

Table II. Equilibrium Constants and Heat for the Reaction $2\text{CrF}(\text{g}) = \text{Cr}(\text{g}) + \text{CrF}_2(\text{g})$

Temp., °K.	K_1'	Log K_1	$\Delta\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$,	
			cal. deg. ⁻¹ mole ⁻¹	ΔH°_{298} , kcal. mole ⁻¹
1259	31.77	1.530	3.83	-13.63
1286	46.57	1.696	3.75	-14.80
1307	37.00	1.596	3.72	-14.40
1269	64.78	1.839	3.82	-15.53
1272	44.98	1.681	3.80	-14.62
1290	43.72	1.668	3.75	-14.68
1294	18.86	1.303	3.74	-12.55
1317	19.19	1.311	3.70	-12.77
Average = -14.12 ± 1.04				

By combining the heat of dissociation of $\text{CrF}_2(\text{g})$ with the heat of reaction listed in Table II, one obtains $D^\circ_{298}(\text{CrF}) = 4.61 \pm 0.15$ e.v. (106.4 ± 3.5 kcal. mole⁻¹). From this value the heat of formation of $\text{CrF}_2(\text{g})$ from the elements in their reference states at 298°K. was computed to be -94.2 kcal. mole⁻¹, in good agreement with the value of -96 kcal. mole⁻¹ estimated by Brewer.¹

It was not possible to determine the dissociation energy by measuring the heat of the heterogeneous reac-

tion $2\text{CrF}(\text{g}) = \text{Cr}(\text{g}) + \text{CrF}_2(\text{s})$ because, as pointed out previously, the activity of the $\text{CrF}_2(\text{s})$ in the Knudsen cell was less than unity. When Al was added to CrF_2 as a reducing agent only AlF_3 -related peaks and Cr^+ were obtained; *i.e.*, CrF was apparently reduced below the sensitivity limit of the instrument.

One may fix an upper limit on the value of $D(\text{CrF})$ in the following manner. The intensities of the ion CrF_2^+ are measured at some voltage much greater than the appearance potentials, in this experiment 70 v. The value of $I(\text{CrF}_2^+)$ must be corrected to account for that amount of $\text{CrF}_2(\text{g})$ undergoing dissociative ionization when exposed to 70-v. electrons. The intensities of the ions Cr^+ and CrF^+ are measured at some value below the breaks at *ca.* 19 and 14 e.v., respectively, and then extrapolated to 70 e.v. Calculating K_1' and K_1 for the reaction $2\text{CrF}(\text{g}) = \text{Cr}(\text{g}) + \text{CrF}_2(\text{g})$ as before, one obtains $\Delta H^\circ_{298} = -7.2 \pm 0.5$ kcal. mole⁻¹ which leads to $D^\circ_{298}(\text{CrF}) \leq 4.76 \pm 0.20$ e.v.

In a similar manner, one can set a lower limit on the value for $D(\text{CrF})$ by using the intensity of CrF_2^+ at 70 v. as above and those of Cr^+ and CrF^+ below the breaks at *ca.* 19 and 14 e.v., *i.e.*, assuming that the ionization efficiency curves level off. Calculating K_1' and K as before, one obtains $\Delta H^\circ_{298} = -18.3 \pm 1.1$ kcal. mole⁻¹ and $D^\circ_{298}(\text{CrF}) \geq 4.52 \pm 0.20$ e.v.

Acknowledgment. This work has been supported by the United States Atomic Energy Commission.

Coordination Compounds with Delocalized Ground States. Bisdithioglyoxalnickel and Related Complexes^{1a,b}

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Received March 19, 1965*

Synthesis properties and electronic structure of the first transition metal complex of the hitherto unknown ligand dithioglyoxal are reported. Bisdithioglyoxalnickel, NiS₄C₄H₄, is a monomeric, planar, diamagnetic nickel complex in which the two positive charges of the nickel atom are compensated by two electrons delocalized over the whole molecule of the complex. Its chemical properties closely resemble those of the related d⁸ metal complexes of α-dithiodiketones, M(S₂C₂R₂)₂; it possesses a low first electron excitation energy and is easily reduced to mono- and dianions. The optical spectra for the species NiS₄C₄H₄^{0,-1,-2} and of substituted derivatives are presented and interpreted on the basis of MO calculations. Satisfactory quantitative agreement with the observed transition energies was achieved using a semiempirical Hückel-type approximation. The Wolfsberg-Helmholtz method was applied as well but afforded less favorable results owing to a basic inadequacy with which the off-diagonal elements H_{ij} are computed. It follows from the available

data that the complexes of this type represent interesting examples of coordination compounds with extensive ground-state π-electron delocalization.

Introduction

The α-dithiodiketones have become some of the most interesting ligands in recent transition metal chemistry. In systems $\text{RC}(=\text{S})\text{C}(=\text{S})\text{R}$ the tendency of the sulfur atoms to form covalent bonds with metals is uniquely combined with a high electron affinity of the ligand which leads to complexes characterized by many unusual and unprecedented chemical and physical properties. Since the characterization of the first complex of this type,² we have developed several methods of synthesis for alkyl- and aryl-substituted complexes $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_z$ ($z = 2$ or 3),^{1b,3-5} while other authors have subsequently

(1) (a) Paper VII of the series "Chemistry of the Coordination Compounds"; (b) paper VI: G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).

(2) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **84**, 3221 (1962).

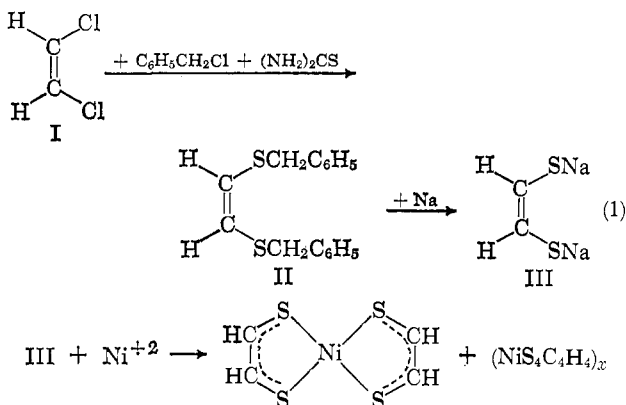
(3) G. N. Schrauzer and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964); G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *ibid.*, **19b**, 1080 (1964).

