sim)$_2$,[23] and Ni(N-isopropyl-3-methylsim)$_2$];[18] for tetrahedrally coordinated Ni(II) the bite is 2.84 Å [Ni(N-isopropylsim)$_2$];[17] and for octahedrally coordinated Ni(II) the bite is 2.91 [Ni(sal)$_2$·2H$_2$O],[42] 2.91 [Ni(acac)$_2$·2H$_2$O],[4] and 3.05 Å [Ni(acac)$_2$].[43] If the difference in coordination configuration is ignored, as in Figure 3, the acac bite distance of 2.584 Å obtained by extrapolation of r/Q to 0 in Figure 3 is in fair agreement with the salicylic acid bite distance of 2.620 Å around the hydrogen ion.[38]

Acknowledgment. This work was supported in part by the U. S. Public Health Service under Research Grant GM-10842, and in part by the U. S. National Science Foundation.

(42) J. M. Stewart, E. C. Lingafelter, and J. D. Breazeale, *Acta Cryst.*, **14**, 888 (1961).
(43) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

Characterization and Electronic Structures of Six-Coordinate Trigonal-Prismatic Complexes

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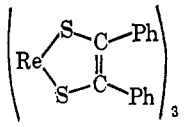
Abstract: The physical properties of the tris(*cis*-stilbenedithiolato) complexes of Mo, W, and Re are described in detail. The three neutral $M(S_2C_2Ph_2)_3$ complexes exhibit MS_6 trigonal-prismatic coordination in the solid state and in solution. The V and Cr complexes in this series are isomorphous with the Mo complex and thus very probably are also trigonal prismatic in the solid state. The syntheses and properties of the tris(toluene-3,4-dithiolato) and tris(benzene-1,2-dithiolato) complexes of Mo, W, and Re are reported. In particular, those properties which have been found to be characteristic of trigonal-prismatic coordination are discussed in detail. It is concluded that at least 12 different well-authenticated complexes, spanning five metals and four different ligands, exhibit a six-coordinate trigonal-prismatic structure. In addition, the existence of numerous other complexes, related to the above by reversible one-electron transfers, is established by polarography. The electronic spectra of all the neutral complexes are discussed in terms of a molecular orbital model of energy levels. The molecular orbital bonding scheme is found to be consistent with the considerable electronic spectral and polarographic data.

Six-coordinate complexes of bidentate, unsaturated sulfur-donor ligands have been the subject of extensive current investigations.[2–7] These studies have recently assumed a new and quite fundamental significance in transition metal chemistry. The structure of $Re(S_2C_2Ph_2)_3$ (I) has been solved by X-ray diffraction analysis[8] and has been found to contain a near-perfect trigonal-prismatic array of sulfur-donor atoms. In addition, this first exception[9] to the maxim "six-coordination equals octahedral complex" has been shown not to stand alone. Thus, we have presented evidence that the complexes $W(S_2C_2Ph_2)_3$[8,10] and $Re(tdt)_3$[10] (II) also have trigonal-prismatic structures.



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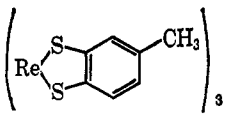

$Re(tdt)_3$

II

In addition, a very recent X-ray study by Smith and co-workers has shown that the $Mo(S_2C_2H_2)_3$ complex is trigonal prismatic.[11] Furthermore, I has been shown to retain trigonal-prismatic coordination in liquid solutions.[10]

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(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) C. H. Langford, E. Billig, S. I. Shupak, and H. B. Gray, *ibid.*, **86**, 2958 (1964).
(5) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *ibid.*, **86**, 4199 (1964).
(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965).
(7) (a) G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964), reported that $S_2C_2Ph_2$ forms bis planar complexes with Os, Ru, Cr, Mo, W, Re, and V. This has since been shown to be in error as these are all tris complexes. See ref 5, 6, and G. N. Schrauzer, H. W. Finck, and V. Mayweg, *Angew. Chem.*, **76**, 715 (1964). (b) The $Mo(tdt)_3$ complex has apparently been prepared previously by T. W. Gilbert, Jr., and E. B. Sandell, *J. Am. Chem. Soc.*, **82**, 1087 (1960). However, an accurate analysis was not obtained and the compound was thus not fully characterized.
(8) R. Eisenberg and J. A. Ibers, *ibid.*, **87**, 3776 (1965); *Inorg. Chem.*, **5**, 411 (1966).
(9) This is the first reported trigonal-prismatic molecular complex. Trigonal-prismatic coordination was first reported [R. G. Dickinson and L. Pauling, *J. Am. Chem. Soc.*, **45**, 1466 (1923)] for the infinitely extended lattices of molybdenite (MoS_2) and tungstite (WS_2). These are not molecular complexes and, although some of the factors stabilizing these systems and the molecular trigonal prisms discussed above may be similar, it is also probable that other factors such as metal–metal interaction and crystal packing requirements are effective in stabilizing trigonal-prismatic coordination in MoS_2 and WS_2.
(10) E. I. Stiefel and H. B. Gray, *ibid.*, **87**, 4012 (1965).
(11) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **87**, 5798 (1965).

In this paper we report in detail the physical properties of $M(S_2C_2Ph_2)_3$ and $M(tdt)_3$ complexes, with M = Mo, W, and Re. We also report the new complexes $M(bdt)_3$ (M = Mo, W, and Re; (bdt) is benzene-1,2-dithiolate) and the new complex $W(S_2C_2(CH_3)_2)_3$. The electronic spectral properties of the complexes are stressed as they apparently provide a probe for the electronic structure which can in turn definitively identify the coordination geometry. We present what we believe is conclusive evidence that at least 12 different six-coordinate complexes, spanning five different metals and four different ligands, possess trigonal-prismatic, rather than octahedral, coordination. In addition, the existence of complexes simply related to the above by reversible one-electron-transfer reactions is established polarographically. Finally, the problem of assigning an oxidation state to the central metal in these complexes is discussed.

Experimental Section

Chemicals. Toluene-3,4-dithiol was obtained from Eastman Organic Chemicals and was used without further purification. Benzene-1,2-dithiol was prepared by the method of Ferretti;[12] a freshly prepared sample was used in all reactions. It was not, however, found to be necessary to distil the product prior to use. The compounds WCl_6, $ReCl_5$, and $MoCl_5$ were obtained from Alfa Inorganics. Hexane and pentane were purified by repeated washing with H_2SO_4, followed by washing with a salt solution and distillation from $CaCl_2$. Hexane and pentane were stored over $CaCl_2$ and filtered before use. All other chemicals were of reagent grade and were used without further purification.

Preparation of Compounds. $Re(S_2C_2Ph_2)_3$. Benzoin (20 g) and P_4S_{10} (20 g) were partially dissolved in 300 ml of xylene. The reaction mixture was refluxed for 3 hr and then cooled; the solution was filtered. Rhenium pentachloride, $ReCl_5$ (2.05 g), was dissolved in EtOH (the nature of this solution is not certain since HCl appears to be given off), and the solution was filtered and added rapidly to the red-orange xylene solution. The resulting solution turned dark brown and was heated for 4 hr on a steam bath, during which time an intense green color appeared. The volume was reduced by vacuum evaporation to *ca.* 50 ml and 300 ml of hexane was added. The solution was allowed to stand overnight, during which time a black substance precipitated. The solution was filtered, and the precipitate was collected and redissolved in CH_2Cl_2. The resulting solution was filtered and evaporated to small volume, whereupon shiny black-green crystals precipitated. These crystals were collected, washed with pentane, and dried under vacuum for 4 hr. The yield was 0.8 g; an attempt was not made to optimize the yield by altering the reaction conditions.

