Coordination Compounds with Delocalized Ground States. Tris(dithioglyoxal) and Related Prismatic α-Dithiodiketone Complexes of Transition Metals[1]

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Abstract: Preparation and properties of prismatic complexes of composition $MS_6C_6H_6$, with ligands derived from dithioglyoxal, $S_2C_2H_2$, and of some of their substituted analogs, $MS_6C_6R_6$, are reported. The bonding is discussed on the basis of molecular orbital and conventional resonance theory, allowing a consistent interpretation of the chemical properties and the infrared and electronic spectra. The metals in the neutral complexes $MS_6C_6R_6$, with M = Cr, Mo, and W, are formally in the +IV state, and the ligands approximately two-thirds intermediate between dithiodiketones and dithiolate dianions. The bonding is characterized by extensive ground-state delocalization. Evidence for aromatic character in closed-shell species $MS_6C_6H_6{}^{z-}$ has been obtained through nmr measurements and a successful Friedel–Crafts alkylation.

The complexes of the type $MS_6C_6R_6{}^{z-}$ ($z = 0, 1, 2$),[2-5] in which the ligands are derived from 1,2-bidentate unsaturated sulfur-containing ligands such as 1,2-dithiodiketones, are connected by reversible oxidation–reduction reactions. However, the reasons for this apparent stabilization of unusual valence states of the metals are not yet understood. The elucidation of their electronic structure has become a matter of prime interest after it was found that $ReS_6C_6Ph_6$ has a trigonal prismatic structure.[6] In the present paper we wish to report the preparation and properties of several of the unsubstituted compounds of composition $MS_6C_6H_6$,[7] with ligands derived from 1,2-dithioglyoxal. The structure of $MoS_6C_6H_6$ is similar to that of $ReS_6C_6Ph_6$, except that the $MoS_2C_2H_2$ chelate rings deviate somewhat from planarity and are identical with that of the tungsten compound, $WS_6C_6H_6$.[8] Together with additional chemical evidence,[9] but with some reservations to be expressed later, it may be concluded that prismatic coordination is general for most members of this class of compounds. The neutral species are all remarkably stable, deeply colored, and strikingly resemble the planar bis complexes $MS_4C_4R_4$. Evidently, the nature of the ligands is primarily responsible for their chemical properties. We have shown recently[10] that the electronic structure of the complexes $MS_4C_4R_4$ may be described in terms of semiempirical molecular orbital as well as conventional resonance theory and was found to involve extensive ground-state delocalization of the vertical π-electron system. We have therefore extended this approach to prismatic tris complexes and describe the results of this work in the following section.

Description of Electronic Structure

For the discussion of the electronic structure, simple Hückel-type molecular orbital theory was used which in view of the complexity of the problem is to be preferred to more sophisticated treatments, particularly at this early stage of development in this field. The main purpose of this paper is to lay the foundation for a qualitative understanding of the bonding in these very unusual compounds. At first the molecular orbital energy levels of a prismatic arrangement of three dithioglyoxal molecules with the symmetry D_{3h}, as shown in Figure 1a, were calculated with appropriate parameters for α_C, α_S, $\beta_{C=C}$, and $\beta_{C=S}$, with neglect of overlap and the original arrangement of the sulfur $3p_\pi$ orbitals as shown in Figure 1b. Although $MoS_6C_6H_6$ was found to actually have C_{3h} symmetry, it is sufficient to assume the higher symmetry as the observed deviation is not very large[11] and actually absent in $ReS_6C_6Ph_6$.[12] Owing to the proximity of the ligands, the $3p_\pi$ orbitals of the sulfur atoms interact, causing a splitting of the originally degenerate set of ligand π-MO's, as indicated in Figure 2. To classify the metal–ligand interactions, a symmetry correlation is shown in Table I; the occurrence of both σ- and π-bonding interactions in the irreducible representations E′ and E″ indicate the important possibility of delocalization involving both the σ- and π-electron systems of the ligands. This is not the case in the planar bis compounds $MS_4C_4R_4$, where the σ- and π-type interactions belong to different symmetries. For the solution of the secular determinant the required matrix elements were suitably approximated (see Appendix); as previously[10] the calculations were carried out over a range of input parameters to

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[1] Paper X of the series "The Chemistry of the Coordination Compounds." Paper IX: G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

[2] R. B. King, *Inorg. Chem.*, **2**, 641 (1963).

[3] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964).

[4] (a) G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Angew. Chem.*, **76**, 715 (1964); (b) G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 1080 (1964); (c) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964).

[5] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965).

[6] R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 3776 (1965).

[7] A preliminary communication has been published: G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Chem. Ind.* (London), 1464 (1965); also see ref 8.

[8] A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **87**, 5798 (1965).

[9] E. I. Stiefel and H. B. Gray, *ibid.*, **87**, 4012 (1965).

[10] G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 3585 (1965).

[11] The observed deviation of the $MoS_2C_2H_2$ rings from planarity is about 18°.[8]

[12] Reference 6. The $ReS_2C_2Ph_2$ rings are planar; the remaining bond distances and angles are practically identical with the molybdenum complex.

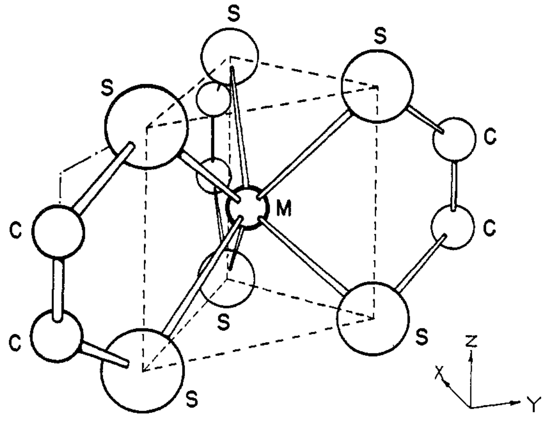


Figure 1a. Model of a prismatic complex $MS_6C_6H_6$ and assumed directions of the axes adopted for the calculation; M–S distance assumed to be 2.23 A.