(4) G. N. Schrauzer and H. W. Finck, *Angew. Chem.*, **76**, 143 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 133 (1964).

prepared analogous CF_3 -substituted complexes and their anion salts.⁶⁻⁸ It was also demonstrated⁷ that these complexes are related to the complex salts of maleonitriledithiol (MNT) first reported by Bähr and Schleitzer⁹ and later studied mainly by Gray and his co-workers.^{10,11} Although a large number of interesting compounds have thus become available, the basic unsubstituted complexes with dithioglyoxal, $\text{HC}(=\text{S})\text{C}(=\text{S})\text{H}$, which would be very important, have never been reported. We now have been able to prepare complexes of this new ligand and describe the first results of this work in the present paper.

Preparation and Properties of Bisdithioglyoxalnickel

The synthesis of the desired unsubstituted nickel dithione complex was at first tried unsuccessfully utilizing methods similar to those yielding the substituted analogs, *e.g.*, by treating acetylene with sulfur in the presence of metallic nickel, or by treating the reaction product of glycol aldehyde with P_4S_{10} with nickelous salts. Quite recently, the preparation of *cis*-dimercaptioethylene and its sodium salt has been reported by Schroth and Peschel.¹² The disodium salt is obtained from *cis*-dichloroethylene according to reaction sequence I.

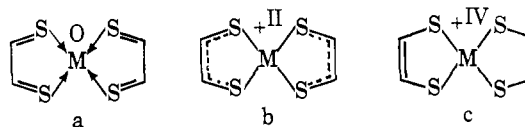


The main product of the reaction of III with nickelous salts in alcohol is a black, amorphous material which analyzes roughly for $\text{NiS}_4\text{C}_4\text{H}_4$. Its infrared spectrum consists of an absorption continuum and its insolubility strongly suggests a polymeric structure. However, careful extraction of the crude product with cold ether yielded purple solutions from which dark glittering crystals of the monomeric bisdithioglyoxalnickel, $\text{NiS}_2\text{C}_4\text{H}_4$, were isolated. The new complex is readily soluble in most organic solvents, stable to air, and decomposes at about 68° . Its n.m.r. spectrum consists of a single sharp peak at 0.8 p.p.m. (in CS_2 solution), indicating "aromatic" environment of the

protons. On the other hand, the proton signal of III in ethanol was observed in the "olefinic" range of 3.62 p.p.m. (relative to TMS). In the infrared spectrum (KBr) the C-H stretching band appears at 2933 cm^{-1} , while the perturbed C=C stretch is assigned to a band at 1349 cm^{-1} . Two bands at 1099 and 873 cm^{-1} may be assigned to the symmetric and asymmetric perturbed C=S stretching modes. Three bands at 740 , 727 , and 717 cm^{-1} are probably C-H deformations, and two weak bands in the CsBr region at 428 and 309 cm^{-1} must be the in-plane Ni-S stretching vibrations. The frequency range of the perturbed C=C, the symmetric C=S, and the two Ni-S stretching bands corresponds to that reported for substituted neutral dithione metal complexes.^{1b} The infrared spectrum of the sodium salt III, on the other hand, differs completely; in particular, the C=C stretch is found at the conventional 1634 cm^{-1} , while there are no bands corresponding to the C=S vibration, a result confirming the absence of ethylenedithiolato dianions in the nickel complex. Polarographic reduction reveals two one-electron reduction steps at 0.188 and -0.98 v. , corresponding to the formation of ions $\text{NiS}_4\text{C}_4\text{H}_4^{-1,2,13}$, the values of the half-wave potentials are thus between those reported for the CF_3 - and CH_3 -substituted complexes. The mono-anion which may be generated in solution by reducing the neutral complex shows one e.p.r. signal at $g = 2.056 \pm 0.001$ (in pyridine), without detectable fine structure. Measurements in the glassy state at 77°K. in pyridine-chloroform allows the observation of a threefold anisotropy of the g -factor, whose principal values are $g_1 = 1.996$, $g_2 = 2.039$, and $g_3 = 2.126$; they are in the same order of magnitude as those reported^{7,8,14} for substituted bisdithione complex monoanions. All available evidence therefore indicates that bisdithioglyoxalnickel behaves just as a substituted complex, and the following discussion of its electronic structure may be generalized to include similar complexes of Pd and Pt.¹⁵

Electronic Structure

We have recently presented evidence^{1b} which leaves no doubt that the unusual properties of certain complexes $\text{M}(\text{RCSCSR})_2$ are a consequence of the particular nature of the unsaturated ligands, a fact which has not received adequate attention by the other workers in this field. For the bonding of two (*cis*-)dithiodiketone molecules to a d^8 -transition metal three possibilities a, b, and c, must be considered. In case a, the meta



would remain zerovalent and the ligands retain their basic dithiodiketonic structure. So far there is no evidence that a complex of this type exists, nor that

(5) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 381 (1964); *Angew. Chem.*, **76**, 715 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 639 (1964).

(6) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963); *Inorg. Chem.*, **2**, 641 (1963).

(7) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).

(8) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963), and subsequent papers.

(9) G. Bähr and G. Schleitzer, *Chem. Ber.*, **90**, 438 (1957).

(10) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(11) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964), and subsequent papers.

(12) W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964).

(13) Extensive polarographic measurements on substituted complexes $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2$ have been performed (G. N. Schrauzer and D. C. Olson) and will be published.

