Polarographic Study of Coordination Compounds with Delocalized Ground States. Substituent Effects in Bis- and Trisdithiodiketone Complexes of Transition Metals

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Abstract: Polarographic half-wave potentials for the reactions $M(S_2C_2R_2)_n + e = M(S_2C_2R_2)^-$ and $M(S_2C_2R_2)_n^- + e = M(S_2C_2R_2)_n^{-2}$ ($n = 2$ for M = Ni, Pd, Pt; $n = 3$ for M = V, Mo, and W) are reported for various substituents R. The $E_{1/2}$ values correlated linearly with inductive substituent constants, a result which is shown to be in principal agreement with the proposed electronic structures of the complexes.

In a series of preceding papers[2-5] certain of the planar bis and the prismatic tris complexes $M(S_2C_2R_2)_n$ of transition metals were described as novel delocalized systems. Although this view accounts for most of the unusual chemical properties of these compounds, it appeared to be of interest to include polarographic data in the discussion. Complexes of this type are excellently suited for such measurements in view of the reversibility of the electron-transfer reactions $M(S_2C_2R_2)_n + xe = M(S_2C_2R_2)_n^{-x}$.[6-10] Although previously published polarographic data indicate pronounced substituent effects, correlations were not possible as yet in view of the limited number of accessible compounds. With the development of a more general method of preparation[11] various substituted complexes $M(S_2C_2R_2)_n$ and, subsequently, a sufficient amount of polarographic data have become available for a quantitative correlation.

Experimental Section

Apparatus. An ORNL-controlled potential polarograph, Model Q-1988 A, and a Varian F-80 X-Y recorder were used to obtain the polarograms. A platinum wire served as the working electrode and a Ag|AgCl electrode in an aqueous 0.10 *M* LiCl solution as the reference. The reference electrode was placed in a 9-mm i.d. Vycor tube having a porous tip (Corning 7900-7930) which was inserted into the sample solution. The resistance across the porous Vycor bridge was 3000 ohms. The rate of leakage of Cl⁻ through the bridge was negligible during the time required for a polarographic measurement. The junction potential was reproducible if the porous tip was stored in DMF containing the supporting electrolyte and both this solution and the aqueous LiCl solution in the tube were replaced daily. The stability of the junction potential was demonstrated by the reproducibility of the $E_{1/2}$ of the first polarographic wave of the $Ni(S_2C_2Ph_2)_2$ complex, which remained essentially unchanged over a period of several days. The characteristics of the dme capillary employed as the indicator electrode were $m = 2.025$ mg/sec and $t = 3.91$ sec, with open circuit, and $h = 70$ cm. A shielded platinum disk or platinum sphere were used as the indicator electrode for the cyclic voltammetry work. The temperature of the cell was maintained at 25 ± 0.1°.

Reagents. The dimethylformamide (DMF) employed as the solvent was Mallinckrodt Reagent Grade treated with anhydrous copper sulfate and distilled at 15 mm. G. F. Smith $LiClO_4$ was recrystallized several times from water and dried under vacuum at 90°, which gave the monohydrate. The equivalent weight of the salt was determined by passing a weighed quantity through a Dowex 50 column in the H^+ form and titrating the eluted acid.

Preparation of the Complexes. All complexes except those with R = H or CN were prepared by the acyloin–P_2S_5 method.[11] Detailed descriptions of the preparative procedure have been given elsewhere as well as for the synthesis of complexes with R = H or CN. Several compounds have not yet been described and are listed in Table I. Compounds of chromium have not been included in this work as their preparation was not always possible and the compounds isolated frequently were too unstable to be obtained in a pure state. For the measurements on the unsubstituted vanadium complex the salt $AsPh_4^+$ $VS_6C_6H_6^-$ was employed.

Polarographic Measurements. Millimolar solutions of the complexes were prepared by dissolving a weighed quantity in a measured volume of DMF which was 0.10 *M* in $LiClO_4$. A solution of the unsubstituted ligand dianion was prepared from solid $Na_2(S_2C_2H_2)$ immediately prior to the measurement. A solution of $S_2C_2(CN)_2^{-2}$ was prepared by dilution of a 1 *M* solution of $Na_2S_2C_2(CN)_2$ in methanol. All solutions were degassed for 20 min with N_2 prior to the measurements.

Complexes of Ni, Pd, and Pt. All complexes of these metals gave two reduction waves. The first wave was well-defined and E *vs.* $\log (i/(i_d - i))$ plots were linear with slopes agreeing within a few millivolts with the theoretical value of 59.1 for a reversible one-electron reduction. The second wave was in most cases distorted near the top by a small post-wave or maximum as seen in Figure 1. The second wave, less the post-wave, was usually 5–25% higher than the first. The log plots of the second waves were reasonably linear, but the slopes were 10–30 mv larger than 59.1 for some of the complexes. For example, a slope of 75 mv was obtained for $Ni(S_2C_2Ph_2)_2$. However, the larger than theoretical slopes did not appear to be due to irreversibility as was shown by a study using cyclic voltammetry. Cyclic voltammograms were obtained for all of the Ni complexes and those Pd and Pt complexes which gave larger than theoretical slopes. Half-wave potentials of the cathodic and anodic peaks (taken as the potential at which the current reaches 85.2% of the peak height[12]) were within several millivolts of each other for both steps which is consistent with reversible behavior. A cyclic voltammogram of $Ni(S_2C_2Ph_2)_2$ is shown in Figure 2. Furthermore, the reversibility of the polarographic