$W(S_2C_2Ph_2)_3$ and $Mo(S_2C_2Ph_2)_3$. These complexes were prepared by a method similar to that for $Re(S_2C_2Ph_2)_3$, using WCl_6 and $MoCl_5$ as starting materials.

$W[S_2C_2(CH_3)_2]_3$. This complex was made using a procedure identical with that for $Re(S_2C_2Ph_2)_3$, using 3-hydroxy-2-butanone (acetoin) instead of benzoin as starting material.

$Re(tdt)_3$. Rhenium pentachloride, $ReCl_5$ (2.4 g, 0.0065 mole), was partially dissolved in 600 ml of CCl_4. The resulting solution-suspension, used without filtration, was added to a 50-ml CCl_4 solution of toluene-3,4-dithiol (3.1 g, 0.020 mole). The mixture turned deep green and was then refluxed for 3 hr, during which time HCl was evolved. The solution was cooled, filtered, and reduced in volume to 50 ml. To this solution was added 750 ml of dry hexane. On standing overnight a precipitate formed. The precipitate was filtered, collected, and redissolved in CH_2Cl_2. This solution was filtered, and the complex was reprecipitated by addition of pentane. The resultant precipitate was washed with 100 ml of pentane and dried under vacuum for 4 hr.

$W(tdt)_3$. Tungsten hexachloride, WCl_6 (4.25 g, 0.00107 mole), was dissolved in 750 ml of CCl_4 and filtered under nitrogen. The filtrate was then added to a solution of toluene-3,4-dithiol (5.0 g, 0.0032 mole) dissolved in about 40 ml of CCl_4, whereupon a deep blue-green color appeared. This solution was refluxed under dry N_2 for 3 hr and allowed to cool to room temperature. The solution was filtered and the filtrate concentrated to 50 ml and then poured into 200 ml of ice-cold *n*-pentane. After several minutes a precipitate formed and was collected, washed with 50 ml of *n*-pentane, and vacuum dried to give 3.9 g of a blue-green powder. The complex was recrystallized (actually reprecipitated) by dissolving it in 200 ml of hot CH_2Cl_2, reducing the volume to 30 ml on a steam bath, and adding the solution to 200 ml of cold *n*-pentane. The resulting precipitate was collected, washed with *n*-pentane, and vacuum dried for several hours.

$Mo(tdt)_3$. Molybdenum pentachloride, $MoCl_5$ (3.8 g, 0.0014 mole), was weighed under dry nitrogen and dissolved in 500 ml of CCl_4 to give a bright red solution. The red solution was filtered and added steadily over a period of 2 hr to a solution of toluene-3,4-dithiol (6.5 g, 0.0042 mole) in 100 ml of CCl_4, during which time a deep green color appeared. The resultant solution was refluxed for 4–5 hr, allowed to cool, and then vacuum evaporated to 150 ml. This solution was added to 750 ml of cold (dried) *n*-pentane. A voluminous green precipitate formed which was collected and washed with 180 ml of cold *n*-pentane. The complex was purified by dissolving in 5:1 cyclohexane–CH_2Cl_2 mixture and chromatographing the solution over silica gel. The eluent solution was evaporated to dryness and the resultant powder dissolved in CH_2Cl_2 and reprecipitated by adding dry *n*-pentane. The green powder was collected and dried *in vacuo* for 6 hr. The yield was 3.6 g (41%) of pure $Mo(tdt)_3$.

$M(bdt)_3$ Complexes. The $M(bdt)_3$ complexes of Re, W, and Mo were prepared by methods analogous to those for the respective $M(tdt)_3$ complexes. However, it was not found necessary to chromatograph the $Mo(bdt)_3$ complex; crystallization occurred readily in this case.

$[(n\text{-}C_4H_9)_4N][CrO(tdt)_2]$. Hydrated chromic chloride, $CrCl_3 \cdot 6H_2O$ (1.8 g, 0.00067 mole), was dissolved in 80 ml of absolute ethanol on a steam bath under nitrogen. Toluene-3,4-dithiol (3.1 g, 0.020 mole) dissolved in 50 ml of absolute ethanol was added to a solution of potassium ethoxide, freshly prepared by treating 1.56 g of potassium metal with 80 ml of absolute ethanol. The resulting solution of the potassium salt of toluene-3,4-dithiolate was added to the ethanolic chromic chloride solution on a steam bath. Tetrabutylammonium bromide (5 g) in absolute ethanol was added and the solution was refluxed for 1 hr to give a light green, misty solution. The solution was allowed to cool to room temperature, and dry oxygen was bubbled through the solution for about 2 hr, producing a color change from green to deep purple and the gradual formation of a purple precipitate. The precipitate was collected and washed with 200 ml of absolute ethanol. The crude precipitate was taken up in methylene chloride and precipitated by addition of absolute ethanol. The product was finally recrystallized from CH_2Cl_2–ether.

Physical Measurements. Electronic spectra were measured by means of a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used throughout. Solid spectra were obtained with the same instrument by using Nujol mulls supported on filter paper. Infrared spectra were obtained with a Perkin-Elmer Model 441 or Model 137 spectrophotometer using the KBr wafer or Nujol mull technique. Static susceptibility measurements were made at ambient room temperature by the Gouy method, using $Hg[Co(SCN)_4]$ as a calibrant. Polarographic measurements were made in DMF solution with a dropping mercury or a rotating platinum electrode using an electronic polarograph described elsewhere.[13] Triangular wave chromoamperometry (oscillopolarography) was utilized, with a platinum electrode serving an indicator electrode. Silver–silver perchlorate was used as the reference electrode [$Ag|AgClO_4$ (0.1 *M*), $[(n\text{-}C_3H_7)_4N]ClO_4$ (0.1 *M*)]. Solutions were approximately 0.001 *M* in complex and 0.1 *M* in tetra-*n*-propylammonium perchlorate. Electron spin resonance spectra were recorded at room temperature using a Varian V4502 spectrometer employing 100-kc/sec field modulation. The klystron frequency was measured directly from a wave meter, and the field was measured from a previously calibrated field dial. Low-temperature spectra were measured at 77°K using a Varian V4546 liquid nitrogen accessory.

Results

The $Re(S_2C_2Ph_2)_3$ complex (I) was prepared by the general method of Schrauzer, *et al.*[7,14] The prepara-

(12) A. Ferretti, *Org. Syn.*, **42**, 54 (1962).

(13) M. J. Kelley, J. D. Fisher, and K. C. Jones, *Anal. Chem.*, **31**, 1475 (1959); **32**, 1262 (1960).