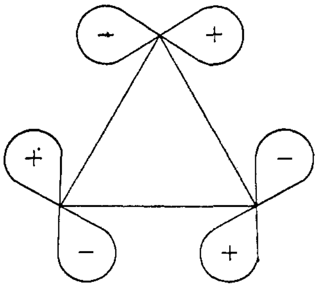


Figure 1b. Assumed initial arrangement of the sulfur 3p orbitals in the isolated prismatic ligand system.

see how sensitively the orbital sequence is affected by changes of the adopted numerical values. The result of a typical calculation is shown in the orbital diagram (Figure 2). It actually represents a complex of a first-row transition metal, but calculations were also carried out for $WS_6C_6H_6$. Although the results indicate reversals in the order of certain of the lowest filled and the higher antibonding orbitals, it may be concluded that there are no essential differences in the electronic structures in the tris complexes of lighter and heavier transition metals. For the neutral complexes, *e.g.*, of Cr, Mo, and W, or the $VS_6C_6R_6^-$ ion, a closed-shell configuration ($(4e')^4$) results. The 4e′ MO is composed of the lowest antibonding (E′) ligand π MO (calcd 41%), the sulfur sp^2(17%), and the metal d and p orbitals of E′ symmetry (25 and 17%, respectively). For $H_M(nd, nd) \cong H_S(3sp^2,3sp^2)$, it is followed by the $3a'_1(d_{z^2}\text{type})$ orbital and the group of nonbonding sulfur sp^2 orbitals; for metals in which $H_M(nd,nd) > H_S(3sp^2,3sp^2)$, the $3a'_1$ orbital becomes more stable than the latter orbitals, but 4e′

Table I. Symmetry Correlation of the Metal–Ligand Interactions in a Tris(dithioglyoxal) Complex of Symmetry D_{3h}

	Irreducible representation					
	A'_1	A''_1	A'_2	A''_2	E'	E''
Sulfur σ orbitals (bonding)	1			1	1	1
Sulfur σ orbitals (nonbonding	1			1	1	1
Ligand π orbitals		2	2		2	2
Metal orbitals, s	1					
p				1	1	
d	1				1	1

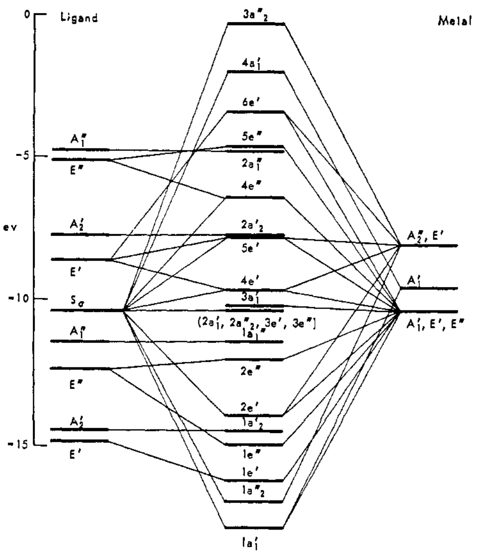
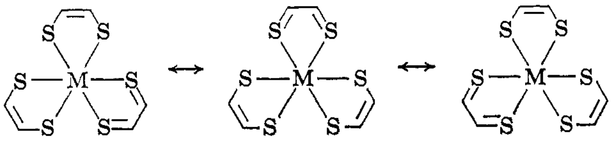


Figure 2. Schematic molecular orbital energy-level diagram for a prismatic complex of the type $MS_6C_6H_6$.

always remains the highest bonding orbital. The lowest unoccupied MO (in closed-shell complexes) is 5e′, closely followed by $2a'_2$. The 5e′ MO is composed similarly as 4e′, but over a relatively broad range of metal input Coulomb terms always has somewhat greater metal character than 4e′. The orbital $2a'_2$, on the other hand, is a pure ligand π MO. The sequence between 5e′ and $2a'_2$ was found to depend critically on the adopted input parameters and, hence, is difficult to predict on the basis of calculations alone. Paramagnetic resonance measurements, to be discussed below, on various species $MS_6C_6R_6^{2-}$ with one unpaired electron in the lowest unoccupied MO, unambiguously indicate significant metal character. This would be consistent with 5e′, but definitely rules out $2a'_2$. On complex formation the C–C bond orders of the free ligands increase, whereas those of the C–S bonds decrease. The C–C bond distance thus should be >1.34 and the C–S distance <1.82 A, respectively, in agreement with the observed 1.37 ± 0.03[13] and 1.70 ± 0.03 A for $MoS_6C_6H_6$.[8] Considering the valence state of the metal in the complex, it follows from the high ligand character of the 4e′ MO that the complexes, *e.g.*, of Cr, Mo, or W, contain the metals in the formal +IV state, whereas vanadium in $VS_6C_6R_6$ would be +III. The ligands, on the other hand, are intermediate between S═C—C═S and $^-$S—C═C—S$^-$ systems. Since one set of ligand MO's ($1a'_2$, $1a''_1$, $2a'_2$, and $2a''_1$) corresponds to unchanged MO's of one S═C—C═S unit, the results of the MO treatment may be expressed with *full justification* in terms of conventional resonance theory. For neutral complexes of Cr, Mo, or W, for example, the ground state may be represented by a set (I) of three canonical formulas.



(I)

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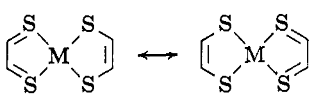
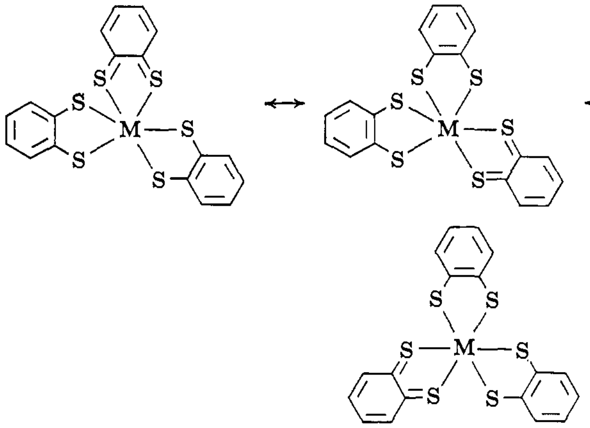
[13] This value is the result of a refinement of the initial measurement,[8] with more data along the z axis; performed by Dr. A E. Smith, Emeryville.

Assuming equal contributions of these structures, the bond lengths calculated from the double-bond characters (1.37 and 1.68 A for C–C and C–S, respectively) are equal or very close to the experimental values. The sulfur atoms thus would be in a state between sp^2 and sp^3 hybridization, a fact which could explain the observed nonplanarity of the $MoS_2C_2H_2$ chelate rings. In addition, the previously suspected[4a,6] close analogy of the bonding in the tris complexes with that in planar d^8 complexes (II) now appears to be fully justified. Evidently this type of ground-state delocalization is the salient feature of complexes with such ligands and is largely responsible for their unusual chemical properties. The same situation also occurs in complexes of toluenedithiol 1,2-(tdt); a set of related valence bond structures III for a neutral complex $M(tdt)_3$ (M, *e.g.*, Cr, Mo, or W) may be written in accord with group-theoretical considerations.

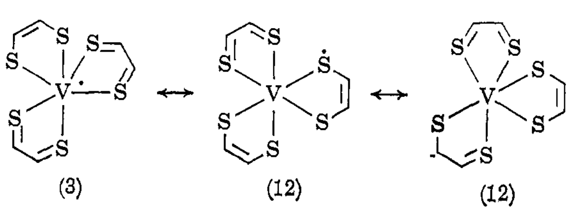


(II)



(III)

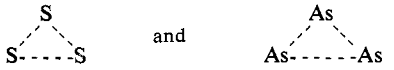
To illustrate further the applicability of conventional valence bond theory we also include a set (IV) of the most important limiting structures of $VS_6C_6H_6$ (the number of equivalent structures is indicated in parentheses).[13a]



(IV)

It is clear that related structures may be used to describe the ground state of complexes with similar *o*-quinoid-type bidentate ligands[14] in which sulfur is partly or completely replaced by other elements, *e.g.*, nitrogen. Complexes of this type may be expected to exhibit properties normally associated with aromatic systems. Experimental evidence in support of this view will be presented.