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

(15) A detailed discussion of bisdithiodiketone complexes of Co and Fe is in preparation. At this point it is only to be mentioned that the ions $\text{CoS}_4\text{C}_4\text{R}_4^-$ and $\text{FeS}_4\text{C}_4\text{R}_4^{2-}$, though formally isoelectronic with the neutral d^8 metal complexes, have a different electronic ground-state configuration.

the planar bis complexes of d^8 -transition metals have this structure. It would only be favored if the dithio-diketones were weakly π -bonding ligands, which is definitely not the case. The other extreme situation is represented by formula c in which the ligands are assumed to be dithiolato dianions $^-S-CR=CR-S^-$. These anions are undoubtedly present in the dianions of bis-dithiodiketone complexes of Ni, Pd, and Pt, or in the salts of some complexes of other metals. They are, however, definitely absent in the d^8 neutral complexes $M(S_2C_2R_2)_2$ as we have already pointed out.^{1b} Their exclusive presence is also unlikely in the complexes of Fe, Co, V,¹⁶ Cr, Mo, W, and Re, the discussion of which we defer for later papers. Likewise not to be considered in this context are complexes of the general composition $(R_2C_2S_2)Fe_2(CO)_6$, of which several have been prepared, and of related species.^{17,18} Case b depicts the intermediate situation between a and c, in which the ligands are spin-paired monoanions; symmetry arguments show that spin pairing of the two monoanions is indeed possible through interaction with suitable metal orbitals. A good representation of the ground state may also be achieved in terms of valence bond formalisms, e.g., by using Kekulé-type structures



To obtain more quantitative information regarding the ordering of the orbitals in the complexes of this type, MO calculations on a model of bisdithioglyoxalnickel (Figure 1) have been performed. To date, molecular orbital calculations on transition metal complexes must be of necessity semiempirical and approximate since there is no way to determine the exact values of the required matrix elements. One can only hope to get results in agreement with observables for a judiciously selected set of input parameters. However, the situation is further complicated by the fact that the eigenvalues may be calculated in various degrees of approximation, e.g., using different methods of calculating the off-diagonal elements and the inclusion of other features such as mutual overlap or nonneighbor interactions, whose effects upon the final energy values may be difficult to assess. We have, therefore, performed calculations using the simplest possible form of the theory first for a range of flexibly selected parameters and then compared the result with that obtained by an extended procedure, namely, in the form first employed by Wolfsberg and Helmholz.¹⁹ In the first approximation mutual overlap was neglected as well as nonneighbor interactions, and the off-diagonal elements were simply set directly proportional to the overlap integrals; a value of 0.135 of S was set equal to 1 e.v. of bond energy. The starting molecular orbitals of the isolated dithioglyoxal molecule were calculated using the Pauling-Wheland method with $\alpha_S = \alpha_C + 0.2\beta$, neglecting sulfur d orbitals and putting $\beta_{C=S} = \beta_{C=C}$. These parameters are well within the range of

(16) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964).

(17) (a) R. B. King, *ibid.*, **85**, 1584 (1963); (b) *ibid.*, **85**, 1587 (1963).

(18) G. N. Schrauzer and W. Heinrich, to be published.

(19) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

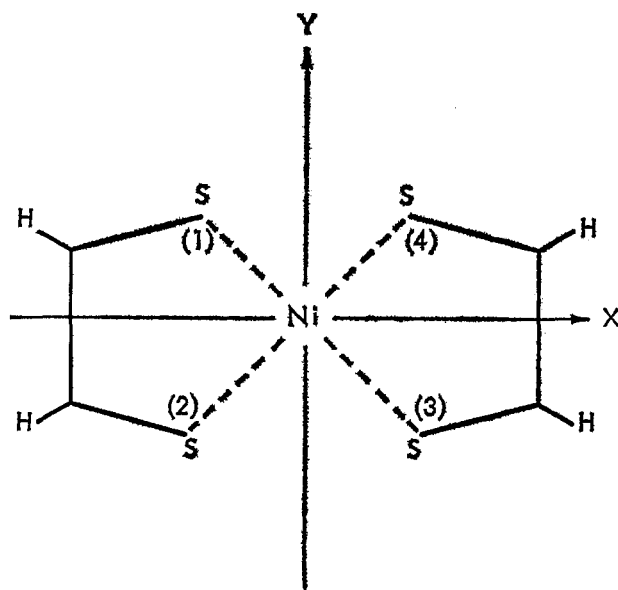


Figure 1. Model of the $NiS_4C_4H_4$ complex used for the calculation (assumed Ni-S distance 2.16 Å.).

recommended values for sulfur compounds.²⁰ The energy of the free electron pairs of the sulfur atoms was given the value of 10.3 e.v., the first ionization potential of sulfur. The highest bonding orbital of dithioglyoxal was placed at 12.05 e.v. and the remaining orbital energies were calculated from the roots of the secular equation with $\beta = 3.00$ e.v. For the energy of the nickel atom, values of around the first ionization potential were employed for the 4s orbital; the 3d and the 4p orbitals were placed 0.5–1.0 e.v. below or 2–3 e.v. above this value, respectively. In Table I the symmetry correlation of the orbital interactions and the overlap integrals are listed, and in Table II the calculated eigenvalues for a specific set of nickel Coulomb terms ($H_{4s4s} = 8.5$, $H_{3d3d} = 9.2$, and $H_{4p4p} = 5.6$ e.v.) are given, leading to the ground-state configuration $\dots(2b_{1u})^2(2b_{2g})^2(3a_g)^2(2b_{3g})^2(4a_g)^2(3b_{2g})^*(3b_{1g})^*\dots$. This configuration represents case b, since the lowest unoccupied MO is both the metal- and ligand-based $3b_{2g}$ orbital which arises from the antibonding combination of the $3d_{xz}$ orbital with the $1/2(\psi_3 - \psi'_3)$ ligand MO set.²¹ The fact that this orbital would be singly occupied in the monoanion would explain the anisotropy of the g factor. Instructive results were obtained from calculations with different metal or ligand Coulomb terms. For instance, decreasing the metal energies or increasing those of the ligand by about 1 e.v. produces an orbital sequence in which both the predominantly ligand-based orbitals $2b_{1u}$ and $3b_{2g}$ would be occupied in the neutral complex, a situation consistent with the less probable structure c. In the anions the $4a_g$ ($d_{x^2-y^2}$ type) orbital would become occupied, a fact which cannot be reconciled with the observed threefold anisotropy of the g factor. A similar ground-state configuration has been recently proposed for the $Ni(MNT)_2^{-1,2}$ anions.²² It may be shown that this result is mainly caused by

(20) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 126.