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

Table I. Analytical Data and Physical Properties of ML_3 Complexes[a]

Complex	Color	Mp,[b] °C	% C Calcd	% C Found	% H Calcd	% H Found	% S Calcd	% S Found	% N Calcd	% N Found
$Re(S_2C_2Ph_2)_3$	Green	>250	55.24	55.26	3.31	3.21	21.07	20.71		
$Re(tdt)_3$	Green	188–192 dec	38.87	38.55	2.80	2.92	29.65	29.18		
$Re(bdt)_3$	Green	232	35.63	36.43	1.99	2.03	31.70	31.69		
$W(tdt)_3$	Blue	160 dec	39.01	39.20	2.81	2.93	29.75	29.97		
$W(bdt)_3$	Blue	>250	35.76	35.93	2.00	2.05	31.82	31.90		
$W(S_2C_2(CH_3)_2)_3$	Blue-green	>250	26.77	26.56	3.37	3.31	35.73	35.36		
$Mo(tdt)_3$	Green	201–204 dec	45.15	44.83	3.25	3.25	34.43	34.76		
$Mo(bdt)_3$	Green	>250	41.85	41.69	2.34	2.41	37.24	36.99		
$[(n\text{-}C_4H_9)_4N][CrO(tdt)_2]$	Purple	181–182	58.21	57.70	7.82	7.83	20.72	20.53	2.26	2.38

[a] Analyses performed by Galbraith Laboratories, Inc. [b] Uncorrected.

tion is described in detail in the Experimental Section since a full description of the preparation of this complex has not yet been published. The $Mo(S_2C_2Ph_2)_3$ and $W(S_2C_2Ph_2)_3$ complexes were also prepared by this method. For the $W(S_2C_2(CH_3)_2)_3$ complex, the same method was used, but with acetoin instead of benzoin. These complexes are crystalline and are dark blue or dark green in the solid. They are soluble and stable indefinitely in nonpolar organic solvents such as CCl_4, $CHCl_3$, CH_2Cl_2, benzene, and dioxane, giving intensely green to blue-green solutions. The complexes are also soluble in DMF and DMSO, but a slow and as yet uncharacterized reaction occurs.

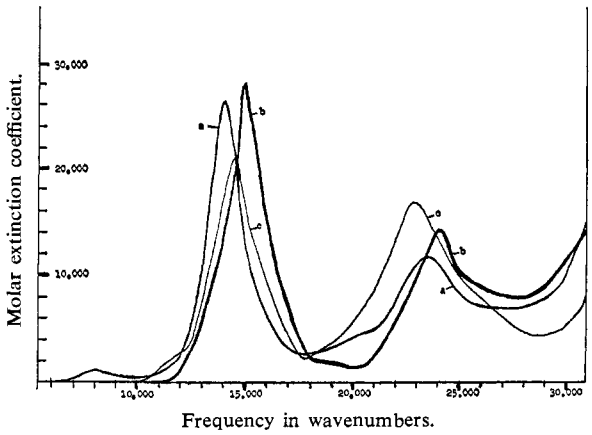

Figure 1. Electronic spectra of selected $M(tdt)_3$ and $M(S_2C_2Ph_2)_3$ complexes: (a) $Re(S_2C_2Ph_2)_3$, (b) $W(S_2C_2Ph_2)_3$, and (c) $Mo(tdt)_3$.

The $M(tdt)_3$ complexes (M = Mo, W, Re) were formed by refluxing the metal chlorides ($MoCl_5$, WCl_6, or $ReCl_5$) in CCl_4[10] with toluene-3,4-dithiol in slight excess of a 3:1 mole ratio. In each case, hydrogen chloride was given off and the complex formed rapidly in good yield. The $M(tdt)_3$ complexes possess approximately the same solubility properties as the $M(S_2C_2Ph_2)_3$ complexes, and the colors of complexes of the same metal in the two series are almost identical. The $M(tdt)_3$ complexes do not crystallize readily and this makes purification somewhat difficult. The fact that they do not crystallize is most probably due to the unsymmetrical nature of the tdt ligand and the fact that there are two possible orientations of the three methyl groups in the complex (in either trigonal-prismatic or octahedral coordination). This may affect the crystallization of the complexes, but in all probability will not affect the coordination geometry and the physical properties of interest. To test this hypothesis, complexes of the symmetrical ligand benzene-1,2-dithiolate (bdt) were prepared.

The $M(bdt)_3$ complexes were prepared by procedures identical with those used for the $M(tdt)_3$ complexes. The physical properties of the crystalline $M(bdt)_3$ complexes are almost identical with the corresponding $M(tdt)_3$ complexes and are not given in full detail in this paper.

The characterization of the complexes consisted of elemental analyses, infrared spectra, electronic spectra, polarography, magnetic susceptibility, and, where applicable, electron spin resonance spectra. The details of the analytical results and certain physical properties are given in Table I.

Electronic Spectral Results. The electronic spectra below 30,000 cm^{-1} of all of the neutral complexes are given in Table II. The spectra of some representative complexes are shown in Figure 1.

It is immediately apparent that the dominant feature of all of the spectra is an intense two-band pattern found in the visible region of the spectrum. The first of these bands occurs around 15,000 cm^{-1} and has $\epsilon \sim$20,000–30,000, whereas the second occurs around 24,000 cm^{-1} and has $\epsilon \sim$15,000. In each case the first band is more intense than the second. It is this characteristic pattern which gives all of the complexes green to blue-green colors in solution, the region of maximum transmission in the visible being in the 18,000–20,000-cm^{-1} range.

The gross similarity of the electronic spectra indicates that the electronic structures (the molecular orbitals) are the same in all the neutral complexes. We interpret this as meaning that all of these complexes have a trigonal-prismatic structure in solution. Additionally, in all cases measured, the solid-state spectra have not differed significantly from the solution spectra. In particular, the band positions in the spectra of $Mo(S_2C_2Ph_2)_3$ in the solid and in solution are essentially identical. Thus we can tentatively conclude that the V and Cr complexes of $(S_2C_2Ph_2)_3$, known to be isomorphous with the Mo complex,[8,11] are also trigonal prismatic in the solid state. This result is of special significance since these are complexes of first-row transition elements, and it is interesting that trigonal-prismatic coordination is apparently not limited to the second- and third-transition rows.

Polarographic Results. The polarographic data are set out in Table III. We can now compare the data for the complexes $M(S_2C_2Ph_2)_3$, $M(tdt)_3$, and $M(S_2C_2$-

Table II. Electronic Spectral Results for Neutral ML_3 Complexes

Complex	Maxima in $CHCl_3$ solution[a] ν_1	ν_2	ν_3	ν_4	ν_5	Solid maxima
$Re(S_2C_2Ph_2)_3$	8230 (1090)		14,050 (24,000)	20,800 sh (~1000)	23,450 (12,300)	8,000, 13,500, 23,000
$Re(tdt)_3$	7920 (300)	9,220 (500)	14,450 (16,000)	22,050 sh (~800)	24,930 (11,000)	
$W(S_2C_2Ph_2)_3$			15,180 (27,800)	19,000 sh (700)	24,010 (12,700)	14,800, 24,400
$W(tdt)_3$		12,400 sh (200)	15,670 (23,400)	23,000 sh (900)	25,890 (15,700)	
$W(bdt)_3$[b]		12,900 sh (1300)	16,060 (20,000)	23,200 sh (2000)	26,140 (16,500)	
$W(S_2C_2(CH_3)_2)_3$			16,450 (20,200)	19,800 sh (1800)	24,750 (9,600)	
$Mo(S_2C_2Ph_2)_3$			14,400 (29,500)		22,300 (17,700)	13,800, 21,600
$Mo(tdt)_3$		11,500 sh (1000)	14,630 (20,900)		22,990 (17,400)	

[a] Frequency in cm^{-1} and molar extinction coefficient in parentheses. Only bands below 30,000 cm^{-1} are reported here. [b] An additional small shoulder occurs at 17,700.