We have also calculated the molecular energy levels for a hypothetical complex $MS_6C_6R_6$ with D_3 symmetry, assuming octahedral metal coordination. The results, which will be reported only briefly, indicate a similar basic orbital sequence. Since the total relative orbital stabilization energy is not drastically different, a telling reason why the prismatic geometry is preferred cannot be given on this basis. Similar coordination geometries are also found in the sulfides MoS_2 and WS_2, as well as in NiAs, indicating that the detailed nature of the ligands actually is not very important. The occurrence of the prismatic coordination in NiAs suggests that it is perhaps the tendency of both sulfur and arsenic to form "bonds"



in a way precursors of polymeric layer structures. It would nevertheless be difficult to dispute the possibility of conformational equilibria $D_{3h} \rightleftarrows D_3$, for instance, in certain oxidation–reduction reactions of complexes $MS_6C_6R_6$. Doubts have been expressed[9] as to whether the trigonal prismatic geometry also extends to the ion $CrS_6C_6(CN)_6{}^{3-}$, which in view of its magnetic properties appears to be a Cr(III) d^3 case in an octahedral ligand field. Attempts in our laboratory to resolve the complex into its optical antipodes have so far met with no success, but it is clear that additional structure determinations are required for a final settlement of these questions.[14c]

Preparation and Properties

The complexes $MS_6C_6R_6$ were prepared by the acyloin–P_4S_{10} method described previously.[15] For the preparation of the parent unsubstituted compounds $MS_6C_6H_6$ (M = V, Mo, W, Re), the disodium salt of *cis*-ethylenedithiol-1,2[16] was allowed to react with various metal salts or oxides in acidic aqueous solution. Although there is evidence for species $CrS_6C_6H_6{}^{2-}$, we so far have been unable to obtain the neutral complex. The reaction of titanium acetylacetonate with $NaS_2C_2H_2$ produced a transient blue solution suggestive of the formation of $TiS_6C_6H_6{}^{2-}$; attempts to isolate it were unsuccessful, however. The complexes $MS_6C_6H_6$ are all well-defined crystalline solids and reasonably stable, except for the vanadium compound which apparently slowly oxidizes in chloroform solution. On heating, metal sulfides and various sulfur-containing products are formed, among which thiophene was identified. In addition, the existence of ions $MS_6C_6H_6{}^{2-}$ was demonstrated by polarographic measurements as well

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[13a] NOTE ADDED IN PROOF. In the meantime structural data on $VS_6C_6Ph_6$ have become available (personal communication, Dr. R. Eisenberg, Columbia University). The compound is also prismatic, but the C–C and C–S distances are 1.40 and 1.69 A, respectively. Using the 27 limiting structures (IV) the calculated bond lengths are 1.39 and 1.69 A, in excellent agreement with the observed values. From the π-bond orders of the MO's in Figure 2 the calculated distances are 1.42 and 1.68 A, respectively. For a complex $ReS_6C_6R_6$ 21 limiting structures can be written; the calculated/observed[6] bond lengths are 1.35/1.34 and 1.75/1.62–1.75 A.

[14] (a) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965); (b) A. L. Balch, F. Röhrscheid, and R. H. Holm, *ibid.*, **87**, 2301 (1965).

[14c] NOTE ADDED IN PROOF. At present the occurrence of prismatic complexes is firmly established for group V, VI, and VII elements. A complex of iron of composition $FeS_6C_6(CF_3)_6$ was reported by A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 3, 814 (1964). We have repeated the preparation exactly as described by these authors and obtained a product with identical properties. Our analyses indicate that it actually is "$FeS_4C_4(CF_3)_4$." A subsequent comparison of the well-resolved X-ray powder patterns proved that the iron complex is isomorphous with the cobalt compound whose structure was determined by J. H. Enemark and W. N. Lipscomb, *ibid.*, **4**, 1729 (1965).

[15] G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **4**, 1615 (1965).

[16] W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964).

as preparation of salts. The polarographic data will not be included here in view of an extensive paper to be published. The unsubstituted complexes thus are analogous to the substituted compounds, except for a somewhat lower thermal stability.

Evidence for Aromatic Character

Owing to the low solubility of the neutral compounds $MS_6C_6H_6$, nmr measurements could not be performed. Salts of the anion $VS_6C_6H_6^-$ are sufficiently soluble in DMSO, however, and the proton signal was observed at τ 0.8 ppm, similarly as in $NiS_4C_4H_4$.[10] The proton resonance is shifted to higher fields, *e.g*, in the ions $ReS_6C_6H_6^-$ and $MoS_6C_6H_6^{2-}$ (τ 2.6 and 2.39 ppm, respectively) but remains well below that in $S_2C_2H_2^{2-}$.[10] The magnetic deshielding thus is similar as in aromatic systems and suggestive of a ring current. To obtain chemical evidence for aromatic character in complexes $MS_6C_6H_6$, a Friedel–Crafts alkylation of $MoS_6C_6H_6$ was attempted. Initial experiments indeed show that alkylation occurs under conditions similar to those employed for benzene derivatives. With *t*-butyl chloride–aluminum chloride, a mixture of isomers, probably mainly consisting of the trialkyl derivative, could be isolated.

$$MoS_6C_6H_6 + 3t\text{-}C_4H_9Cl \xrightarrow{AlCl_3} MoS_6C_6H_3(C_4H_9)_3 + 3HCl$$

Although the nickel complex $NiS_4C_4H_4$ should behave similarly, it is less stable and was found to decompose under analogous conditions of reaction.