(21) The metal character of the $3b_{2g}$ orbital is calculated from the eigenvectors to 18.32%.

(22) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

the choice of input parameters of these authors; it also disagrees with the results of the e.p.r. analysis on the $\text{Ni}(\text{MNT})_2^-$ ion¹⁴ and must be now considered less likely. The authors of ref. 22 used Coulomb terms of 12.9 and 13.5 e.v. for the 3d orbitals, assuming a positively charged nickel atom. For the MNT ligands their input parameters were derived from experimental and theoretical data on bis(methylthio)-maleonitrile. They have thus *a priori* introduced a considerable charge separation between the metal and the ligands. In view of the small electronegativity difference between Ni and S, an essentially covalent model as used by us with a ligand system $\text{S}=\text{C}-\text{C}=\text{S}$ will certainly produce results more suitable at least for the description of the neutral molecules $\text{NiS}_4\text{C}_4\text{R}_4$ and the monoanions. In going from the mono- to the dianions, pronounced changes within the ligand system occur.^{1b} To obtain the best quantitative results for the dianions, the set of input parameters would have to be altered to account for the conversion of the ligands into dithiolato dianions.

Lowering the ligand or increasing the metal energies again by about 1 e.v. does not seriously affect the ground-state configuration. However, the $3b_{2g}$ MO is now above the $3b_{1g}$ (d_{xy} type) orbital, which would lead to an improbable configuration for the lowest excited states or the complex anions. Hence, there is only a relatively narrow range of parameters which leads to an electronic structure consistent with the available experimental evidence, and the failure to consider the possible effects of small changes of the adopted Coulomb terms may lead to misinterpretations.

Table I. Symmetry Correlation of the Orbital Interactions and Calculated Group Overlap Integrals for the Model of Bisdithioglyoxalnickel Shown in Figure 1

Irreducible representation in D_{2h} symmetry	Metal function	Ligand function ^a	S_{ij} ^b
a_g	$3d_{z^2}$	$1/2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$	0.128
	4s	$1/2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$	0.857
	$3d_{x^2-y^2}$	$1/2(\pi_{1h} + \pi_{2h} + \pi_{3h} + \pi_{4h})^c$	0.078
a_u	...	$(1/\sqrt{2})(\psi_2 + \psi'_2)$...
	...	$(1/\sqrt{2})(\psi_4 + \psi'_4)$...
b_{1g}	$3d_{xy}$	$1/2(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$	0.239
	$3d_{xy}$	$1/2(-\pi_{1h} + \pi_{2h} - \pi_{3h} + \pi_{4h})$	0
b_{1u}	$4p_z$	$(1/\sqrt{2})(\psi_1 + \psi'_1)$	0.186
	$4p_z$	$(1/\sqrt{2})(\psi_3 + \psi'_3)$	0.356
b_{2g}	$3d_{xz}$	$(1/\sqrt{2})(\psi_1 - \psi'_1)$	0.041
	$3d_{xz}$	$(1/\sqrt{2})(\psi_3 - \psi'_3)$	0.077
	$4p_y$	$1/2(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4)$	0.790
b_{2u}	$4p_y$	$1/2(-\pi_{1h} + \pi_{2h} + \pi_{3h} - \pi_{4h})$	0.180
	$3d_{yz}$	$(1/\sqrt{2})(\psi_2 - \psi'_2)$	0.065
b_{3g}	$3d_{yz}$	$(1/\sqrt{2})(\psi_4 - \psi'_4)$	0.048
	$4p_x$	$1/2(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$	0.790
b_{3u}	$4p_x$	$1/2(-\pi_{1h} - \pi_{2h} + \pi_{3h} + \pi_{4h})$	0.180

^a The adopted notation is similar to that in ref. 22; σ - or π -type interactions in the molecular plane are denoted by σ_i or π_{ih} ($i = 1-4$, h for horizontal). The π_{ih} 's are the orthogonal components to the sp^2 -hybrids of sulfur in the Ni-S bond directions. The ψ_i 's are the ligand π -MO's vertical to the plane of the molecule. ^b See Appendix. ^c Overlap of this ligand function with 4s is small and was neglected.

In the next approximation, the orbital energies of $\text{NiS}_4\text{C}_4\text{H}_4$ were calculated by the Wolfsberg-Helmholz (W.H.) method,¹⁹ using the same H_{ii} values. The off-diagonal elements in this method are $H_{ij} - ES$, where the H_{ij} are usually estimated by the formula $H_{ij} = KS\sqrt{H_{ii}H_{jj}}$, with $k = 2.00$. The resulting eigenvalues are also included in Table II. As may be seen, several changes in the orbital sequence are introduced through this approximation, which, however, do not seriously affect the basic conclusion derived from our previous calculation. It is, however, rather disturbing that positive energies are calculated for the highest antibonding orbitals. This absurd result is caused by the fact that for the strongest orbital interactions, much too large H_{ij} values are calculated. But even for the weaker interactions the particular method to obtain the off-diagonal elements produces eigenvalues of questionable physical significance. Thus, considering the combination of two orbitals with largely differing H_{ii} values, the calculation will affect the antibonding levels much more than the bonding ones, an effect which is essentially caused by the basic inadequacy with which the H_{ij} elements are calculated. Until a better method to determine the off-diagonal elements is at hand, it should be kept in mind that this method offers at best a fair description of the ground state without actually improving the results over a simple Hückel-type calculation. For excited states it is actually a worse approximation.²³