Table III. Polarographic Data for ML_3 Complexes

Complex	$E_{1/2}$ for[a] $n = 1 \rightarrow n = 0$	$n = 0 \rightarrow n = -1$	$n = -1 \rightarrow n = -2$	$n = -2 \rightarrow n = -3$
$Re(S_2C_2Ph_2)_3^n$	+0.163	−0.340	−1.812	−2.591
$Re(tdt)_3$	+0.387	−0.065	−1.577	−2.375
$W(S_2C_2Ph_2)_3^n$		−0.542	−1.135	
$W(tdt)_3^n$		−0.247[c]	−1.075[c]	
$W(S_2C_2(CH_3)_2)_3^n$		−0.839[c]	−1.405[c]	
$W(S_2C_2(CF_3)_2)_3^n$		(+0.35)[b]	(−0.21)[b]	
$Mo(S_2C_2Ph_2)_3^n$		−0.489	−1.095	−2.92
$Mo(tdt)_3^n$		−0.219[c]	−0.895[c]	−2.62[c]
$Mo(S_2C_2(CF_3)_2)_3^n$		(+0.42)[b]	(−0.17)[b]	(?)[d]

[a] See Experimental Section for details. [b] From ref 3. The potentials in this reference were determined in CH_3CN against a saturated calomel electrode. We have arrived at an empirical conversion factor of −0.53 v to convert the sce values to our scale. See text for discussion. [c] Tetraethylammonium perchlorate was used as supporting electrolyte. [d] This wave probably exists but was not reported in ref 3. We would expect this wave at −2.0 v *vs.* Ag|$AgClO_4$ or *ca.* −1.5 v *vs.* sce.

$(CF_3)_2)_3$. The values for the $M(S_2C_2(CF_3)_2)_3$ complexes are adjusted from literature[3] values where a saturated calomel electrode was used as reference and acetonitrile as the solvent. For a comparison of complexes investigated for both sets of conditions,[15,16] we have arrived at an approximate conversion factor between the two scales. Thus the values recorded in parentheses under $M(S_2C_2(CF_3)_2)_3$ have been adjusted to our scale and must be viewed with some caution. Nevertheless, the values are considered to be of sufficient accuracy for the qualitative comparative purposes for which we use them.

It is clear from the half-wave potentials that the order of ease of reduction from $0 \rightarrow -1$ and from $-1 \rightarrow -2$ for a given metal is $S_2C_2(CF_3) > tdt > S_2C_2Ph, > S_2C_2(CH_3)_2$. Data are not yet complete, but preliminary results[17] indicate that the mnt complexes are the easiest of all to reduce. This parallels the order found in bis-planar complexes formed by these same ligands.[15,16] A key point to be stressed is the large variation of the potentials for the different ligands Any attempt to elucidate the electronic structure of these complexes must be consistent with this result.

The question of the geometry of the reduced (or oxidized in the Re case) species cannot be answered unequivocally at this time. However, due to the reversibility of all waves, it is probable that the observed species in the polarographic experiments possess the trigonal-prismatic structure. It is possible, however, that isomerization occurs slowly and that in trying to isolate a reduced species, a complex of octahedral or distorted octahedral structure may be obtained. It is not likely that (trigonal-prismatic) octahedral isomerization is rapid enough to give reversible polarographic waves. Further work will help to elucidate this point.

A more complete exposition of polarographic results will be given in a forthcoming paper on tris(mnt) complexes of transition metals.[17]

Esr and Magnetic Susceptibility Results. All of the neutral complexes of Mo and W are diamagnetic in the solid state, whereas the Re complexes are paramagnetic to the extent of one unpaired electron. The magnetic moments of $Re(S_2C_2Ph_2)_3$ and $Re(tdt)_3$ are 1.79 and 1.55 BM, respectively. Each Re complex shows a single, broad electron spin resonance signal in solid and in solution. The g values given in Table IV are rather close to the free-electron value of 2.0023, indicating the probability of an orbitally nondegenerate ground state.

The polarographic data have indicated that the complexes $M(tdt)_3$ and $M(S_2C_2Ph_2)_3$ are capable of being reduced by reaction with chemical reducing agents. In fact, the complexes $M(S_2C_2(CF_3)_2)_3^-$ with M = Cr, Mo, W have been isolated,[3] and the existence of the $M(S_2C_2Ph_2)_3^-$ complexes with M = Cr, Mo, W has been demonstrated[5] by chemical and electron spin resonance studies. To further compare the esr results for the $M(S_2C_2(CF_3)_2)_3$ and $M(S_2C_2Ph_2)_3$ complexes, we have measured the frozen-glass spectra of the $M(S_2C_2Ph_3)_2$ complexes in 2-Me-THF. Reduction of the neutral complexes was accomplished by addition of $[(n\text{-}C_4H_9)_4N]BH_4$ to a solution of the complex kept under

(15) H. B. Gray, *Progr. Transition Metal Chem.*, 1, 239 (1965).
(16) R. Williams, Ph.D. Thesis, Columbia University, 1966.
(17) T. Crawford, C. Simo, E. I. Stiefel, and H. B. Gray, to be published.

Table IV. Electron Spin Resonance Results for ML_3 Rhenium, Tungsten, and Molybdenum Complexes

Complex	Solvent	$\langle g \rangle$	$\langle A \rangle$, gauss	Glass Solvent	Glass $g_{\parallel}$	Glass $g_{\perp}$
$Re(S_2C_2Ph_2)_3$	$CHCl_3$	2.015 ± 0.003	...[a]	DMF-$CHCl_3$	...[a]	...[a]
$Re(tdt)_3$	$CHCl_3$	2.010 ± 0.003	...[a]	DMF-$CHCl_3$	...[a]	...[a]
$W(S_2C_2Ph_2)_3^-$	Diglyme	1.992	...[a]	2-Me-THF	1.987 ± 0.002	1.996 ± 0.002
$W(S_2C_2(CF_3)_2)_3^-$ [b]	CH_2Cl_2	1.9910 ± 0.0005	...[a]	CH_3OH	1.987 ± 0.002	1.993 ± 0.002
$[W(tdt)_3^-]$[c]	THF	1.974 ± 0.005	50 ± 10			
$Mo(S_2C_2Ph_2)_3^-$	Diglyme	2.011	11.4 ± 0.4	2-Me-THF	2.010 ± 0.002	2.010 ± 0.002
$Mo(S_2C_2(CF_3)_2)_3^-$ [b]	CH_2Cl_2	2.0097 ± 0.0003	12.2 ± 0.5	CH_3OH	2.011 ± 0.001	2.009 ± 0.001
$[Mo(tdt)_3^-]$[c]	Acetone	2.003	29.1 ± 1			

[a] Not observed or not resolved. [b] From ref 3; glass spectrum measured at 100°K. [c] See text for discussion of the uncertain nature of this species.

a stream of nitrogen. The solution was then rapidly frozen and its esr spectrum observed. On defrosting, the esr spectrum in the 2-Me-THF solution had g values (and hyperfine splitting in the Mo case) identical with those already reported[5] in diglyme solution. The pertinent data are set out in Table IV.