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Table I. Melting Points and Analyses of Complexes Previously Not Described in the Literature

M	R	R′	Mp, °C	Calcd, %	Found, %
Ni	i-C_3H_7	i-C_3H_7	304 dec	C, 47.2; H, 6.9	C, 47.4; H, 6.8
Ni	n-C_3H_7	n-C_3H_7	52–54	C, 47.2; H, 6.9	C, 48.5; H, 6.8
Ni	C_6H_5	H	174–5	C, 49.1; H, 3.1	C, 49.3; H, 3.0
Ni	CH_3	C_6H_5	152	C, 51.6; H, 3.8; S, 30.6; Ni, 14.0	C, 51.8; H, 3.6; S, 30.2; Ni, 13.5
Pd	CH_3	CH_3	360 dec	C, 281; H, 3.5; S, 37.6; Pd, 30.8	C, 28.3; H, 3.6; S, 34.4; Pd, 30.0
Pd	p-$C_6H_4OCH_3$	p-$C_6H_4OCH_3$	294 dec	C, 54.0; H, 4.0; S, 18.0	C, 54.1; H, 3.9; S, 18.2.
Pt	p-$C_6H_4OCH_3$	p-$C_6H_4OCH_3$	341	C, 48.1; H, 3.5; S, 16.0; Pt, 24.4	C, 48.0; H, 3.5; S, 15.8; Pt, 24.0
Pt	C_6H_5	CH_3	350	C, 52.5; H, 3.8; S, 17.4, Pt, 26.6	C, 52.2; H, 3.8; S, 17.6; Pt, 26.6

waves of $Ni(S_2C_2Ph_2)_2$, taken as a representative bis complex, was also tested by constant potential electrolysis. A 1 m*M* solution was partially electrolyzed at a mercury pool at both −0.3 v and −1.2 v. The composite cathodic–anodic polarographic waves of the resulting solutions have the shape expected for a reversible reaction as seen in Figure 1.

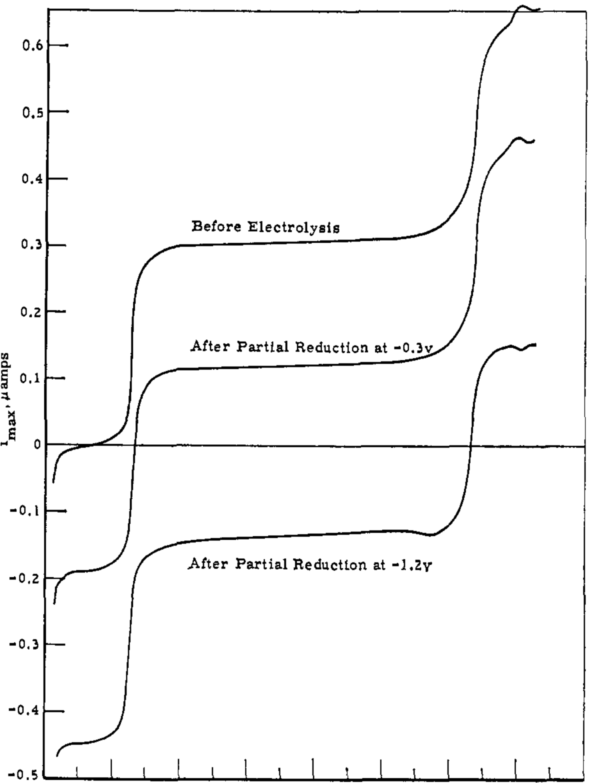


Figure 1. Constant potential electrolysis of a 1 m*M* solution of $Ni(S_2C_2)_2(C_6H_5)_2$.

The dependence of the limiting current of both waves of the phenyl-substituted complexes on the height of the mercury reservoir (uncorrected for back pressure) was tested and found to be consistent with diffusion control. Due to the similarity in structure of the complexes, this test was not made for all of the members of the series. Log *i* *vs.* log *h* plots gave slopes slightly larger than the expected value of 0.50 for a diffusion-controlled process, probably because *h* was not corrected for back pressure. Where solubility was sufficient, diffusion coefficients were determined from the height of the first wave.

Half-wave potentials and diffusion coefficients are given in Table II. In several instances half-wave potential data published by the Harvard group[6–10] have been used by us. These were converted to our scale by the addition of 0.033 v. This value was determined by taking the difference in the $E_{1/2}$ reported for the couple $Ni(S_2C_2(CN)_2)^- + e \rightleftharpoons Ni(S_2C_2(CN)_2)^{-2}$ and the same measured by us in DMF.

Complexes of Mo, W, and V. The Mo and W complexes gave two waves in the accessible range except $W(S_2C_2(C_6H_4OCH_3)_2)_3$, which gave three waves of nearly equal height. The first wave in all cases was well-defined and gave linear log plots having slopes in agreement with a reversible one-electron reduction. The second wave was generally somewhat higher than the first; log plots of the second wave were linear but in most cases had slopes larger than theory for a one-electron reversible wave. However, cyclic voltammograms obtained for these complexes indicated that the electrode reactions were reversible. A constant potential electrolysis experiment similar to the one described for $Ni(S_2Ph_2)_2$ was also carried out with one of the tris complexes, $W(S_2C_2(CH_3)_2)_3$. The composite cathodic–anodic polarographic waves obtained following partial electrolysis had the shape expected for reversible reactions. Monoanion salts, *e.g.*, $N(C_2H_5)_4{}^+V(S_2C_2R_2)_3{}^-$, were used for the measurements in the vanadium series. In all cases except with R = p-$C_6H_4OCH_3$ one anodic and two cathodic waves were observed. In the one exception three cathodic waves were observed. Linear log plots with slopes characteristic of reversible one-electron reactions were obtained for all of the waves except two. The anodic wave of the unsubstituted complex was irreversible, and the second cathodic wave of the p-$C_6H_4OCH_3$-substituted complex had a large maximum in the middle of the wave.