Electronic Spectra

(a) *Neutral Complexes.* The electronic spectra of $\text{NiS}_4\text{C}_4\text{H}_4$ and of some substituted derivatives are shown in Figure 2. Using eigenvalues of Table II as calculated by the first method, the transitions were assigned systematically, with the results shown in Table III. It is remarkable that the simple independent electron model even affords a good quantitative agreement with the observed transition energies. Obviously, our parameters are particularly suited for this purpose, and the future application of similar methods to other complexes may prove valuable. With the orbital energy values calculated by the W.H. method, the same assignments result for most transitions, but the over-all agreement is not quite as good. In the spectrum of $\text{NiS}_4\text{C}_4\text{H}_4$ the first absorption is a shoulder at $11,857 \text{ cm}^{-1}$ ($\epsilon 1 \times 10^3$) which is assigned to a group of orbitally forbidden $M \rightarrow \pi$ charge-transfer transitions. (It must be pointed out at this time that this description of the band type is, of course, oversimplified since almost all orbitals involved in the observed transitions have both ligand and metal character.) In this region also the weak ligand field transitions are to be expected, which in the neutral complex are covered by the more intense bands. The $M \rightarrow \pi$ transitions in this energy range are no longer observed in most of the substituted complexes as they are usually completely covered by the next and very intense $2b_{1u} \rightarrow 3b_{2g}$ transition (previously^{1b} designated $2b_{1u} \rightarrow 2b_{2g}$). For this band the deviation between the calculated and the found energy is only 681 cm^{-1} , a result which could, of course, still be improved by a slight parameter change. This band could also cover the forbidden transition $2b_{1u} \rightarrow$

(23) For a very recent and more extensive criticism of the W. H. method, see R. F. Fenske, *Inorg. Chem.*, 4, 33 (1965).

Table II. Calculated Orbital Energies for the Set of Coulomb Terms Indicated in the Text

Simple MO theory			W. H. method		
MO	Type ^a	Energy, e.v.	MO	Type ^a	Energy, e.v.
3b _{3u} , 3b _{2u}	(4p)	-1.511	5a _g	(4s)	51.154
5a _g	(4s)	-2.926	3b _{3u} , 3b _{2u}	(4p)	23.456
3b _{1u}	(4p _x)	-3.857	3b _{1u}	(4p _x)	-2.178
3b _{3g}	(L)	-5.317	3b _{3g}	(L)	-5.305
2a _u	(L)	-5.346	2a _u	(L)	-5.346
3b _{1g}	(3d _{xy})	-7.896	3b _{1g}	(3d _{xy})	-6.633
3b _{2g}	(L)	-7.978	3b _{2g}	(L)	-7.830
4a _g	(3d _{x²-y²)}	-8.914	4a _g	(3d _{x²-y²)}	-8.749
2b _{3g}	(3d _{yz})	-9.153	2b _{1u}	(L)	-8.959
3a _g	(3d _{z²)}	-9.185	2b _{3g}	(3d _{yz})	-9.014
2b _{2g}	(3d _{xz})	-9.455	3a _g	(3d _{z²)}	-9.182
2b _{1u}	(L)	-9.782	2b _{2g}	(3d _{xz})	-9.456
2b _{2u} , 2b _{3u} , 2b _{1g}	(S)	-10.300	2b _{2u} , 2b _{3u} , 2b _{1g}	(S)	-10.300
2a _g	(S)	-10.585	2a _g	(S)	-10.632
1b _{1g}	(S)	-11.603	1b _{2u} , 1b _{3u}	(S)	-11.661
1a _u	(L)	-12.050	1b _{1g}	(S)	-11.689
1b _{3g}	(L)	-12.129	1a _u	(L)	-12.050
1b _{2u} , 1b _{3u}	(S)	-14.398	1b _{3g}	(L)	-12.163
1b _{2g}	(L)	-15.016	1a _g	(S)	-13.787
1b _{1u}	(L)	-15.220	1b _{2g}	(L)	-15.021
1a _g	(S)	-15.888	1b _{1u}	(L)	-15.040

^a L = orbital significantly centered on the ligand π-orbital system vertical to the molecular plane; S = orbital significantly centered on the π-plane sulfur orbitals.

3b_{1g} which is expected to occur at a similar energy. The next band occurs in most complexes with the intensity of about 10³ and was previously assigned to a n_{=S}: → π transition, which is in agreement with our calculation. A poorly resolved shoulder at about 19,360 cm.⁻¹ and a shoulder at 22,746 cm.⁻¹ may be due to forbidden n_{=S}: → M or n_{=S}: → π transitions, in fair agreement with the calculated values. In the following region between 24,000 and 30,600 cm.⁻¹, the spectra of all complexes show substituent dependent bands which are of medium intensity and not well resolved. According to our calculation, eight transitions, mostly M → π and n_{=S}: → π, of which only one is orbitally allowed, are expected in this region and may indeed cause the broad absorption range. The strongest absorptions occur in the range between 30,600 and 38,700 cm.⁻¹ (the maximum for the unsubstituted complex is at about 34,000 cm.⁻¹) which must be due to the allowed 1a_u → 3b_{2g} transition for which the energy of 32,845 cm.⁻¹ is calculated. This assignment is again supported by the observed substituent dependence.^{1b} Several other transitions (seven in total, mostly π → π and M → π transitions, four of which are orbitally allowed) are expected in this energy range and may account for the mighty absorption. The last band observed was found at 42,590 cm.⁻¹ and is tentatively assigned to the 4a_g → 3b_{1u} transition, for which the energy of 40,800 cm.⁻¹ is calculated (Table III).