Results of Magnetic and Electron Paramagnetic Resonance Measurements

The magnetic moments of species with one unpaired electron are in the right order of magnitude and require no comments. It is important, however, that the ions $CrS_6C_6R_6^{2-}$ ($R = CF_3$, CN) are paramagnetic, suggesting a $S = 1$ ground state[3] consistent with the proposed configuration $\langle 5e' \rangle^2$. The fact that the corresponding species of W and Mo are diamagnetic[3] does not contradict this proposal in view of the various mechanisms which are possible for the removal of the degeneracy of 5e′. That the ions $MoS_6C_6R_6^-$ exhibit a $Mo^{95,97}$ hyperfine splitting (Table II) in addition indicates that the 2a′$_2$ MO is not being occupied in the relevant compounds of the heavier transition metals. The epr spectra of the neutral vanadium complexes and their dianions consist of eight-line signals due to V^{51} ($I = {}^7/_2{}^5$). In all cases the isotropic hyperfine splitting is larger in the dianions than in the neutral compounds as the result of the greater metal character of 5e′ compared to 4e′.[17]

Table II. Results of Paramagnetic Reonance Measurements

Compound	Solvent	$\langle g \rangle$	$\langle A \rangle$, gauss
$VS_6C_6Ph_6^{2-}$ [a]	CH_3CN	1.9811	63.9 ± 0.2 (V^{51}, $I = {}^7/_2$)
$VS_6C_6Ph_6$ [a]	CH_2Cl_2	1.9900	61.5 ± 0.2
$VS_6C_6H_6^{2-}$ [b]	$CHCl_3$	1.981	67.8 ± 0.2
$VS_6C_6H_6$ [b]	$CHCl_3$	1.991	62.6 ± 0.2
$VS_6C_6(CF_3)_6^{2-}$ [a]	CH_2Cl_2	1.9829	62.4 ± 0.2
$V(S_2C_6H_3\text{-}CH_3)_3^{2-}$ [a]	CH_2Cl_2	1.9782	65.8 ± 0.3
$CrS_6C_6(CF_3)_6^-$ [c]	CH_2Cl_2	1.994	16.3 ± 0.5 (Cr^{53}, $I = {}^3/_2$)
$CrS_6C_6Ph_6^-$ [d]	$CHCl_3$	1.996	19.0 ± 0.5 (Cr^{53}, $I = {}^3/_2$)
$MoS_6C_6(CF_3)_6^-$ [c]	CH_2Cl_2	2.0097	12.2 ± 0.5 ($Mo^{95,97}$, $I = {}^5/_2$)
$MoS_6C_6Ph_6^-$ [c]	$CHCl_3$	2.011	11.2 ± 0.4 ($Mo^{95,97}$, $I = {}^5/_2$)
$WS_6C_6(CF_3)_6^-$ [c]	CH_2Cl_2	1.991	
$WS_6C_6Ph_6^-$ [d]	$CHCl_3$	1.992	
$ReS_6C_6Ph_6$ [b,e]	THF	2.015	
$ReS_6C_6H_6$ [b]	Solid	2.010	

[a] Reference 5. [b] Measurements by Dr. E. E. Genser, Emeryville. [c] Reference 3. [d] Reference 4c. [e] Reference 9.

Infrared Spectra

The infrared spectra of complexes $MS_6C_6R_6$ are nearly identical with those of the bis complexes. The observed characteristic frequencies, ω_1–ω_5, of various complexes are listed in Table III. The bands have been assigned[18] previously to the perturbed C═C, C═S, RC(═S)C, and M—S stretching vibrations; in D_{3h} or C_{3h} symmetry ω_1 is of the type A''_2 and ω_2 and ω_3 are expected to consist significantly of the two C═S stretchings E' and A''_2, whereas ω_4 and ω_5 are the E' and A''_2 M—S bands. In principle, the changes in the C═C and C═S bond orders could parallel the infrared frequencies; that is, ω_1 should increase and ω_2 and ω_3 should decrease with increasing z in the species $MS_6C_6R_6^{z-}$ ($z = 0, 1, 2$). For ω_1 and ω_3, this is indeed the case, *e.g.*, for $VS_6C_6H_6^{z-}$ ($z = 0, 1, 2$) as shown in Table III and the data reported in ref 3. The changes of ω_2, on the other hand, evidently can no longer be explained on such a simple basis. In the complexes $MS_6C_6Ph_6$ (M = Cr, Mo, W), ω_1 and ω_2 increase, and ω_3 decreases, indicating an increase in π-backbonding interactions in the complexes of the heavier elements. Similarly, electron back-donation is stronger in $VS_6C_6Ph_6^-$ than in $CrS_6C_6Ph_6$ and is caused by the metal d-orbital expansion in the anions relative to the neutral compounds. The M—S stretching frequencies do not vary significantly with the central metal; the M—S bonds should have considerable double-bond character. In a

Table III. Characteristic Infrared Bands of Various Bis- and Tris(dithiodiketone) Complexes (all in KBr)

M	R	ω_1	ω_2	ω_3	[a]	ω_4	[a]	ω_5
Ni	Ph	1359	1136	882		408		354
Pd	Ph	1342	1136	884		401		352
Pt	Ph	1351	1139	877		403		373
V	Ph	1372	1150	892		406		346
Cr	Ph	1398	1160	891		421		356
V^-	Ph	1428	1165	869	(418)	398		349
Mo	Ph	1400	1165	878		403	(387)	356
W	Ph	1422	1165	872		403		359
Re	Ph	1430	1172	879	(398)	373		359
Re^-	Ph	1481	1030	?	(374)	361		350
Ni	H	1333	1097	872		428		309
V	H	1347	1113	894	(401)	385		361
V^-	H	1416	1118	849	(431)	392		363
V^{2-}	H	1494	952	799		367		350
Mo	H	1402	1121	866		380		354
W	H	1408	1118	854	(430)	369		329
Re	H	1418	1106	856	(422)	338		333
Re^-	H	1450	1099	824	(422)	361	(351)	333

[a] Usually low-intensity bands of uncertain origin or shoulders.

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[17] This is in agreement with the calculated eigenvectors of 4e′ and 5e′. The per cent d and p metal orbital character of 4e′ and 5e′ is 42 and 52% for the MO's of Figure 2.

[18] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 87, 1483 (1965).

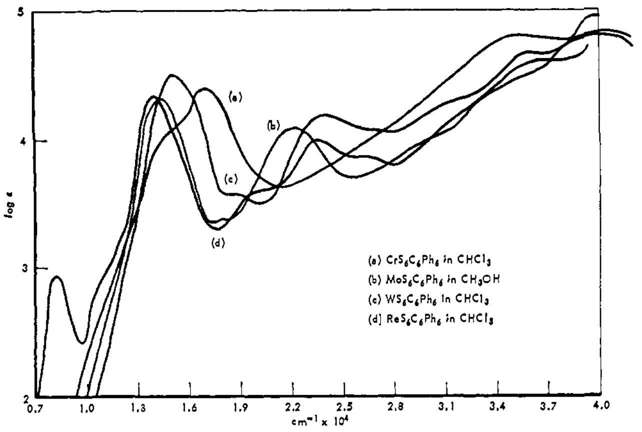

Figure 3. Spectra of four neutral complexes of the type $MS_6C_6Ph_6$.

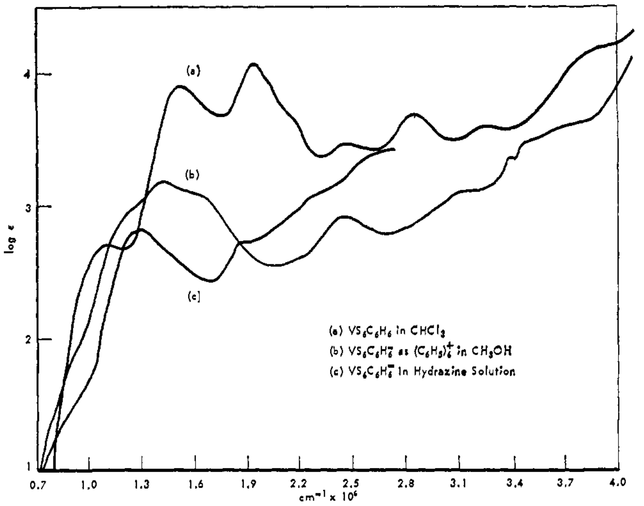

Figure 4. Spectra of $VS_6C_6H_6$ and its anions.