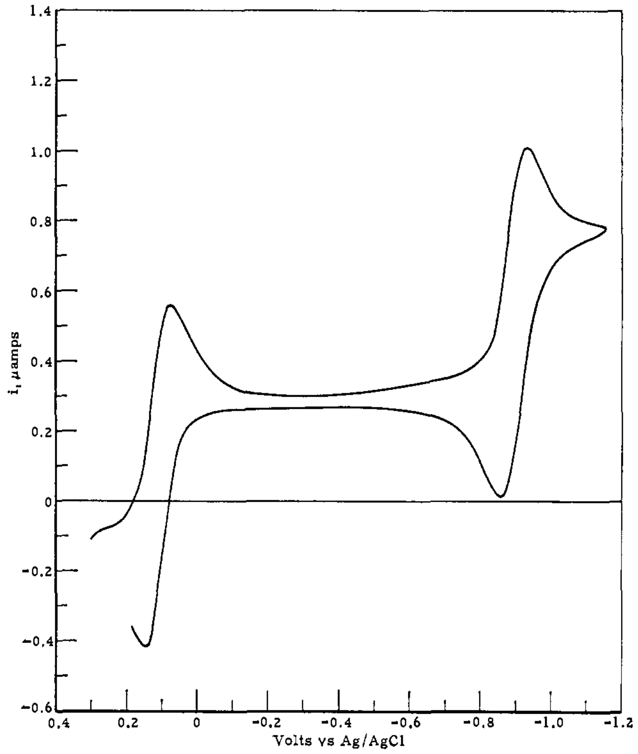


Figure 2. Cyclic voltammogram of a 1 m*M* solution of $Ni(S_2C_2(C_6H_5)_2)_2$ using a Pt indicator electrode.

The dependence of the limiting current on the height of the mercury reservoir for both waves of the CH_3-substituted complexes of Mo and W, and the anodic and first cathodic waves of the p-C_6H_4-

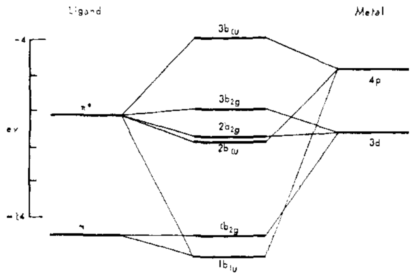


Figure 3. Molecular orbital energy level scheme for the irreducible representations B_{1u} and B_{2g} in $NiS_4C_4H_4$.

OCH_3-substituted complex of V, was found to be consistent with diffusion control. Diffusion coefficients were calculated from the height of the first polarographic waves of the Mo and W complexes and the wave corresponding to the couple $V(S_2C_2R_2)_3^- + e = V(S_2C_2R_2)_3^{-2}$.

The determined half-wave potentials and diffusion coefficients are listed in Table III.

Table II. Polarographic Half-Wave Potentials and Diffusion Coefficients for Complexes $MS_4C_4R_4$, with M = Ni, Pd, Pt

No.	R	R′	$E_{1/2}$, $ML_2^0 + e \rightleftharpoons ML_2^-$	$E_{1/2}$, $ML_2^- + e \rightleftharpoons ML_2^{-2}$	$D \times 10^6$ cm² sec⁻¹
		Nickel			
1	CN	CN	1.049	−0.259	b
2[a]	CF_3	CF_3	1.030	−0.088	b
3	p-C_6H_4Cl	p-C_6H_4Cl	0.218	−0.757	3.64
4	C_6H_5	C_6H_5	0.134	−0.881	5.15
5	H	C_6H_5	0.115	−0.879	5.75
6	H	H	0.120	−0.921	9.00
7	p-$C_6H_4CH_3$	p-$C_6H_4CH_3$	0.083	−0.960	b
8	CH_3	C_6H_5	0.025	−0.988	5.34
9	p-$C_6H_4OCH_3$	$C_6H_4OCH_3$	0.035	−0.945	3.68
10	CH_3	CH_3	−0.107	−1.114	6.36
11	C_2H_5	C_2H_5	−0.119	−1.138	5.64
12	n-C_3H_7	n-C_3H_7	−0.121	−1.154	4.41
13	i-C_3H_7	i-C_3H_7	−0.151	−1.204	7.90
		Palladium			
1[a]			b	0.473	
2[c]			0.996	0.114	
4			0.182	−0.636	4.21
6			0.165	−0.718	5.52
9			0.086	−0.720	3.21
10			−0.060	−0.870	b
		Platinum			
1[a]			b	0.243	
2[c]			0.852	−0.234	
4			0.090	−0.844	2.27
7			0.043	−0.900	b
9			−0.004	−0.919	5.30
10			−0.133	−1.069	b

[a] Data from ref 7. [b] Not determined or not reported. [c] Data from ref 8.