(b) *The Monoanions.* The spectra of the ions NiS₄C₄H₄⁻ and NiS₄C₄(C₆H₅)₄⁻ are shown in Figure 3. Theoretically, occupation of the 3b_{2g} orbital by one electron should leave the basic spectrum of the neutral complex essentially unaltered, except in the region around 20,000–22,000 cm.⁻¹, where the allowed 3b_{2g} → 2a_u transition is expected, while the 3b_{2g} → 3b_{3g} transition, which should lie very close, would probably not be resolved. Indeed, this has been found to be the case. The occupation of the 3b_{2g} orbital somewhat alters the separation 2b_{1u} → 3b_{2g} through secondary

interactions. Although the relevant part in the spectra is not well-resolved, there is definite indication for a new band at 20,200 cm.⁻¹ (ε 787) which we assign to

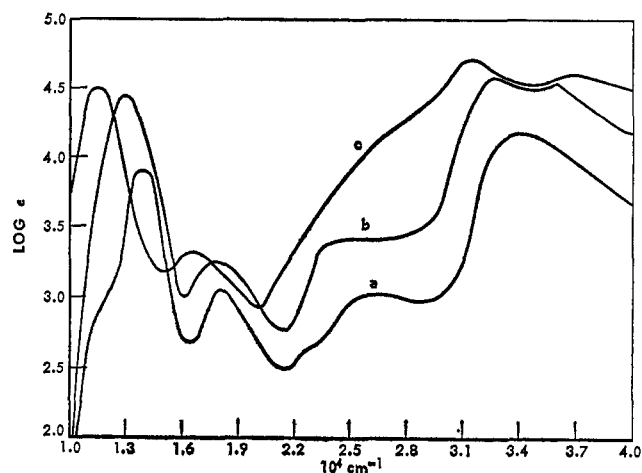


Figure 2. Electronic spectra of NiS₄C₄H₄ (a, in CH₃OH), of NiS₄C₄(CH₃)₄ (b, in CHCl₃), and of NiS₄C₄(C₆H₅)₄ (c, in CHCl₃).

the 3b_{2g} → 2a_u transition. The same conclusion may also be drawn from the spectrum of the NiS₄C₄(C₆H₅)₄⁻ ion. The reported spectrum of Ni(MNT)₂⁻ is very similar to that of NiS₄C₄H₄⁻ and is therefore included in our assignments in Table IV.

(c) *The Dianions.* The spectra of the dianions are shown in Figure 4. The occupation of the 3b_{2g} orbital by two electrons should cause all intense low-energy transitions to vanish; the first allowed inter-π-transition would be expected at fairly high energy. Absence of strong bands in the visible is indeed the most characteristic feature of the spectra of all dianions studied. This makes it possible to detect the weak ligand-field bands appearing between 7000 and 13,000 cm.⁻¹. Although these bands are not well-resolved, it is notable

Table III. Observed, Calculated, and Assigned Transitions in NiS₄C₄H₄

—Transition energy, cm. ⁻¹ —		Possible assignments ^b	Predominant band component	—Intensity—	
Obsd. ^a	Calcd.			Expected ^d	Obsd.
11,857 ^c	7,560	4a _g → 3b _{2g} (F)	M → π (F)	~10 ² -10 ³	1 × 10 ³
	9,478	2b _{3g} → 3b _{2g} (F) (all M → π)	(2b _{2g} → 3b _{2g})		
13,870	9,736	3a _g → 3b _{2g} (F)	π → π (A)	~10 ⁴	0.77 × 10 ⁴
	11,914	2b _{2g} → 3b _{2g} (F)			
18,150	14,551	2b _{1u} → 3b _{2g} (A) (π → π)	n=s: → π (A)	~10 ² -10 ³	1.14 × 10 ³
	15,222	2b _{1u} → 3b _{1g} (F) (π → M)			
19,360 ^c	19,390	2b _{2u} , 2b _{3u} , 2b _{1g} → 3b _{2g} (F)	n=s: → M ? (F)	Weak	4.3 × 10 ²
	22,750	2a _g → 3b _{2g} (F) (n=s: → π)	n=s: → π (F)		
24,000-30,600 (broad absorption)	21,030	2a _g → 3b _{1g} (F) (n=s: → M)	n=s: → M (F)	Together ~10 ² -10 ³	10 ³
	21,689	4a _g → 2a _u (F); 5a _g → 3b _{3g} (F); 1b _{1g} → 3b _{2g} (F); 1b _{1g} → 3b _{1g} (F); 2b _{3g} → 2a _u (A); 4a _g → 2a _u (F); 2b _{3g} → 3b _{3g} (F); 4a _g → 3b _{3g} (F)	Six M → π (5F, 1A) One n=s: → M (F), One n=s: → π (F)		
30,600-38,700 (max. at 34,000) (broad absorption)	32,845	1a _u → 3b _{2g} (A) (π → π)	π → π, (1a _u → 3b _{2g} (A))	Together ~10 ⁴	1.45 × 10 ⁴
	33,122	2b _{2g} → 2a _u (A) (M → π)			
42,590	33,482	1b _{3g} → 3b _{2g} (F) (π → π)	M → π (A)	~10 ³	4.4 × 10 ³
	33,387	2b _{2g} → 3b _{3g} (F) (M → π)			
42,590	33,506	1a _u → 3b _{1g} (A) (π → M)	(M → M) ?	~10 ³	4.4 × 10 ³
	35,781	2b _{1u} → 2a _u (F) (π → π)			
42,590	36,013	2b _{1u} → 3b _{3g} (A) (π → π)	(M → M) ?	~10 ³	4.4 × 10 ³
	40,193	2b _{2u} , 2b _{3u} , 2b _{1g} → 3b _{3g} (A) (n=s: → π)			
	40,800	4a _g -3b _{1u} (M → M) (A)			

^a In CH₃OH. ^b Abbreviations: A, orbitally allowed band; F, orbitally forbidden band. For bands involving the free electron pairs of the sp²-hybridized sulfur atoms, the symbol n=s: is used, regardless of whether these orbitals are bonding or nonbonding in the complex. ^c Shoulder. ^d Intensities were predicted on an empirical basis.