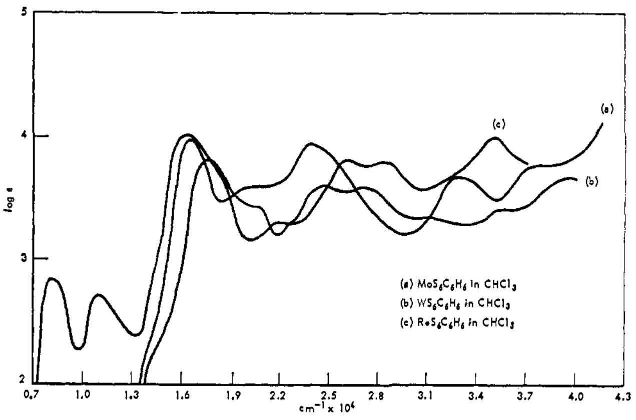

Figure 5. Spectra of three complexes of the type $MS_6C_6H_6$.

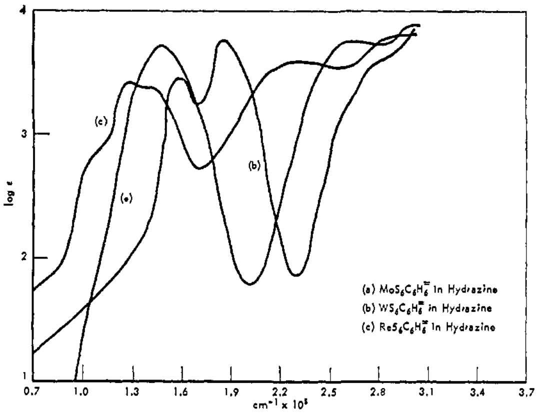

Figure 6. Spectra of three dianions in hydrazine solution.

recently characterized nickel complex[19] of composition $C_{28}H_{22}P_2S_8Ni$ in which the metal-sulfur bonds are more nearly single, the M—S stretchings are at 349 and 323 cm^{-1}, 59 and 31 cm^{-1} lower than in $NiS_4C_4Ph_4$. The infrared data thus in general agree with our model considerations, although a more detailed correlation would require a normal coordinate analysis and extended MO calculations.

Electronic Spectra

We shall now briefly attempt the interpretation of the relatively complicated electronic spectra shown in Figures 3-6. In principle, five types of transitions listed in the order of decreasing intensity are to be expected: $\pi \rightarrow \pi^*$, M → π^*, $n_{=\mathrm{S}:} \rightarrow \pi^*$, $\pi \rightarrow$ M, and d → d. Of these only the first three will be observable and will almost certainly submerge the remaining two. In the closed-shell complexes, the 4e′ → 5e′ transition should be the first allowed low-energy band. It is of the π-π^* type and principally resembles the characteristic intense $2b_{1u} \rightarrow 3b_{2g}$ transitions of the planar d^8 metal bis complexes.[10] Three additional transitions, namely 4e′ → 2a′$_2$, 3a′$_1$ → 5e′, and 3a′$_1$ → 2a′$_2$, should follow closely. The first of these is of the $\pi \rightarrow \pi^*$, and the remaining are of the M → π^* type. These bands should also be relatively intense (log ϵ ~4.0) but not necessarily resolved. The frequency of the M → π^* transitions should depend on the metal and, in general, increase with increasing ionization potential. An intense band in $VS_6C_6H_6^-$ at 18,680 cm^{-1}, for instance, shifts to 24,210 and 24,750 cm^{-1} in $MoS_6C_6H_6$ and $WS_6C_6H_6$, respectively, and therefore is assigned to these metal-ligand charge-transfer transitions (Table IV).

The next bands expected are the $n_{=\mathrm{S}:} \rightarrow$ 5e′ and $n_{=\mathrm{S}:} \rightarrow$ 2a′$_2$, respectively, which both are of the n → π^* type, followed by the $\pi \rightarrow$ M transition 4e′ → 4e″. These bands should be weaker and not necessarily observable. Proceeding systematically according to Figure 2, plausible assignments may be offered for the remaining intense bands. Since the parameters used for the calculation are related to those employed in our previous treatment of $NiS_4C_4H_4$,[10] it is not surprising that there is even a remarkably good quantitative correlation which strongly supports at least the assignments for the most intense $\pi \rightarrow \pi^*$ transitions. The spectra of $VS_6C_6H_6$ and $VS_6C_6Ph_6$ resemble those of the monoanions. In addition, however, a low-energy band assigned to the expected 1a″$_1$ → 4e′ transition is observed. The assignments made in Tables IV and V are furthermore supported by a consistent comparative analysis of the spectra of additional neutral and anionic complexes of various metals with several types of ligands. Term level schemes may be constructed from the observed and assigned transitions which are in accord with the proposed orbital scheme. The spectra of

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(19) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Inorg. Chem.*, 4, 1615 (1965).

Table IV. Expected and Observed Transitions in Complexes $MS_6C_6H_6$[a]

Transition	Type	Calcd (Figure 2), cm^{-1}	Intensity predicted, log ϵ	Obsd (in $CHCl_3$), cm^{-1} (log ϵ) $VS_6C_6H_6$	$MoS_6C_6H_6$	$WS_6C_6H_6$
1a″–4e′[b]	$\pi \rightarrow \pi$	14,911	~3.0	11,620 (2.72)	...[b]	...[b]
4e′–5e′	$\pi \rightarrow \pi$	14,480	4.0	14,990 (3.903)	...[c]	...[c]
4e′–2a′$_2$	$\pi \rightarrow \pi$	14,980	4.0	16,130 sh (3.81)	16,580 (3.98)	17,360 (3.826)
3a′$_1$*–5e′*	$M \rightarrow \pi$	19,280	3.0–4.0	19,460 (4.057)	...[c]	...[c]
3a′$_1$*–2a′*$_2$	$M \rightarrow \pi$	19,740	2.0–3.0	20,700 sh (3.77)	24,210 (3.96)	24,750 (3.616)
S–5e′	$N_{-S}: \rightarrow \pi$	20,471	2.0–3.0	...[c]	20,410 sh (3.59)	20.000 sh (3.45)
S–2a′2	$N_{-S} \rightarrow \pi$	20,931	2.0–3.0	...[c]	...[c]	...[c]
2e″–4e′[b]	$\pi \rightarrow \pi$	19,880	~3.0	24,750 (3.43)?	...[b]	...[b]
4e′–4e″	$\pi \rightarrow M$	25,480	2.0–3.0	...[c]	...[c]	...[c]
1a″$_1$*–5e′*	$\pi \rightarrow \pi$	29,473	~4.0	28,410 (3.67)	27,000 sh (3.5)	27,170 (3.60)
1a″$_1$*–2a′*$_2$	$\pi \rightarrow \pi$	29,925	~4.0	...[c]	...[c]	...[c]
3a′$_1$–4e″	$M \rightarrow M$	30,280	2.0–3.0	...[c]	...[c]	...[a]
S–4e ′	$N_{-S} \rightarrow M$	31,474	~2.0–3.0	...[c]	...[c]	31,250 sh (3.34)
2e″–5e′	$\pi \rightarrow \pi$	34,360	~4.0	32,680 (3.59)	33,000 (3.68)	35,970 sh (3.42)
2e″–2a′$_2$	$\pi \rightarrow \pi$	34,813	~4.0			
4e′–2a″$_1$	$\pi \rightarrow \pi$	38,420	~4.0	39,220 sh (4.18)	38,800 (3.79)	39,200 sh (3.68)
4e″–5e″	$\pi \rightarrow \pi$	39,902	~4.0			