Free Ions $S_2C_2H_2^{-2}$ and $S_2C_2(CN)_2^{-2}$. The ions were oxidized in DMF at a platinum electrode. Both ions gave two irreversible anodic waves at potentials given below.

R	I	II
H	−0.81	−0.21
CN	−0.31	0.00

Discussion

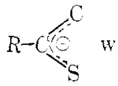
Planar Complexes. According to the proposed molecular orbital bonding scheme shown in Figure 3, the B_{1u} combination of the lowest unoccupied ligand

Table III. Polarographic Half-Wave Potentials and Diffusion Coefficients for Complexes $MS_6C_6R_6$, with M = Mo, W, V

Ligand[a] no.	$ML_3^0 + e \rightleftharpoons ML_3^-$	$ML_3^- + e \rightleftharpoons ML_3^{-2}$	$D \times 10^6$, cm² sec⁻¹
	Molybdenum		
2[b]	0.98	0.39	c
4	0.009	−0.617	4.42
6	−0.090	−0.745	7.52
10	−0.307	−0.936	5.86
	Tungsten		
2[b]	0.91	0.35	c
4	−0.041	−0.684	3.78
6	−0.133	−0.845	6.86
7	−0.091	−0.681	2.41
9	−0.138	−0.751	2.32
10	−0.333	−0.994	5.30
	Vanadium		
1[b]	c	0.69	c
2[d]	c	0.50	c
4[d]	+0.33	−0.68	c
6	+0.25[e]	−0.722	8.12
7	+0.323	−0.745	3.46
9	+0.260	−0.783	2.83

[a] Numbering of the ligands as in Table II. [b] Data from ref 8. [c] Not reported. [d] Data from ref 9. [e] Irreversible anodic wave.

MO's becomes stabilized on interaction with the metal p_z orbital and is occupied in the neutral complexes.[3] The B_{2g} combination of the same orbitals, on the other hand, becomes weakly antibonding on interaction with the metal d_{xz} orbital and is filled with one or two electrons during the reduction of the neutral d^8 transition metal complexes. Both orbitals are delocalized over the whole molecule but consist to a significant extent of the π MO's of the ligands.[3] The polarographic $E_{1/2}$ values thus should be substituent dependent to a similar degree as the free ligands. A correlation with Taft's inductive substituent constants[13] σ^* is to be expected, particularly in view of the similarity of the system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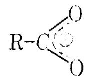

and is indeed found as shown in Figures 4, 5, and 6. Since the σ^* values are given relative to the methyl group, plots of $\Delta E_{1/2}/0.0591$ vs. $\Sigma\sigma^*$ were made, where $\Delta E_{1/2} = E_{1/2}(R) - E_{1/2}(CH_3)$. The linear relation fits for all substituents studied except for the second anodic potential of the nickel complex with R=CN which may be due to irreversiblity. Thus, it may be concluded that the substituent effects are essentially inductive. To correlate this fact with the proposed electronic structure, we have performed a model calculation. At first the molecular orbital energies for the isolated S=C—C=S system were calculated, neglecting mutual overlap, with $\alpha_S = \alpha_C^0 + 0.2\beta$ and $\beta_{C=C} = \beta_{C=S}$ (β = 3 ev). The inductive substituent effect was approximated by chang-

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(13) The σ^* values were taken from R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13. The σ^* value for the CN group was obtained by multiplying $\sigma^*_{CH_2CN}$ by 2.8, as suggested by Taft, and $\sigma^*_{CH_3}$ by multiplying $\sigma^*_{CH_2CF_3}$ by the ratio $\sigma^*_{CH_2CF_3}/\sigma^*_{(CH_2)_2CF_3}$, or 2.87. The σ^* constants for the aryl substituents were those reported for the *ortho*-substituted benzene derivatives. These values are given relative to the unsubstituted phenyl rings and were converted to the scale of the aliphatic series by the addition of 0.60, which is the σ^* value for C_6H_5 in the aliphatic series.

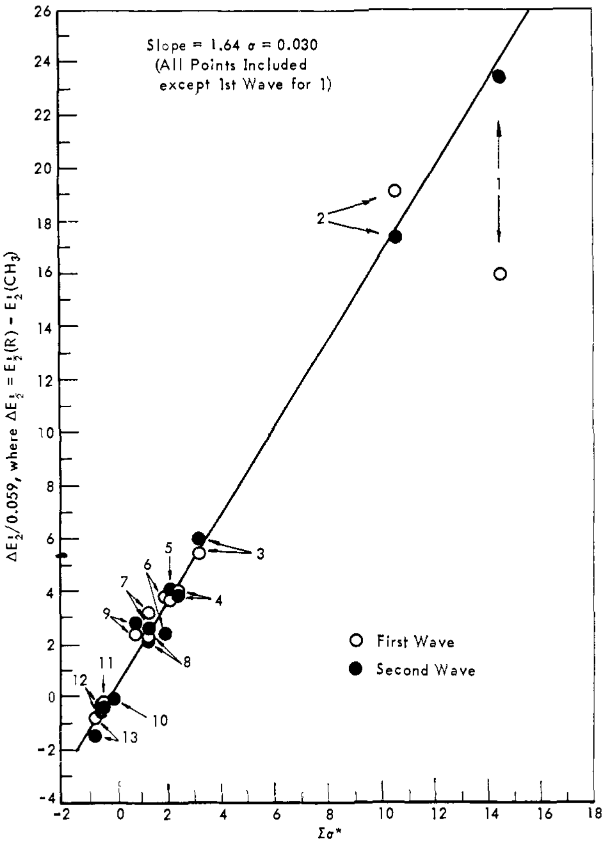

Figure 4. Plot of $\Delta E_{1/2}/0.059$ *vs.* Taft substituent constant weighted for number of R groups present for $Ni(S_4C_4R_4)$ complexes.