Table IV. Transitions and Assignments in the Spectra of Ions NiS₄C₄R₄⁻

—Observed bands, cm. ⁻¹ —			Assignment ^d	Calcd., cm. ⁻¹ ^e	Classification of predominant band component
NiS ₄ C ₄ H ₄ ^{-a}	NiS ₄ C ₄ (C ₆ H ₅) ₄ ^{-b}	NiS ₄ C ₄ (CN) ₄ ^{-c}			
7,246 (53.7) ^h	4a _g → 3b _{2g} (F)	7,560	² A _g → ² B _{2g} (M → π) (F)
8,695 (323) ^h	...	8,330 (329)	2b _{3g} → 3b _{2g} (F)	9,478	² A _g → ² B _{1g} or ² B _{2g} (M → π) (F)
			3a _g → 3b _{2g} (F)	9,736	
11,495 (2374)	11,100 (7950)	11,790 (8000)	2b _{1u} → 3b _{2g} (A)	14,551	² A _g → ² B _{3g} (π → π) (A)
15,748 (85)	15,600 (400) ^h	16,700 (500)	2b _{1u} → 3b _{1g} (F)	15,222	² A _g → ² A _u (π → M) (F)
19,120 (833) ^h	17,200 (720)	18,350 (690)	n=s: → 3b _{2g} (A)	18,729	² A _g → ² A _u , ² B _{1u} (n=s: → π) (A)
19,685 (956)	19,400 (1570) ^h		n=s: → 3b _{1g} (F)	19,390	² A _g → ² B _{2u} , ² B _{3u} (n=s: → M) (F)
20,284 (787) ^h	20,800 (1900)	20,800 (2500)	2a _g → 3b _{2g} (F) (?)	21,030	
22,989 (360)	3b _{2g} → 2a _u (A)	21,689	² A _g → ² B _{2u} (π → π) (A)
23,529 (512) ^h	2a _g → 3b _{1g} (F)	21,044	² A _g → ² B _{1g} (n=s: → M) (F)
28,571 (2720)	28,000 (13,000) ^h	27,300 (13,650)	Not assigned		
33,898 (7516)	31,400 (38,400)	31,800 (42,350)	2b _{3g} → 2a _u (A)	30,708	² A _g → ² B _{3u} (M → π) (A)
			1a _u → 3b _{2g} (A)	32,845	² A _g → ² B _{2u} (π → π) (A)

^a In pyridine. ^b In tetrahydrofuran. ^c From ref. 22. ^d Notation for NiS₄C₄H₄. ^e Calcd. for NiS₄C₄H₄. ^f Not observed or not resolved. ^g Intensities in brackets. ^h Shoulder.

that they appear in the calculated range. That these weak bands are indeed d-d transitions is strongly supported by comparison with the spectra of corresponding dianions of Pd and Pt; the general increase of the d-d splitting in the sequence Ni, Pd, Pt, is in accord with the expectation and of the right order of magnitude. The effective ligand field strength was found to depend to some extent on the substituents R of the dithione ligands. From the observed values of the d-d transitions it is thus possible to devise a spectrochemical series of increasing ligand-field strength: R = CN < H < p-ClC₆H₄ = C₆H₅ = p-CH₃C₆H₄ = p-CH₃OC₆H₄

< C₂H₅ < n-C₃H₇ = i-C₃H₇ < CH₃ < CF₃. In most cases this sequence plausibly reflects inductive effects of the substituents. The position of the electronegative CF₃ group in this series is somewhat surprising, suggesting that other factors also influence the ligand-field strength. It is possible that overcrowding causes a slight deformation leading to a somewhat greater chelating ability of the ligand. In the spectra of the NiS₄C₄H₄⁻² ion and in most of the alkyl-substituted dianions of nickel, two additional bands of medium intensity are observed which are probably due to the n=s: → 3b_{1g} and 2a_g → 3b_{1g} transitions; these bands

Table V. Transitions and Assignments of the Low-Energy Transitions in Ions $MS_4C_4R_4^{2-}$

Ion ^a	Transitions, cm. ⁻¹				
$NiS_4C_4(CN)_4^{2-}$ ^b	...	11,690 (30)	...	17,500 (570) ^e	19,250 (1250) ^e
$NiS_4C_4H_4^{2-}$...	11,765 (30) ^e	12,987 (38) ^e	18,182 (167)	23,256 (384)
$NiS_4C_4(CH_3)_4^{2-}$	11,110 (5.3)	12,739 (20)	...	18,520 (55)	24,691 (343)
$NiS_4C_4(C_2H_5)_4^{2-}$	10,753 (4.8)	12,658 (22)	...	18,520 (64)	25,000 (434)
$NiS_4C_4(CF_3)_4^{2-}$...	12,900 (18) ^e	...	17,000 (82) ^e	26,312 (2500) ^e
$NiS_4C_4(C_6H_5)_4^{2-}$...	12,579 (121)	23,529 (4610)
$PdS_4C_4(CN)_4^{2-}$ ^d	...	15,700 (64)	22,700 (5700)
$PdS_4C_4(C_6H_5)_4^{2-}$...	16,340 (33)	24,270 (6590)
$PtS_4C_4(CH_3)_4^{2-}$	18,018 (7)	20,833 (51)
$PtS_4C_4(C_6H_5)_4^{2-}$...	19,608 (4915) ^e
Assignment	$^1A_g \rightarrow ^3B_{1g}$	$^1A_g \rightarrow ^1B_{1g}$	$^1A_g \rightarrow ^1B_{3g}$	$^1A_g \rightarrow ^1B_{2u}, ^1B_{3u}$	$^1A_g \rightarrow ^1B_{1g}$
Classification	$(d_{x^2-y^2} \rightarrow d_{xy})$	$(d_{x^2-y^2} \rightarrow d_{xy})$	$(d_{xz} \rightarrow d_{xy})$	$(n \rightarrow s, \rightarrow M)$	$(n \rightarrow s, \rightarrow M)$

^a Measured in hydrazine solution, if not stated otherwise. ^b Data from ref. 22. ^c Shoulder. ^d Data from ref. 22. ^e Not observed or not resolved.