[a] Main transitions in italics. [b] Transitions to be expected in the neutral vanadium complex only. [c] Not observed or not resolved.

Table V. Expected and Observed Transitions in $VS_6C_6H_6^-$ and Isoelectronic Complexes[a]

Transition	Type	Calcd (Figure 2), cm^{-1}	Intensity predicted, log ϵ	Obsd in $CHCl_3$, cm^{-1} $VS_6C_6H_6^-$	$VS_6C_6Ph_6^-$	$CrS_6C_6Ph_6$	$MoS_6C_6Ph_6$	$WS_6C_6Ph_6$
4e′–5e′	$\pi \rightarrow \pi$	14,480	~4.0	15,500 sh (2.95)	14,490 (4.08)	15,000 (4.05)	14,490 (4.32)	15,150 (4.4456)
4e′–2a′$_2$	$\pi \rightarrow \pi$	14,980	~4.0	17,240 (3.165)	16,750 (4.17)	17,200 (4.382)	15,150 (3.412)	18,520 (3.48)
3a′$_1$*–5e′*,	$M \rightarrow \pi$	19,280	~3.0–4.0	18,680 (3.086)	18,380 (4.02)	...[b]	22,270 (4.087)	23,980 (4.0682)
3a′$_1$*–2a′*$_2$	$M \rightarrow \pi$	19,740	~3.0–4.0					
S–5e′	$N_{-S} \rightarrow \pi$	20,471	~2.0–3.0	...[b]	...[b]	...[b]	...[b]	...[b]
S–2a′$_2$	$N_{-S}: \rightarrow \pi$	20,931	2.0–3.0	...[b]	...[b]	...[b]	...[b]	...[b]
4e′–4e″	$\pi \rightarrow M$	25,480	2.0–3.0	...[b]	...[b]	23,250 sh (3.60)	...[b]	...[b]
1a″$_1$*–5e′*,	$\pi \rightarrow \pi$	29,473	~4.0	27,500 (3.44)	30,760 sh	...[b]	31,440 sh (4.065)	...[b]
1a″$_1$*–2a′*$_2$	$\pi \rightarrow \pi$	29,925	~4.0					
3a′$_1$—4e″	$M \rightarrow M$	30,280	2.0–3.0	...[b]	...[b]	...[b]	...[b]	...[b]
S–4e″	$N_{-S}: \rightarrow M$	31,474	2.0–3.0	...[b]	...[b]	...[b]	...[b]	...[b]
2e″–5e′,	$\pi \rightarrow \pi$	34,360	~4.0	33,900 (3.53)	33,500 sh (4.50)	35,200 (4.80)	34,960 sh (4.395)	33,330 (4.250)
2e″–2a′$_2$	$\pi \rightarrow \pi$	34,813	~4.0					
4e′–2a″$_1$,	$\pi \rightarrow \pi$	38,420	~4.0	40,820 (3.611)	42,010 (4.806)	40,700 (4.805)	40,000 (4.79)	40,000 (4.93)
4e″–5e″	$\pi \rightarrow \pi$	39,902	~4.0					

[a] Main transitions in italics. [b] Not observed or not resolved.

the anionic species $MS_6C_6R_6^{2-}$ (M = *e.g.*, Cr, Mo, W) are generally less well resolved, but all show an intense broad low-energy band arising from transitions from the 4e′ MO to the partly filled 5e′ shell, or to 2a′$_2$. The spectrum of $ReS_6C_6H_6$ is similar to that of $WS_6C_6H_6$ but contains two additional low-energy bands arising from the transitions of the electron in 5e′ into the next higher MO's. The spectrum of the ion $CrS_6C_6(CN)_6^{3-}$, on the other hand, differs completely and lacks intense low-energy transitions. This may be taken as good indication that in this case the ligands are present as "conventional" dithiolate dianions which do not have chromophoric properties. It thus may be concluded that all chemical properties as well as the electronic and infrared spectra of the complexes $MS_6C_6R_6^{z-}$ correlate with the proposed "delocalized" model of bonding, providing a telling argument for the correctness of our description.

Experimental Section[20]

Preparation of the Complexes. A. Substituted Complexes of Mo, W, and Re. To a "thioester solution" (obtained by refluxing 100 g of the acyloin, *e.g.*, benzoin, with 100 g of P_4S_{10} in 500 ml of dioxane) was added 30 g of Na_2MoO_4 or Na_2WO_4, or 3.0 g of Re_2O_7 or $ReCl_5$, respectively, in 150 ml of 1 *N* HCl. The mixture was vigorously stirred and heated on a steam bath for 2 hr. After cooling, the lower layer was evaporated *in vacuo* and the oily, green residue was redissolved in 500 ml of benzene. The solution was treated with water in a separatory funnel until the washings became colorless. After removal of the last portion of water, the benzene solution was extracted with 50 ml of 95% hydrazine solution. The complex was converted into the anionic form, which was soluble in the hydrazine solution. The supernatant benzene layer, now yellow, was discarded. For further purification the hydrazine solution was washed twice with 100-ml portions of benzene. Subsequently, 500 ml of benzene was added and the two-phase system was carefully acidified with concentrated hydrochloric acid. The benzene layer containing the complex was washed with water, dried over Na_2SO_4, and evaporated to dryness. The crude complex was obtained by addition of acetone and was finally recrystallized from a mixture of methylene chloride and acetone.