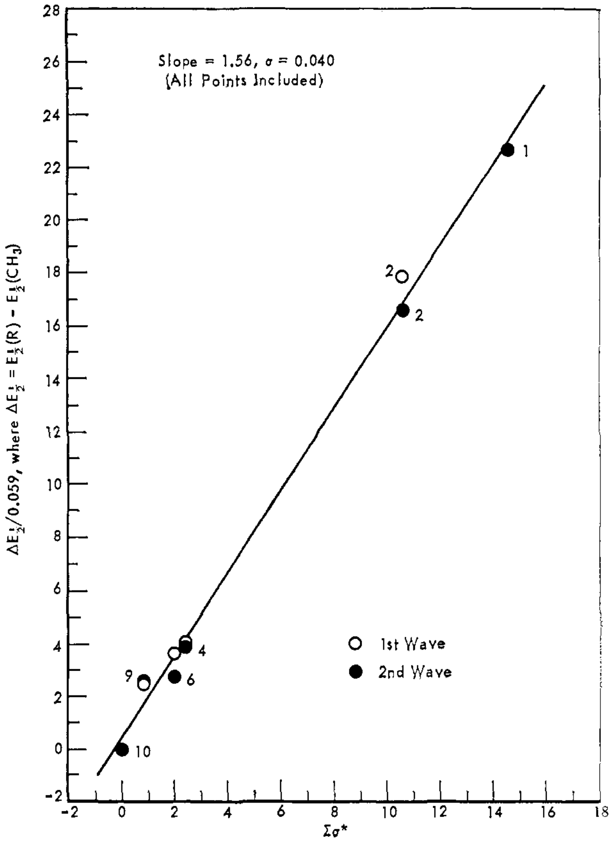

Figure 5. Plot of $\Delta E_{1/2}/0.059$ *vs.* Taft substituent constant weighted for number of R groups present for $Pd(S_4C_4R_4)$ complexes.

ing the effective carbon atom Coulomb terms, $\alpha_C = \alpha_C^0 \pm m\beta$. From the eigenvectors and eigenvalues obtained for several values of m the elements of the secular determinants of the representations B_{1u} and B_{2g} were obtained. (The input Coulomb terms of the metal were identical with those used in the previous calculation of $NiS_4C_4H_4$,[3] and the resonance integrals were approximated from the relevant group-overlap integrals[3].) The numerical results will not be presented in detail. They indicate, however, that $-I$ substituents should increase, and $+I$ groups decrease the absolute energy of both $3b_{2g}$ and $2b_{1u}$, which for $3b_{2g}$ is in qualitative agreement with the polarographic data. No direct experimental information is available to test the behavior of orbital $2b_{1u}$, but there is spectroscopic evidence suggesting that it behaves as expected. According to Figure 7, a hypsochromic shift of the $2b_{1u}$–$3b_{2g}$ transition is predicted. As the energy of the latter is available from the optical spectra,[2,3] the validity of this prediction may be tested, with the result given in Table IV. In Table IV there are also included three calculated transition energies for given values of the inductive substituent parameter m (in ev). The experimentally observed frequency increase of the $2b_{1u} \rightarrow 3b_{2g}$ transition is not only actually observed, it may also be reproduced within a reasonable range of values of m. The general agreement between the theory and experiment thus strongly supports the proposed orbital scheme as well as the assignment of the characteristic low-energy transition in the electronic spectra. For substituents with σ^* between —0.115 and +0.60, the frequency increase of this transition is roughly pro-

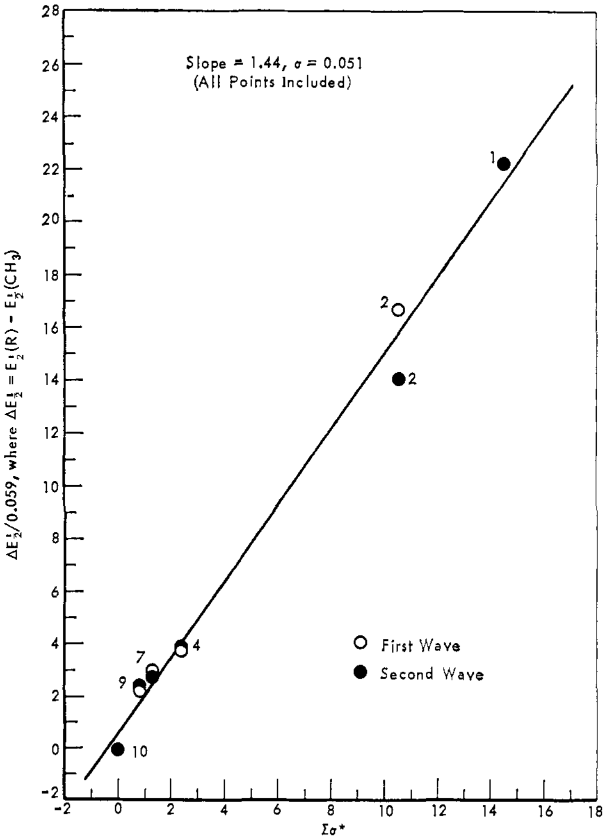

Figure 6. Plot of $\Delta E_{1/2}/0.059$ *vs.* Taft substituent constant weighted for number of R groups present for $Pt(S_4C_4R_4)$ complexes.