Complications arose when the above reduction technique was used with the $M(tdt)_3$ complexes, and the species which showed the esr signal could not always be reversibly oxidized to the neutral complex. It was therefore not certain that the observed esr signal came from a simple one-electron reduction product. Here, we report the observed signal, but we wait until the chemistry involved in the reduction and reoxidation process is more thoroughly understood before attempting to interpret the result. In this respect it is significant that $[(n\text{-}C_4H_9)_4N][CrO(tdt)_2]$ has actually been isolated and is paramagnetic to the extent of 1.74 BM. This compound shows a sharp esr signal in CH_2Cl_2 at $g = 1.994$ with $A(^{53}Cr) = 14.9$ gauss. Thus there is a reasonable possibility that analogous compounds of W and Mo may be producing the observed esr signals.

Molecular Orbitals for $Re(S_2C_2Ph_2)_3$

Structure of $Re(S_2C_2Ph_2)_3$. The structure of the neutral complex $Re(S_2C_2Ph_2)_3$ has been determined by X-ray diffraction techniques.[8] The crystal structure

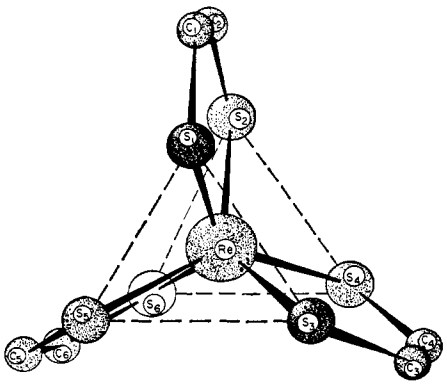

Figure 2. Perspective drawing of the coordination geometry of $Re(S_2C_2Ph_2)_3$. The six phenyl rings are not shown.

consists of well-separated monomers. In the molecule, rhenium is surrounded by six sulfur atoms in trigonal-prismatic coordination. The average Re–S distance is 2.325 A, and the average S–Re–S angle is 81.4°. A perspective drawing of the coordination geometry is shown in Figure 2. The metal–ligand planes defined by the five-membered ring radiate out from the threefold axis in a "paddle-wheel" fashion. The phenyl rings, which are omitted from Figure 2, are twisted out of the planes of the chelate rings and appear not to be conjugated. Although the over-all molecular symmetry is C_3, the coordination geometry is D_{3h}, and thus the calculation was carried out in D_{3h} symmetry.

Coordinate System for Molecular Orbitals. The coordinate system and the numbering used in the molecular orbital scheme are shown in Figure 3.

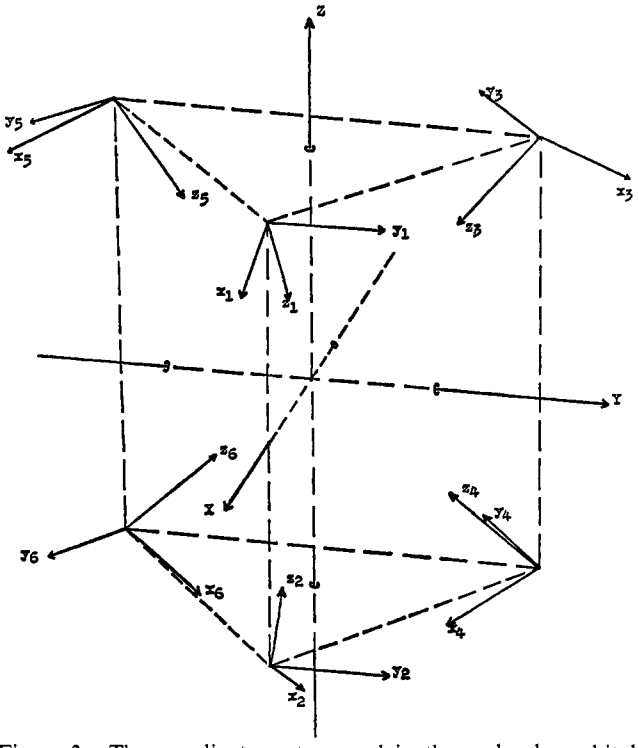

Figure 3. The coordinate system used in the molecular orbital calculation.

The z axis of the coordinate system of the central Re coincides with the threefold symmetry axis of the molecule. The x and y axes are equivalent in D_{3h} symmetry. However, the x axis is chosen to bisect one of the ligands along its twofold axis, while the y axis is set normal to the xz plane to form a right-handed coordinate system. The local ligand coordinate systems are established with the z_L axes pointing directly at the metal. The x_L axes which are orthogonal to z_L are contained in the planes of the chelate rings. Finally, the y_L axes are set normal to the chelate planes in such a manner as to make the ligand coordinate systems left-handed.

Valence Orbitals. The rhenium valence orbitals are the 5d, 6s, and 6p functions. Sulfur sp^2 hybrid orbitals

Table V. Orbital Transformation Scheme in D_{3h} Symmetry

Irreducible representation	Metal orbitals	Ligand orbitals
A_1'	$5d_{z^2}$, 6s	$\frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$
		$\frac{1}{\sqrt{6}}(\pi_{1h} + \pi_{2h} + \pi_{3h} + \pi_{4h} + \pi_{5h} + \pi_{6h})$
A_2'	...	$\frac{1}{\sqrt{3}}(1\pi_{1v,2v} + 1\pi_{3v,4v} + 1\pi_{5v,6v})$
		$\frac{1}{\sqrt{3}}(3\pi_{1v,2v} + 3\pi_{3v,4v} + 3\pi_{5v,6v})$
E'	$(5d_{xy}, 5d_{x^2-y^2})$, $(6p_x, p_y)$	$\frac{1}{2\sqrt{3}}(2\sigma_1 - \sigma_3 - \sigma_5 + 2\sigma_2 - \sigma_4 - \sigma_6)$
		$\frac{1}{2}(\sigma_3 - \sigma_5 + \sigma_4 - \sigma_6)$
		$\frac{1}{2\sqrt{3}}(2\pi_{1h} - \pi_{3h} - \pi_{5h} + 2\pi_{2h} - \pi_{4h} - \pi_{6h})$
		$\frac{1}{2}(\pi_{3h} - \pi_{5h} + \pi_{4h} - \pi_{6h})$
		$\frac{1}{\sqrt{2}}(1\pi_{3v,4v} - 1\pi_{5v,6v}), \frac{1}{\sqrt{6}}(2(1\pi_{1v,2v}) - 1\pi_{3v,4v} - 1\pi_{5v,6v})$
		$\frac{1}{\sqrt{2}}(3\pi_{3v,4v} - 3\pi_{5v,6v}), \frac{1}{\sqrt{6}}(2(3\pi_{1v,2v}) - 3\pi_{3v,4v} - 3\pi_{5v,6v})$
A_1''	...	$\frac{1}{\sqrt{3}}(2\pi_{1v,2v} + 2\pi_{3v,4v} + 2\pi_{5v,6v})$
		$\frac{1}{\sqrt{3}}(4\pi_{1v,2v} + 4\pi_{3v,4v} + 4\pi_{5v,6v})$
A_2''	$6p_z$	$\frac{1}{\sqrt{6}}(\sigma_1 + \sigma_3 + \sigma_5 - \sigma_2 - \sigma_4 - \sigma_6)$
		$\frac{1}{\sqrt{6}}(\pi_{1h} + \pi_{3h} + \pi_{5h} - \pi_{2h} - \pi_{4h} - \pi_{6h})$
E''	$(5d_{xz}, 5d_{yz})$	$\frac{1}{2\sqrt{3}}(2\sigma_1 - \sigma_3 - \sigma_5 - 2\sigma_2 + \sigma_4 + \sigma_6)$
		$\frac{1}{2}(\sigma_3 - \sigma_4 - \sigma_5 + \sigma_6)$
		$\frac{1}{2\sqrt{3}}(2\pi_{1h} - \pi_{3h} - \pi_{5h} - 2\pi_{2h} + \pi_{4h} + \pi_{6h})$,
		$\frac{1}{2}(\pi_{3h} - \pi_{4h} - \pi_{5h} + \pi_{6h})$
		$\frac{1}{\sqrt{2}}(2\pi_{3v,4v} - 2\pi_{5v,6v})$,
		$\frac{1}{\sqrt{6}}(2(2\pi_{1v,2v}) - 2\pi_{3v,4v} - 2\pi_{5v,6v})$
		$\frac{1}{\sqrt{2}}(4\pi_{3v,4v} - 4\pi_{5v,6v})$,
		$\frac{1}{\sqrt{6}}(2(4\pi_{1v,2v}) - 4\pi_{3v,4v} - 4\pi_{5v,6v})$