B. $CrS_6C_6Ph_6$. To the "thioester solution" (obtained form 50 g of benzoin and 50 g of P_4S_{10} in 500 ml of xylene), 100 ml of 95% hydrazine solution was added. The mixture was shaken in a separatory funnel for 10 min. To the hydrazine solution 50 g of $CrCl_3 \cdot 6H_2O$, dissolved in 100 ml of water, was added. The mixture was agitated and heated on a steam bath for 30 min. After cooling, the warm solution was covered with 250 ml of benzene and carefully acidified with 1:1 HCl. The benzene layer subsequently turned blue and after separation from the aqueous phase was washed with water, dried, and evaporated *in vacuo*. The crude was recrystallized at first from a mixture of methylene chloride and *n*-hexane and finally from chloroform–ethanol. Only moderate

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(20) In cooperation with W. Heinrich and H. W. Finck, both at University of Munich, Germany.

Table VI. Analyses of Neutral Complexes

	Calcd (Found), %					
Compound	C	H	S	Metal	Mol wt	Mp, °C
$VS_6C_6Ph_6$	64.8	3.9	24.7	6.5	778.0	252 dec
	(64.8)	(4.1)	(24.4)	(6.6)		
$VS_6C_6H_6$	22.4	1.9	59.9	15.9	321.5	~95 dec
	(22.8)	(2.3)	(60.2)	(16.2)		
$MoS_6C_6Ph_6$	61.2	3.6	23.2	11.6	823.0	>360
	(61.0)	(3.6)	(23.1)	(11.6)	(810)	
$MoS_6C_6(CH_3)_6$	32.0	4.0	42.7	21.2	450.6	>360
	(31.6)	(4.0)	(41.9)	(21.4)		
$MoS_6C_6(p\text{-}C_6H_4CH_3)_6$	62.8	4.4	18.2	10.9	907.2	306 dec
	(62.4)	(4.1)	(18.6)	(10.5)	(900)	
$MoS_6C_6H_6$	19.6	1.7	52.5	26.2	366.5	~76 dec
	(20.0)	(1.6)	(53.0)	(25.9)		
$WS_6C_6Ph_6$	55.4	3.3	21.1	20.2	911.0	>360
	(55.3)	(3.1)	(20.6)	(20.9)		
$WS_6C_6(CH_3)_6$	26.8	3.4	35.7	34.1	538.6	360
	(27.4)	(3.6)	(35.5)	(34.0)		
$WS_6C_6H_6$	15.9	1.3	42.3	40.7	454.4	~103 dec
	(15.7)	(1.3)	(43.0)	(40.0)		
$WS_6C_6(p\text{-}C_6H_4CH_3)_6$	57.0	4.0	16.5	19.0	995.2	312 dec
	(56.2)	(4.0)	(16.2)	(19.8)		
$WS_6C_6(p\text{-}C_6H_4OCH_3)_6$	54.5	3.7	15.5	17.7	1091.2	315 dec
	(54.4)	(3.6)	(15.3)	(18.0)		
$CrS_6C_6Ph_6$	64.7	3.9	24.7	6.6	779.1	241 dec
	(64.7)	(4.3)	(24.5)	(6.7)	(825)	
$ReS_6C_6H_6$	15.8	1.3	42.2	40.7	456.8	~104 dec
	(15.7)	(1.5)	(42.5)	(40.5)		
$ReS_6C_6Ph_6$	55.23	3.3	21.1	20.4	913.4	>340
	(54.9)	(3.1)	(20.6)	(19.9)		

Table VII. Analyses of Salts of Anionic Species

	Calcd (Found), %						
Compound	C	H	S	M	As	N	Mp, °C
$N(C_2H_5)_4{}^+VS_6C_6Ph_6{}^-$	68.5	5.7	18.3	5.9		1.6	245 dec
	(68.0)	(5.4)		(5.8)		(1.6)	
$[N(C_2H_5)_4{}^+]_2VS_6C_6Ph_6{}^{2-}$	69.2	7.0	16.0	5.0		2.8	235 dec
	(68.7)	(7.0)				(2.9)	
$AsPh_4{}^+VS_6C_6H_6{}^-$	52.9	3.9	23.8	7.6	11.2	11.0	245 dec
	(52.7)	(4.2)	(24.2)				
$N(C_2H_5)_4{}^+VS_6C_6(p\text{-}C_6H_4CH_3)_6{}^-$	69.6	6.2	17.2	5.5		1.5	240 dec
	(69.9)	(5.9)	(16.9)			(1.8)	
$N(C_2H_5)_4{}^+VS_6C_6(p\text{-}C_6H_4OCH_3)_6{}^-$	65.0	5.9	16.1	5.1		1.4	203 dec
	(65.2)	(5.8)	(16.2)				
$[N(C_2H_5)_4{}^+]_2MoS_6C_6Ph_6{}^{2-}$	66.2	6.7	15.2	9.1		2.7	235 dec
	(65.8)	(6.3)				(2.4)	
$N(C_2H_5)_4{}^+ReS_6C_6(p\text{-}C_6H_4CH_3)_6{}^-$	58.7	5.7	17.4	16.9		1.3	262
	(58.5)	(5.8)	(17.2)			(1.5)	
$N(C_2H_5)_4{}^+ReS_6C_6Ph_6{}^-$	57.5	4.7	18.4			1.3	293–297 dec
	(56.8)	(4.4)				(1.7)	
$As(C_6H_5)_4{}^+ReS_6C_6H_6{}^-$	38.5	3.3	24.7		9.6		151 dec
	(37.9)	(3.4)	(25.0)				

yields (about 1 g of pure $CrS_6C_6Ph_6$) were usually achieved. The complex forms dark red crystals, mp 291° dec, which are isomorphous with the analogous compounds of V, Mo, and W.

C. $VS_6C_6Ph_6$. To a hydrazine solution of the thioester obtained as described in part B, a solution of 15 g of vanadyl acetylacetonate and 10 g of $N(C_2H_5)_4Br$ in 120 ml of methanol was added. The solution was carefully acidified with 1:1 hydrochloric acid. On standing overnight the salt of the complex monoanion, $N(C_2H_5)_4{}^+VS_6C_6Ph_6{}^-$ precipitated and was collected on a filter. The salt is dissolved in methylene chloride and 1 equiv of I_2 was added to obtain the neutral complex. After 5 min of agitation, the solution was poured into 1 l. of ethanol. The crystals of the complex were collected and recrystallized by extraction from methylene chloride.

D. Tris(dithioglyoxal) Complexes of Mo, W, and Re. To a slurry of 10 g of Na_2WO_4 in 200 ml of 30% HCl, 10 g of the sodium salt of *cis*-dimercaptoethylene[16] was added in small portions with simultaneous stirring. The resulting dark precipitate was filtered off and washed with water, dried, and extracted with methylene chloride. After cooling, the complex crystallized and was collected by filtration. It was recrystallized from methylene chloride. Similar procedures led to the complexes of Mo and Re, using Na_2MoO_4, Re_2O_7, or $ReCl_5$ as the inorganic starting materials.

E. $VS_6C_6H_6$. Vanadyl acetylacetonate (10 g) and 10 g of $Na_2S_2C_2H_2$ were suspended in 100 ml of methanol and stirred for about 60 min. The reaction mixture was acidified with concentrated hydrochloric acid. Dark crystals of the complex precipitated and were recrystallized by extraction from methylene chloride.