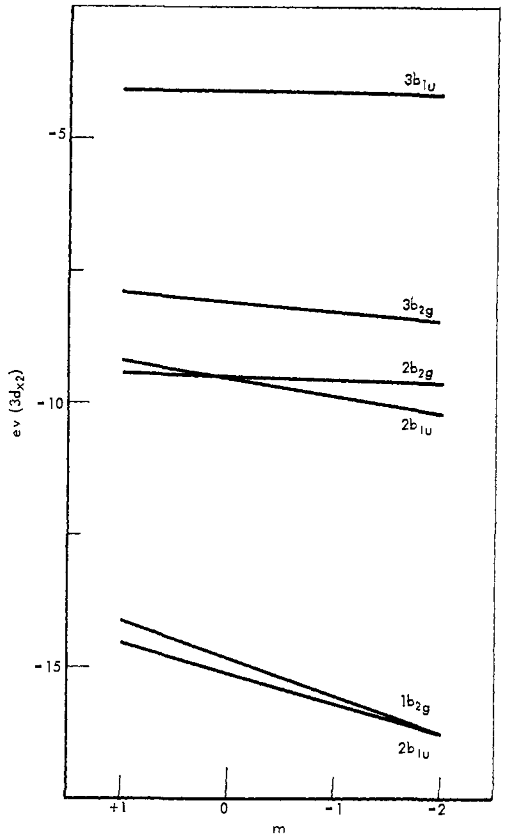

Figure 7. Dependence of the B_{1u} and B_{2g} group orbitals on the magnitude of the inductive substituent parameter m (calculated for the $NiS_4C_4H_4$ model).

portional to the magnitude of σ^*; substituents with $\sigma^* > +0.60$ produced smaller frequency increments, which may be due to resonance effects. Other authors[14,15] have proposed an orbital scheme for complexes $NiS_4C_4(CN)_4^{-z}$ in which the highest occupied orbital would have the symmetry A_g and be of the $d_{x^2-y^2}$ type. We have criticized this orbital scheme previously and have also shown that it arises from a somewhat less realistic choice of input parameters for the isolated systems.[3] It should be emphasized that it would not explain the unusual nature of these bidentate ligands and that it apparently is no longer considered a valid description by the originators themselves.[16,16a] The slope of the $\Delta E_{1/2}/0.0591$ *vs.* $\Sigma\sigma^*$ plots slightly decreases in going from Ni to Pd and Pt (Table V), indicating that the $3b_{2g}$ orbital acquires a somewhat higher metal character in the complexes of the heavier transition metals. A direct polarographic determination of the substituent effects in the free dithiodiketones, on the other hand, is not possible due to the instability of these compounds. However, the voltammetric oxidation of the ions $S_2C_2H_2^{-2}$ and $S_2C_2(CN)_2^{-2}$ gave two irreversible waves whose potentials proved to be substituent dependent to quite a similar degree as in the case of the metal complexes. The dithiodiketones also formally resemble the quinones. It is of interest that the (first) cathodic $E_{1/2}$ potentials determined for p-benzoquinone, duroquinone, and 2,3-dichloro-4,5-dicyanoquinone nearly fit the line in Figure 4, with a calculated slope of 1.76. The $3b_{2g}$ orbital of the nickel complexes may be estimated to have about 80% ligand character, in agreement with the MO calculations.[3]

Table IV. Observed and Calculated Substituent Dependence of the $2b_{1u}$–$3b_{1g}$ Transition in Nickel Complexes of Dithiodiketones

R	σ^*	$2b_{1u}$–$3b_{2g}$, cm^{-1} Obsd	Calcd
		Aliphatic Series	
n-C_3H_7	−0.115	12,821	12,055 for $m = 0$
C_2H_5	−0.010	12,870	
CH_3	0	12,900	13,000 for $m = +1$
H	0.475	13,870	
CF_3	2.65	13,990	14,083 for $m = +2$
		Aromatic Series	
p-$C_6H_4OCH_3$	+0.20	10,820	
p-$C_6H_4CH_3$	+0.33	11,300	
C_6H_5	+0.60	11,550	
p-$C_{11}H_4Cl$	+0.80	11,561	

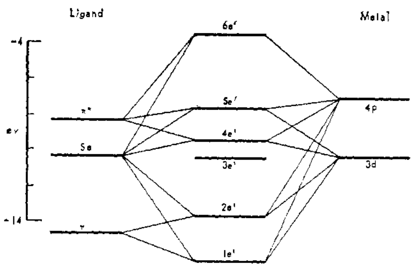

Figure 8. Molecular orbital energy level scheme for the E′ irreducible representation in complexes $MS_6C_6H_6$ (the nonbonding sulfur sp^2 orbital (3e′) is included).