(one-third 3s and two-thirds 3p) were used for the in-plane σ and π_h bonding (see below). The wave functions for the ligand π_v orbitals were obtained from a separate Hückel calculation for the planar S–C–C–S system. The contribution of the phenyl rings to the π_v bonding is justifiably ignored. The radial functions for Re are analytical approximations to the numerical Hartree–Fock–Slater wave functions.[18] Clementi's[19] SCF functions were used for the carbon and sulfur valence orbitals.[20]

The transformation scheme for the metal and ligand orbitals in D_{3h} symmetry is given in Table V.

Description of the Calculation. The analytical expressions for the group-overlap integrals G_{ij} between the properly normalized ligand and metal basis functions are presented in Table VI. The normalization of the ligand orbitals included consideration of ligand–ligand overlap, although this is not shown in Table V. Numerical G_{ij} values for $Re(S_2C_2Ph_2)_3$ are given in Table VII.

(18) H. Basch and H. B. Gray, *Theoret. Chim. Acta*, in press.
(19) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).
(20) For a more detailed discussion of the possible valence orbitals and of the type of calculation performed, see S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

Table VI. Analytical Expressions for Group-Overlap Integrals in D_{3h}[a]

A_1'	$G_{A_1'}(s,\sigma) = \dfrac{6S(s_M,\sigma_L)}{[6 + 18S_{12}(\sigma_L,\sigma_L) + 12S_{14}(\sigma_L,\sigma_L)]^{1/2}}$
	$G_{A_1'}(s,\pi_h) = \dfrac{6S(s_M,\pi_{h_\sigma})}{[6 + 6S_{12}(\pi_{h_L},\pi_{h_L}) + 12S_{13}(\pi_{h_L},\pi_{h_L}) + 12S_{14}(\pi_{h_L},\pi_{h_L})]^{1/2}}$
	$G_{A_1'}(d_{z^2},\sigma) = \dfrac{6(1 - {}^3/_2\sin^2\delta)S(d_\sigma,\sigma_L)}{[6 + 18S_{12}(\sigma_L,\sigma_L) + 12S_{14}(\sigma_L,\sigma_L)]^{1/2}}$
	$G_{A_1'}(d_{z^2},\pi_h) = \dfrac{6(1 - {}^3/_2\sin^2\delta)S(d_\sigma,\pi_{h_\sigma}) + 6\sqrt{3}\sin\delta\cos\delta\, S(d_\pi,\pi_{h_\pi})}{[6 + 6S_{12}(\pi_{h_L},\pi_{h_L}) + 12S_{13}(\pi_{h_L},\pi_{h_L}) + 12S_{14}(\pi_{h_L},\pi_{h_L})]^{1/2}}$
E'	$G_{E'}(p,\sigma) = \dfrac{2\sqrt{3}\sin\delta\, S(p_\sigma,\sigma_L)}{2[1 - S_{14}(\sigma_L,\sigma_L)]^{1/2}}$
	$G_{E'}(p,\pi_h) = \dfrac{2\sqrt{3}\sin\delta\, S(p_\sigma,\pi_{h_\sigma}) - 2\sqrt{3}\cos\delta\, S(p_\pi,\pi_{h_\pi})}{2[1 + S_{12}(\pi_{h_L},\pi_{h_L}) - S_{13}(\pi_{h_L},\pi_{h_L}) - S_{14}(\pi_{h_L},\pi_{h_L})]^{1/2}}$
	$G_{E'}(p,1\pi_v) = \dfrac{-2\sqrt{3}[c_{1s}S(p_\pi,p_{L_s\pi}) + c_{1c}S(p_\pi,p_{L_c\pi})]}{[2 + 4c_{1s}^2S_{12}(p_{L_s},p_{L_s}) + 4c_{1c}^2S(p_{L_c},p_{L_c}) - 4c_{1s}^2S_{13}(p_{L_s},p_{L_s})]^{1/2}}$
	$G_{E'}(p,3\pi_v) = \dfrac{-2\sqrt{3}[c_{3s}S(p_\pi,p_{L_s\pi}) + c_{3c}S(p_\pi,p_{L_c\pi})]}{[2 + 4c_{3s}^2S_{12}(p_{L_s},p_{L_s}) + 4c_{3c}^2S_{12}(p_{L_c},p_{L_c}) - 4c_{3c}^2S_{13}(p_{L_s},p_{L_s})]^{1/2}}$
	$G_{E'}(d,\sigma) = \dfrac{-3\sin^2\delta\, S(d_\sigma,\sigma_L)}{2[1 - S_{14}(\sigma_L,\sigma_L)]^{1/2}}$
	$G_{E'}(d,\pi_h) = \dfrac{-3\sin^2\delta\, S(d_\sigma,\pi_{h_\sigma}) + 2\sqrt{3}\sin\delta\cos\delta\, S(d_\pi,\pi_{h_\pi})}{2[1 + S_{12}(\pi_{h_L},\pi_{h_L}) - S_{13}(\pi_{h_L},\pi_{h_L}) - S_{14}(\pi_{h_L},\pi_{h_L})]^{1/2}}$
	$G_{E'}(d,1\pi_v) = \dfrac{2\sqrt{3}\sin\delta\,[c_{1s}S(d_\pi,p_{L_s\pi})] + 2\sqrt{3}\sin\delta'\,[c_{1c}S(d_\pi,p_{L_c\pi})]}{[2 + 4c_{1s}^2S_{12}(p_{L_s},p_{L_s}) + 4c_{1c}^2S_{12}(p_{L_c},p_{L_c}) - 4c_{1s}^2S_{13}(p_{L_s},p_{L_s})]^{1/2}}$
	$G_{E'}(d,3\pi_v) = \dfrac{2\sqrt{3}\sin\delta\,(c_{3s}S(d_\pi,p_{L_s\pi})) + 2\sqrt{3}\sin\delta'\,(c_{3c}S(d_\pi,p_{L_c\pi}))}{[2 + 4c_{3s}^2S_{12}(p_{L_s},p_{L_s}) + 4c_{3c}^2S_{12}(p_{L_c},p_{L_c}) - 4c_{3s}^2S_{13}(p_{L_s},p_{L_s})]^{1/2}}$
A_2''	$G_{A_2''}(p,\sigma) = \dfrac{6\cos\delta\, S(p_\sigma,\sigma_L)}{[6 + 6S_{12}(\sigma_L,\sigma_L) - 12S_{14}(\sigma_L,\sigma_L)]^{1/2}}$
	$G_{A_2''}(p,\pi_h) = \dfrac{6\cos\delta\, S(p_\sigma,\pi_{h_\sigma}) + 6\sin\delta\, S(p_\pi,\pi_{h_\pi})}{[6 - 6S_{12}(\pi_{h_L},\pi_{h_L}) + 12S_{13}(\pi_{h_L},\pi_{h_L}) - 12S_{14}(\pi_{h_L},\pi_{h_L})]^{1/2}}$
E''	$G_{E''}(d,\sigma) = \dfrac{6\sin\delta\cos\delta\, S(d_\sigma,\sigma_L)}{[4 - 8S_{12}(\sigma_L,\sigma_L) + 4S_{14}(\sigma_L,\sigma_L)]^{1/2}}$
	$G_{E''}(d,\pi_h) = \dfrac{6\sin\delta\cos\delta\, S(d_\sigma,\pi_{h_\sigma}) - \sqrt{3}\cos(2\delta)\, S(d_\pi,\pi_{h_\pi})}{[4 - 4S_{12}(\pi_{h_L},\pi_{h_L}) - 4S_{13}(\pi_{h_L},\pi_{h_L}) + 4S_{14}(\pi_{h_L},\pi_{h_L})]^{1/2}}$
	$G_{E''}(d_\pi,2\pi_v) = \dfrac{-2\sqrt{3}\cos\delta\,(c_{2s}S(d_\pi,p_{L_s\pi})) - 2\sqrt{3}\cos\delta'\,(c_{2c}S(d_\pi,p_{L_c\pi}))}{[2 - 4c_{2s}^2S_{12}(p_{L_s},p_{L_s}) - 4c_{2c}^2S_{12}(p_{L_c},p_{L_c}) - 4c_{2s}^2S_{13}(p_{L_s},p_{L_s})]^{1/2}}$
	$G_{E''}(d_\pi,4\pi_v) = \dfrac{-2\sqrt{3}\cos\delta\,(c_{4s}S(d_\pi,p_{L_s\pi})) - 2\sqrt{3}\cos\delta'\,(c_{4c}S(d_\pi,p_{L_c\pi}))}{[2 - 4c_{4s}^2S_{12}(p_{L_s},p_{L_s}) - 4c_{4c}^2S_{12}(p_{L_c},p_{L_c}) - 4c_{4s}^2S_{13}(p_{L_s},p_{L_s})]^{1/2}}$