F. Salts of the Anionic Species. For the preparation of these compounds similar methods as outlined in the literature[3,5] were adopted.

Analyses of the neutral complexes and salts of the anionic species are shown in Tables VI and VII, respectively.

Friedel–Crafts Alkylation of $MoS_6C_6H_6$. Tris(dithioglyoxal)-molybdenum (110 mg) was dissolved in 80 ml of CS_2. After the addition of 1 ml of freshly distilled *t*-butyl chloride and of a mixture of 1 g of anhydrous $ZnCl_2$ with 0.5 g of $AlCl_3$, the solution turned brown. A brown oil separated and was subsequently redissolved by adding 50 ml of methanol. After 30 min the color of the reaction solution was green again. Benzene (50 ml) was added and the solution extracted twice with water. The organic phase was dried with Na_2SO_4 and evaporated *in vacuo*. The product was chromatographed on a column of silica gel in isooctane, and the green zone separated. The residue, a mixture of incompletely substituted complexes, crystallized slowly. After drying *in vacuo* it melted between 30 and 110° and decomposed at 230°. *Anal.* Calcd for $MS_6C_6R_3H_3$: C, 25.4; H, 7.0. Found: C, 25.8; H, 7.4. The presence of *t*-butyl groups was unambiguously demonstrated by nmr measurements and residual protons (peak maxima at τ 8.57 and 0.8, respectively, with the intensity ratio of approximately 9:1). The bands in the visible spectrum with maxima or shoulders at 619 (ϵ 15,000), 510 (sh) (4750), and 420 mμ (13,500), respectively, are between those observed for $MoS_6C_6H_6$ (Table IV) and $MoS_6C_6(CH_3)_6$ (λ_{max} (observed) 640 (ϵ 13,550), 513 (3110), and 435 mμ (10,750)). In the infrared spectrum (KBr), the perturbed C=C stretch is split into two bands at 1360 and 1372 cm^{-1}, and ω_2 and ω_3 are observed at 1110 and 875 cm^{-1}, respectively.

Appendix

The orbital transformation scheme and the overlap integrals used for the calculation of the orbital diagram shown in Figure 2 are given in Table VIII. The MO energies and coefficients for the prismatic ligand system were obtained by solving the Hückel matrix (neglecting mutual overlap) with $\alpha_S = \alpha_C + 0.2\beta$ and $\beta_{C=S} = \beta_{C=C}$, with $\beta = -3.0$ ev, and with the absolute value of $\alpha_S = -10.3$ ev, corresponding to the ground-state ionization potential of sulfur (configuration $3p^4$). The value of β', describing the interaction of adjacent $3p_\pi$ orbitals of sulfur in the prism, was put at +0.4 ev. The Coulomb terms of the 3d orbitals of vanadium and the $3sp^2$ orbitals of sulfur were both assumed to be -10.3 ev, a value about midway between the first and second ionization potentials of vanadium. The 4s and 4p orbitals of the metal were placed 0.8 and 3.3 ev above 3d, and the presence of 3d orbitals of sulfur was neglected. Trial calculations were also carried out by varying the metal Coulomb terms about ±1.5 ev around the adopted values. The off-diagonal elements were estimated assuming $H_{ij} = kG_{ij}$, using the same proportionality factor ($G_{ij} = 0.135 \equiv 1$ ev) as in the previous calculation.[10] With these data, the numerical results from which Figure 2 was constructed may be reproduced and, therefore, they are not presented in detail.

Table VIII. Orbital Transformation Scheme for D_{3h}^- Symmetry, and Group-Overlap Integrals Used for the Calculation

Irreducible representation	Metal function	Ligand function	G_{ij}[a]
A'_1	4s	$(1/\sqrt{6})(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$	0.966
	$3d_{z^2}$	$(1/\sqrt{6})(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$	0.462
E'	$3d_{x^2-y^2}$	$(1/\sqrt{12})(2\sigma_1 - \sigma_2 - \sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6)$	0.492
	$3d_{xy}$	$(1/2)(\sigma_2 - \sigma_3 + \sigma_5 - \sigma_6)$	0.492
	$4p_x$	$(1/\sqrt{12})(2\sigma_1 - \sigma_2 - \sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6)$	0.501
	$4p_y$	$(1/2)(\sigma_2 - \sigma_3 + \sigma_5 - \sigma_6)$	0.501
	$3d_{xy}$	$(1/\sqrt{12})(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6)$, (1e′)	0.210
	$3d_{xy}$	$(1/\sqrt{12})(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6)$, (2e′)	0.269
	$3d_{x^2-y^2}$	$(1/2)(\pi_2 - \pi_3 + \pi_5 - \pi_6)$, (1e′)	0.210
	$3d_{x^2-y^2}$	$(1/2)(\pi_2 - \pi_3 + \pi_5 - \pi_6)$, (2e′)	0.269
	$4p_y$	$(1/\sqrt{12})(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6)$, (1e′)	0.086
	$4p_y$	$(1/\sqrt{12})(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6)$, (2e′)	0.113
	$4p_x$	$(1/2)(\pi_2 - \pi_3 + \pi_5 - \pi_6)$, (1e′)	0.086
	$4p_x$	$(1/2)(\pi_2 - \pi_3 + \pi_5 - \pi_6)$, (2e′)	0.113
A''_1	$4p_z$	$(1/\sqrt{6})(\sigma_1 + \sigma_2 + \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$	1.105
E''	$3d_{xz}$	$(1/\sqrt{12})(2\sigma_1 - \sigma_2 - \sigma_3 - 2\sigma_4 + \sigma_5 + \sigma_6)$	0.559
	$3d_{yz}$	$(1/2)(\sigma_2 - \sigma_3 - \sigma_5 + \sigma_6)$	0.559
	$3d_{xz}$	$(1/2)(\pi_2 - \pi_3 - \pi_5 + \pi_6)$, (1e″)	0.282
	$3d_{xz}$	$(1/2)(\pi_2 - \pi_3 - \pi_5 + \pi_6)$, (2e″)	0.154
	$3d_{yz}$	$(1/\sqrt{12})(2\pi_1 - \pi_2 - \pi_3 - 2\pi_4 + \pi_5 + \pi_6)$, (1e″)	0.282
	$3d_{yz}$	$(1/\sqrt{12})(2\pi_1 - \pi_2 - \pi_3 - 2\pi_4 + \pi_5 + \pi_6)$, (2e″)	0.154

[a] Calculated, using Slater orbitals for S and V, with σ 6.7 and τ 0.118 (R_{V-S} = 2.23 A). Atomic overlap integrals or interactions with 4s and 4p were taken from L. Leifer, F. A. Cotton, and J. R. Leto (*J. Chem. Phys.*, **28**, 364 (1958)), and S($3p_\pi$, $4p_\pi$) was extrapolated. The G_{ij} values are not corrected for ligand–ligand overlap.