Table V. Observed $\Delta E_{1/2}/0.0591$ *vs.* $\Sigma\sigma^*$ Slopes

Metal	Slope	a
Ni	1.64	0.030
Pd	1.56	0.040
Pt	1.44	0.051
Mo	1.40	0.027
W	1.40	0.053
V	1.33[b]	0.091

[a] Standard deviation. [b] Slope of $E_{1/2}/0.0591$ *vs.* $\Sigma\sigma^*$ since $V(S_2C_2CH_3)_3$ was not available.

Prismatic Complexes. In the closed-shell prismatic tris compounds, the lowest unoccupied MO 5e′ originates from the lowest unoccupied π MO's of the isolated ligands, the metal d and p orbitals as well as a component of the sp^2 sulfur electron pairs of the appro-

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(15) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966).

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(16a) Note Added in Proof. Similar criticism must be expressed with respect to a recently proposed electronic structure for $ReS_6C_6Ph_6$ (E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2956 (1966)). The Coulomb terms assumed to be valid for the isolated ligands were undoubtedly too large relative to the input energy assumed for the d orbitals of the metal. Consequently, too many electrons were placed into the ligands, leading to an incorrect representation of the bonding in these and related complexes.

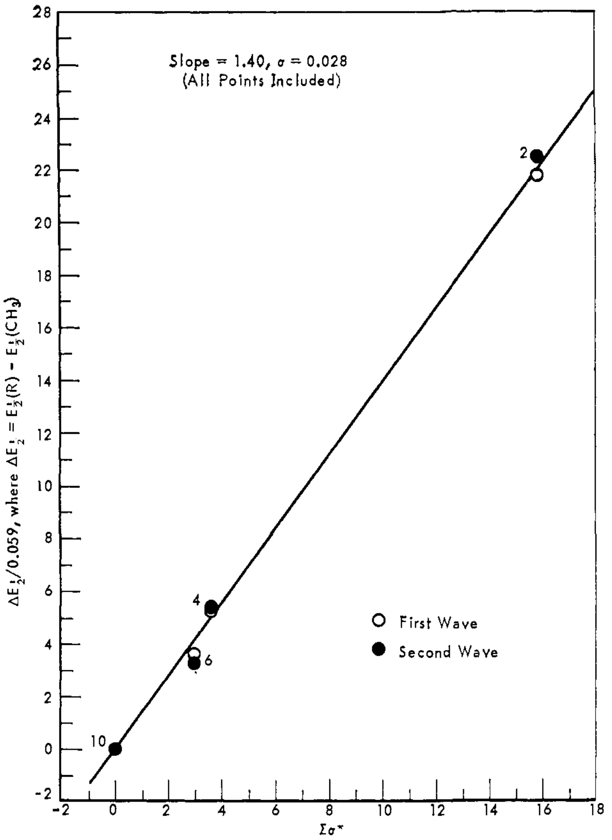

Figure 9. Plot of $\Delta E_{1/2}/0.059$ *vs.* Taft substituent constant weighted for number of R groups present for $Mo(S_6C_6R_6)$ complexes.

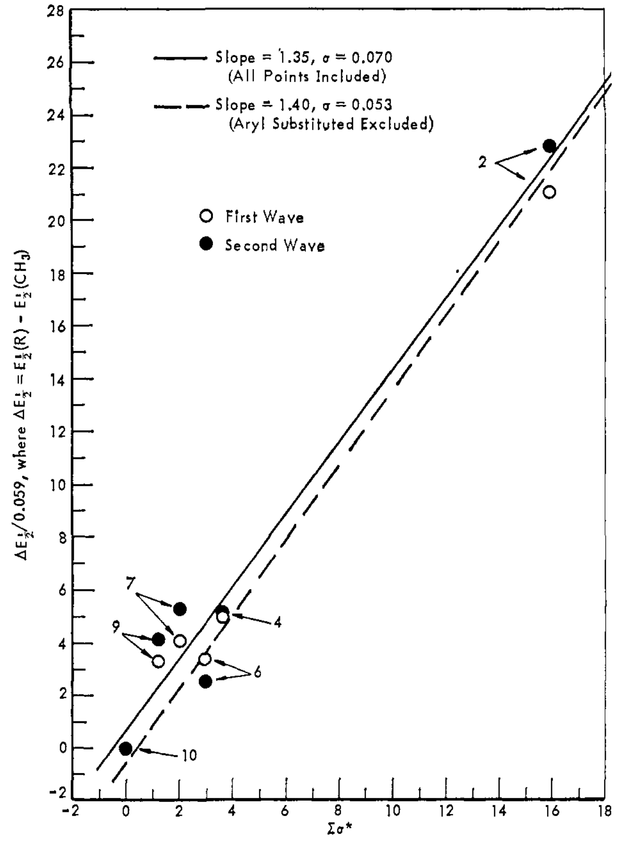

Figure 10. Plot of $\Delta E_{1/2}/0.059$ *vs.* Taft substituent constant weighted for number of R groups present for $W(S_6C_6R_6)$ complexes.

