. J. Watkin, *Chem. Commun.*, 440 (1969).

(24) W. M. Macintyre, J. M. Robertson, and R. F. Zahrosky, *Proc. Roy. Soc., Ser. A*, **289**, 161 (1966).

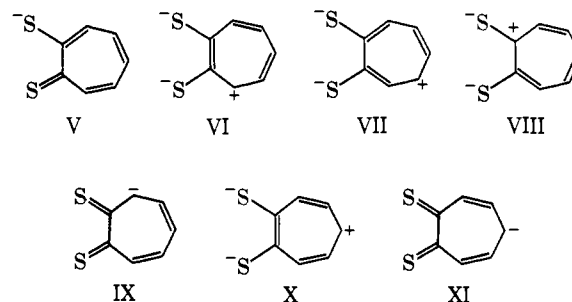
This lack of symmetry in the ligand is partially attributed to packing effects.

The C–H distances in the structure are found to average 0.95 (3) Å. This value, while significantly shorter than the accepted 1.08-Å distance, is consistent with the generally short C–H distances determined from X-ray structural analyses.

The packing of the $\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2$ complex consists of the stacking of planar molecules in the c direction. The closest intermolecular contacts are H(5)–H(5)' (2.858 Å), S(2)–H(5)' (2.926 Å), H(5)–H(6)' (3.057 Å), and S(2)–H(3)' (3.067 Å). The closest Ni–Ni distance is 6.914 Å.

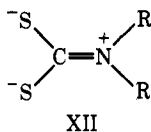
Discussion

It is possible on the basis of valence-bond theory to formulate numerous resonance structures for the dithiotropolonate anion. These resonance structures are written as V–XI, with V–IX representing one of



two equivalent forms in C_{2v} symmetry. The structural results obtained for $\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2$ are consistent with the notion that the dominant resonance structures for the dithiotropolonate ligand are V and its symmetry-related form, as suggested by Forbes and Holm.⁵ This conclusion is similar to that drawn by Shiono²² for sodium tropolonate. In addition, the structural parameters of $\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2$ and, in particular, the shortness of the C(1)–C(2) bond of 1.448 (4) Å relative to the single-bond value of 1.504 Å imply that resonance structures VI (and its equivalent form) and X make significant, but not major, contributions to a complete description of the electronic structure of the dithiotropolonate ligand in this system. Canonical forms of types VI and X serve to increase the C(1)–C(2) bond order while reducing both the S–C and C(2)–C(3) bond orders relative to the C(3)–C(4) and C(4)–C(5) bonds in accord with the structural results. It is interesting to note that these dipolar resonance structures parallel the dipolar resonance forms such as XII which are

suggested as being of considerable importance in descriptions of the 1,1-dithiolato complexes.²⁵



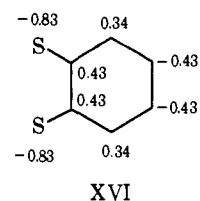
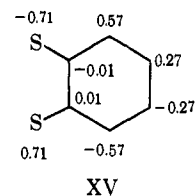
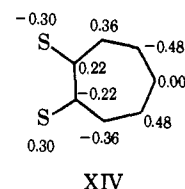
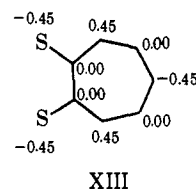
The lack of dithiolene character in the $\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2$ complex, which seems apparent from the large C(1)-C(2) distance in the structure, has been demonstrated electrochemically by Forbes and Holm.⁵ The significant differences in the properties and electron affinities of the dithiopolonate complexes from the stereochemically similar dithiolene complexes can be explained from a molecular orbital point of view as well as from valence-bond formalisms. The notion of ligand π acidity and electron delocalization in metal chelate complexes is intimately related to the symmetry of the highest filled and lowest unfilled molecular orbitals of the ligand. For the purpose of symmetry arguments, we can consider the π molecular orbitals of 1-heptafulvenylmethyl²⁶ as being characteristic of the π system of dithiotropolonate. XIII and XIV represent the highest filled and lowest unfilled molecular orbitals for the dithiotropolonate anion (1-heptafulvenylmethyl), whereas XV and XVI represent the corresponding orbitals for benzene-1,2-dithione.²⁷ The numbers refer to the coefficients for the molecular orbitals. It is clearly seen that the symmetry properties of the highest filled and lowest unfilled molecular orbitals are reversed in the two cases.

In order to compare the electron affinities of similar complexes of the two ligands, attention should focus on the lowest unfilled ligand molecular orbitals which

(25) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature (London)*, 177, 1042 (1956); *Suom. Kemistilehti B*, 29, 75 (1956).

(26) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I, Pergamon Press, New York, N. Y., 1965, p 61.

(27) M. J. B. Hawkes, Ph.D. Thesis, Columbia University, 1966. The d_{zz} orbital is designated as such on the basis of the coordinate system employed by Hawkes.



may serve as the π -acceptor functions. A molecular orbital calculation for $[\text{Ni}(\text{S}_2\text{C}_6\text{H}_4)_2]^-$ ²⁷ has shown that there exists an important interaction between XVI (as well as other ligand π functions of the same symmetry) and the metal d_{zz} function, with the resultant molecular orbitals delocalized over the entire complex. The delocalized molecular orbital, which is composed principally of XVI and d_{zz} , is unoccupied in the neutral complex and half-filled in the monoanionic system. The calculations show and chemical studies^{4d,e} verify that this molecular orbital is easily accessible energetically and hence, the complex undergoes facile electron-transfer reactions. On the other hand, no such molecular orbital formation is possible in the $\text{Ni}(\text{S}_2\text{C}_7\text{H}_5)_2$ complex, and, as a consequence, a low-lying π -acceptor orbital is not readily available for reduction. Dithiotropolonate thus appears to be analogous to the "odd" ligand systems as designated by Schrauzer in his discussion of metal dithienes.²

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