[a] δ is defined as one-half the supplement of the S–Re–S intraligand angle. δ' is defined as one-half the supplement of the C–Re–C intraligand angle. c_{is} and c_{ic} are, respectively, the coefficients of the sulfur and carbon p orbitals in the ith molecular orbital for the planar S–C–C–S system. Overlap between adjacent carbon and sulfur orbitals was ignored in deriving the normalization constants, as were interligand C–C overlaps and S–S overlaps of type S_{14}.

The Coulomb integrals H_{ii} for the atomic orbitals of Re were taken as the valence orbital ionization potentials (VOIP's) which have been described in detail previously.[21] The H_{ii} values for the sulfur hybrids are based on the results obtained previously from theoretical and experimental work on bis(methylthio)-maleonitrile,[22] whereas the ligand π_v energies were obtained from a separate calculation.

The off-diagonal integrals were approximated as $H_{ij} = FG_{ij}[(H_{ii} + H_{jj})/2]$, where H_{ii} and H_{jj} are the diagonal elements uncorrected for ligand–ligand overlap. The F factor was set equal to 2.0 and was used unchanged.

The secular equations were of order 4(a_1'), 6(e'), 3(a_2''), and 5(e''). The a_2' and a_1'' basis orbitals are ligand π_v combinations which are nonbonding with respect to the metal orbitals. The secular equations were solved for the eigenvalues and eigenvectors using an IBM 7094 Fortran program written by P. T. Manoharan of these laboratories. A Mulliken population analysis was performed for each of the occupied levels. Successive cycles were carried out until the computed charge and configuration (output) agreed with the

(21) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta*, 3, 458 (1965).
(22) J. Halper, W. D. Closson, and H. B. Gray, *ibid.*, in press.

Table VII. Numerical Values for Group-Overlap Integrals for $Re(S_2C_2Ph_2)_3$[a]

$G_{A_1'}(s,\sigma)$	=	0.8092
$G_{A_1'}(s,\pi_h)$	=	0.0403
$G_{A_1'}(d_{z^2},\sigma)$	=	0.0525
$G_{A_1'}(d_{z^2},\pi_h)$	=	0.1321
$G_{E'}(p,\sigma)$	=	0.6969
$G_{E'}(p,\pi_h)$	=	−0.0404
$G_{E'}(p,1\pi_v)$	=	−0.3294
$G_{E'}(p,3\pi_v)$	=	−0.2070
$G_{E'}(d,\sigma)$	=	−0.1673
$G_{E'}(d,\pi_h)$	=	0.0474
$G_{E'}(d,1\pi_v)$	=	0.0997
$G_{E'}(d,3\pi_v)$	=	0.0697
$G_{A_2''}(p,\sigma)$	=	0.8055
$G_{A_2''}(p,\pi_h)$	=	0.4471
$G_{E''}(d,\sigma)$	=	0.3238
$G_{E''}(d,\pi_h)$	=	0.0198
$G_{E''}(d,2\pi_v)$	=	−0.0968
$G_{E''}(d,4\pi_v)$	=	−0.0407

[a] The overlap between nonadjacent sulfurs of type S_{14} was set equal to zero in the normalization of the ligand functions, except for the σ set.

assumed charge and configuration (input) to within reasonable limits. At this point, the calculation was considered self-consistent.

Although variation of the F factor can be used to obtain a better fit with spectral data,[23] it was decided not to attempt to achieve detailed agreement between calculated and observed results at this time, owing to the approximate nature of the Re wave functions and VOIP's used. When the structural work on $V(S_2C_2Ph_2)_3$ now in progress is complete,[24] we will attempt to construct a more quantitative model of molecular orbitals for trigonal-prismatic complexes.

Discussion of Electronic Structure

The molecular orbitals derived for $Re(S_2C_2Ph_2)_3$ will be used as a guide in discussing the electronic structures of the neutral trigonal-prismatic complexes of Mo, W, and Re. Although derived from the quantitative semiempirical calculation described above, the ordering of the molecular orbitals in our model system can be understood from simple qualitative arguments based on symmetry and overlap considerations. To understand the resultant molecular orbitals, we first look at the starting ligand orbitals. These are of three types.