priate symmetry. The MO energy level scheme describing the E′ group orbitals is shown in Figure 8. The bonding situation thus is very similar to that proposed for the planar d^8 neutral complexes, except that the important orbitals 4e′ and 5e′ have a somewhat smaller ligand π orbital character (calcd for a model compound $MS_6C_6R_6$: 47%[5]; calcd for $NiS_4C_4H_4$: 82%[3]). This causes the $\Delta E_{1/2}/0.0591$ *vs.* Σσ* slope to decrease (Table V). On the whole, the linear relation is still fulfilled (Figures 9–11). Interestingly, however, a somewhat greater deviation for the aromatic substituents is observed in the complexes of tungsten, which may be the result of weak resonance effects.[16b] As in the planar complexes, a hypsochromic shift of the first intense band which was assigned to the 4e′ → 5e′ transition is observed with increasing −I effect of the substituents. This effect can be rationalized by a calculation similar to that performed above. However, in addition to considering the substituent effect onto the π molecular orbitals of the ligands it is also necessary to vary the adopted energy of the sulfur sp^2 orbitals. If this is not done a slight bathochromic effect for the 4e′ → 5e′ transition on substitution with −I substituents is predicted. There is no doubt, on the other hand, that the effective Coulomb term of the sp^2 orbitals will increase with increasing −I effect of the substituents and it may thus be stated that the substituent effect on

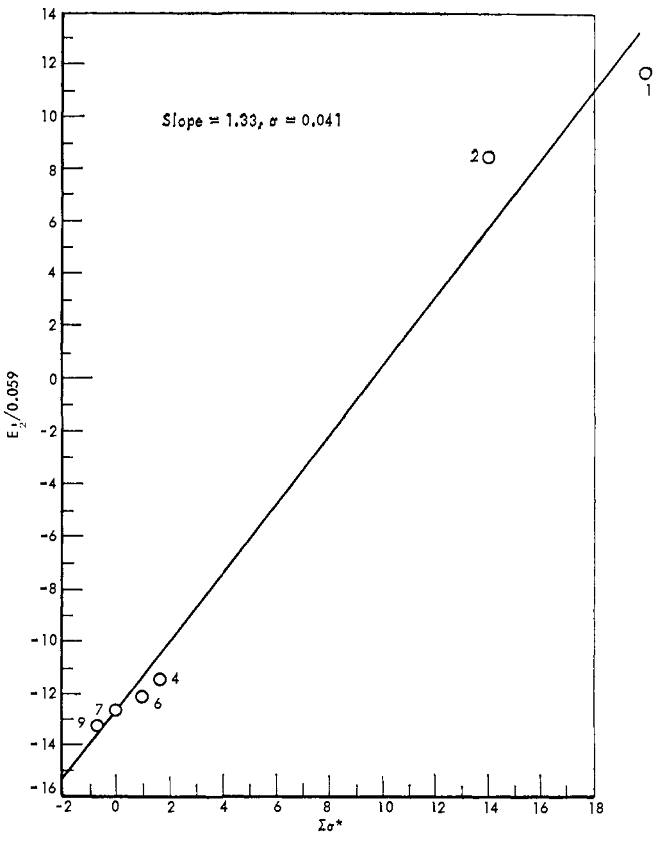

Figure 11. Plot of $E_{1/2}/0.059$ *vs.* Taft substituent constant weighted for number of R groups present for $V(S_6C_6R_6)^- + e = V(S_6C_6R_6)^{-2}$ couple.

(16b) Note Added in Proof. The fact that the phenyl groups in complexes $MS_6C_6Ph_6$ are twisted out of the MS_2C_2 planes in the solid state (see, *e.g.*, R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 3776 (1965)), does not exclude weak resonance effects at room temperature in solution. Under these conditions the phenyl groups will undoubtedly rotate about the *c*–*c* axes.

Table VI. Calculated and Observed Substituent Dependence of the First Allowed Optical Transition in Complexes $MS_6C_6R_6$

R	Adopted Coulomb term of the sp^2 orbitals of sulfur, ev[a]	Inductive parameter m, ev	Calcd $4e'$-$5e'$, cm^{-1}	Energy (cm^{-1}) of the first transition in complexes of Mo	W
CH_3	−10.30	0	14,480	15,625	16,450
H	−10.58	−1	14,865	16,600	17,360
CF_3	−10.80	−2	15,164	17,400	18,451

[a] The energy assumed for $m = 0$ corresponds to the first ionization potential of sulfur. The remaining values in this column were obtained by assuming a parallel increase of the sp^2 sulfur orbital energy with the energy of the lowest unoccupied π MO of the isolated S=C—C=S system calculated for $m = -1$ and -2. In this calculation the interactions between the $3p\pi$ orbitals of sulfur in the prism were neglected.

the energy of the first transition may be understood in terms of our model (Table VI). The fact that the tungsten complex with R = p-$C_6H_4OCH_3$ exhibits three reduction waves in the measurable range is not inconsistent with the proposed electronic structure. It suggests the existence of a trianion which would have the ground-state configuration $\langle 5e' \rangle^3$. Similarly, the existence of a $ReS_6C_6Ph_6^{-2}$ anion has been inferred from polarographic measurements,[17] an ion in which the ground-state configuration would be $\langle 5e' \rangle^4$. The polarographic results from the vanadium complexes are quite similar to those of the tris complexes studied. In the neutral compounds, the ground-state configuration is $\langle 4e' \rangle^3$. Although it would be of interest to obtain information on the composition of orbital $4e'$ relative to $5e'$, only limited data for the first reduction wave are available so that these values could not be plotted against $n\sigma^*$. For the second wave the linear relation is satisfactorily demonstrated, however. It thus may be concluded that the polarographic measurements clearly reflect the ligand π-orbital origin of the orbitals which become occupied during the reduction, in complete agreement with the proposed "delocalized" electronic structures of the complexes.

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(17) E. I. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, 87, 4012 (1965).