are obscured in the aryl-substituted complex dianions. The observed and assigned transitions of some representative dianions are given in Table V. No com-

in *vacuo*. During evaporation crystals appeared which were collected on a filter, washed with cold methanol, and dried at room temperature under vacuum. The black

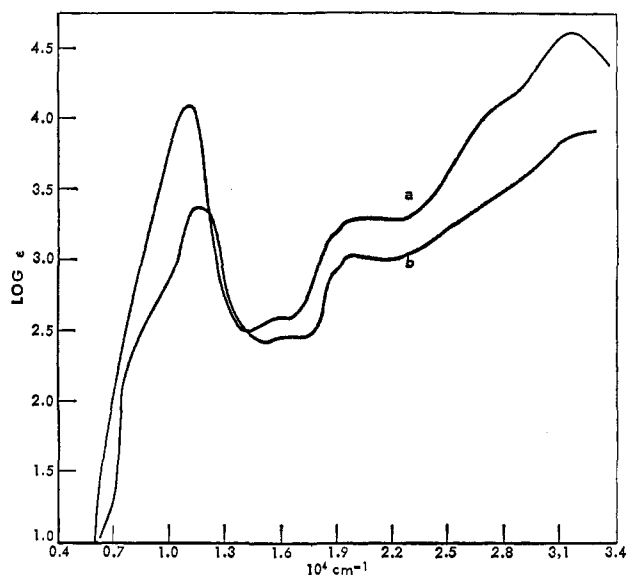


Figure 3. Absorption spectra of $NiS_4C_4H_4^-$ in pyridine (a) and of $NiS_4C_4(C_6H_5)_4^-$ in acetonitrile (b).

parison with calculated values was performed for the d-d transitions in the $MS_4C_4R_4^{2-}$ anions. As was pointed out before, this would require a complete recalculation to account for the changes in the ligand system (conversion of $RC(=S)C(=S)R$ into $RC(-S^-)=C(-S^-)R$).

Experimental

Preparation of $NiS_4C_4H_4$. The sodium salt of *cis*-dimercaptoethylene (III) was prepared according to the published procedure.¹² The compound (10 g.) was dissolved in 50 ml. of cold ethanol and a solution of 10 g. of $NiCl_2 \cdot 6H_2O$, dissolved in 100 ml. of ethanol-water (1:1), was added. A brown-black precipitate formed immediately. The slurry was acidified adding 5 ml. of concentrated HCl and diluted with 500 ml. of cold water. Repeated extraction with ether gave purple solutions of the complex. The ether phase was washed with water, dried over sodium sulfate, and evaporated

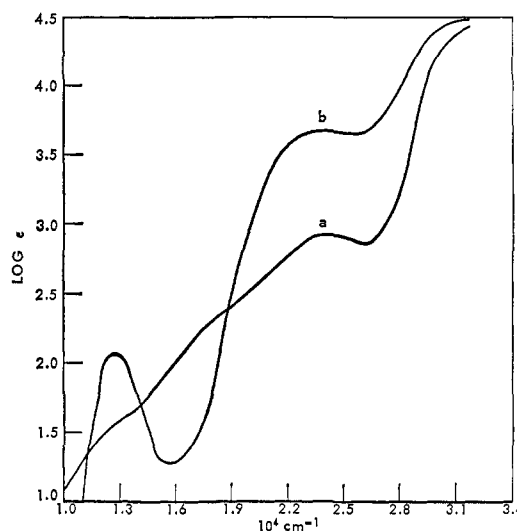


Figure 4. Absorption spectra of $NiS_4C_4H_4^{2-}$ (a) and of $NiS_4C_4(C_6H_5)_4^{2-}$ (b), both measured in hydrazine solution.

crystals start to decompose at about 68°. In solution extensive decomposition occurred during attempts of recrystallization from higher boiling solvents. The yield obtained was 271 mg. or 3%, based on the amount of III.

Anal. Calcd. for $NiC_4H_4S_4$: C, 20.1; H, 1.7; Ni, 24.6; S, 53.6; mol. wt., 239.1. Found: C, 20.4; H, 1.8; Ni, 24.5; S, 52.6; mol. wt., 225.

Isolation of Polymeric $NiS_4C_4H_4$. The precipitate obtained in the above experiment was filtered after acidification, washed with water, methanol, and acetone, and dried at 110° *in vacuo*.²⁴

Anal. Calcd. for $NiC_4H_4S_4$: C, 20.1; H, 1.7; Ni, 24.6. Found: C, 20.1; H, 2.9; Ni, 24.3.

Infrared spectra were recorded on a Beckman IR 4

(24) NOTE ADDED IN PROOF. The yield of complex is significantly increased (up to 24%) if the solutions of III and of the nickel salt are combined at about -20°: unpublished experiments with W. Heinrich, Munich.

Table VI

Orbital	Atom				Energy, β	Adopted Coulomb integral value, e.v.
	S ₁	C ₂	C ₃	S ₄		
1	0.3408	0.6196	0.6196	0.3408	1.818	15.00
2	0.5473	0.4477	-0.4477	-0.5473	0.818	12.05
3	0.6527	0.2728	-0.2728	0.6527	-0.418	8.25
4	0.4079	-0.5768	0.5768	-0.4079	-1.418	5.346

spectrophotometer and are described in the text. Ultraviolet spectra were obtained from a Cary 14 instrument. The polarographic measurements were performed on a ORNL controlled potential instrument (using an Ag-AgCl reference electrode in 0.1 *N* aqueous LiCl and a porous Vycor bridge) in a 0.1 *M* solution of LiClO₄ in dimethylformamide.

Appendix

The atomic overlap integrals were taken from ref. 22, and, where necessary, the group overlap integrals were recalculated for our eigenvectors. Eigenvalues and -vectors for the isolated dithioglyoxal molecule (with $\alpha_S = \alpha_C + 0.2\beta$ and $\beta_{C=S} = \beta_{C=C}$) are shown in Table VI.