Six σ Orbitals. These are sp^2 hybrids pointing toward the metal. They overlap most strongly with the d_{xz} and $d_{yz}(e'')$ metal d orbitals.

Six π_h Orbitals. These are sp^2 hybrids on sulfur whose orientation is at 120° to the σ orbitals. They are in the plane of the chelate ring and overlap most strongly with $d_{z^2}(a_1')$ of the metal d orbitals. It should be noted that this overlap is of both σ and π character.

Twelve π_v Orbitals. These are the four ligand π orbitals situated perpendicular to the plane of each of the three chelate rings and delocalized over the S–C–C–S framework. These are designated in order of increasing energy as $1\pi_v$, $2\pi_v$, $3\pi_v$, and $4\pi_v$, with the $3\pi_v$ orbital being of comparable energy to the d orbitals of Re and therefore capable of interacting strongly with them. In the neutral form of the ligand the $1\pi_v$ and $2\pi_v$

(23) See, for example, P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, 87, 3340 (1965).

(24) R. Eisenberg and H. B. Gray, to be published.

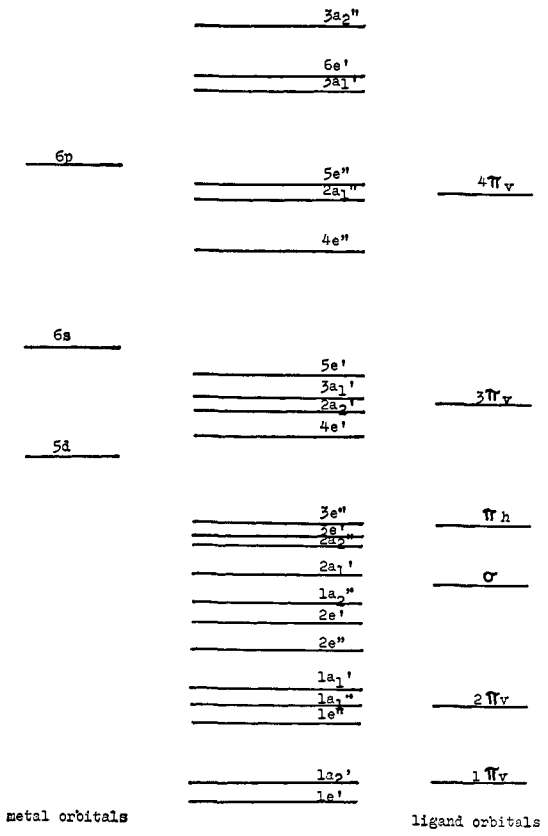

Figure 4. Complete molecular orbital energy level diagram for $Re(S_2C_2Ph_2)_3$.

are occupied by two electrons each, whereas the $3\pi_v$ is empty. Of course, the $3\pi_v$ is filled in the dianionic modification of the ligand. If the $3\pi_v$ is half-filled, the ligand is a radical anion. This becomes an important consideration in an attempt to describe the ground state of the complex in terms of some initial configuration of the ligand.

A molecular orbital correlation diagram showing all of the levels as well as the starting ligand and metal orbitals is shown in Figure 4. The principal levels of spectroscopic interest are shown in Figure 5. We now can explain the principal features of the scheme using simple qualitative arguments concerning the interaction of the metal d orbitals with the ligand orbitals.

The d_{xz} and d_{yz} orbitals transform as e'' and interact most strongly with the e'' symmetry orbitals of the σ set. This interaction gives rise to a strongly bonding level (2e'') localized predominantly on the ligand orbitals, and a strongly antibonding level (4e'') localized primarily on the metal (d_{xz},d_{yz}) set.[25]

The d_{z^2} orbital, transforming as a_1', interacts moderately strongly with the a_1' symmetry orbital of the π_h set. This gives rise to a bonding orbital mainly localized on the π_h ligand orbital ($2a_1'$) and an anti-

(25) It should be noted that this discussion is only valid as a first approximation, since the only interaction of e'' symmetry considered is between (d_{xz},d_{yz}) and the σ orbitals. It must be noted that π_h, $2\pi_v$, and $4\pi_v$ contain symmetry orbitals transforming as e''. These are, of course, included in the secular equation for e'', but the principal interaction which gives rise to the 2e'' and 4e'' is between (d_{xz},d_{yz}) and σ. We are thus justified in discussing these levels in the above manner. This same type of argument may be presented for all of the interactions discussed.

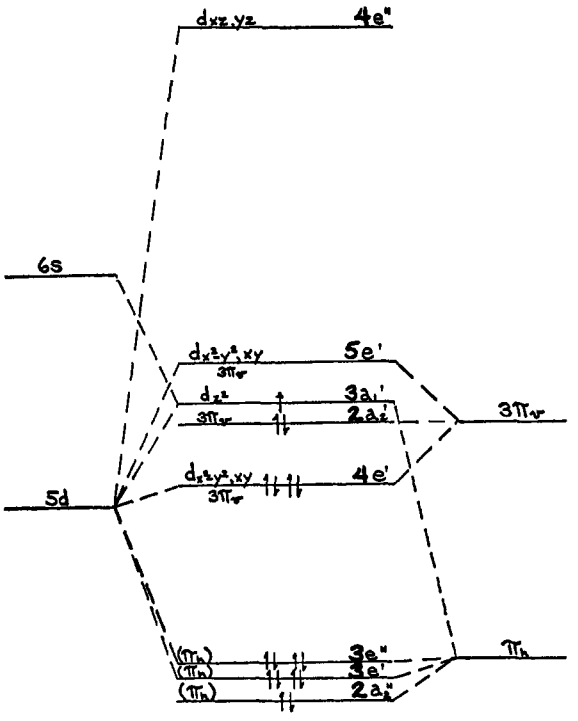

Figure 5. A diagram showing the orbital levels of interest in formulating the ground state and low excited states of $Re(S_2C_2Ph_2)_3$.

bonding orbital ($3a_1'$) which is largely metal d_{z^2} in character.

The (d_{xy},$d_{x^2-y^2}$) metal orbitals transform as e′ and interact strongly with the e′ symmetry orbitals of the $3\pi_v$ set. However, the d orbitals and the ligand $3\pi_v$ orbitals are of comparable energy such that the principal orbitals derived from this interaction (4e′ and 5e′) both contain considerable d and $3\pi_v$ character. That is, the 4e′ and 5e′ are thoroughly delocalized over d_{xy}, $d_{x^2-y^2}$, and $3\pi_v$.

The remaining symmetry orbital of the $3\pi_v$ set transforms as a_2' and thus does not possess the correct symmetry to combine with any of the metal orbitals. This orbital ($2a_2'$) is therefore nonbonding in the complex and in our approximate scheme is located at the same energy as the initial $3\pi_v$ orbital level, as shown in Figure 4.

The predicted ground state for $Re(S_2C_2Ph_2)_3$ is thus $\ldots(4e')^4(2a_2')^2(3a_1')^1 = {}^2A_1'$. The orbitally nondegenerate ground state is compatible with the gross features of the esr and magnetic susceptibility results of $Re(S_2C_2Ph_2)_3$.

Let us now consider the oxidation state assignment for Re in $Re(S_2C_2Ph_2)_3$. If we consider 4e′ as an orbital derived from (d_{xy},$d_{x^2-y^2}$), and 5e′ (empty) as essentially a $3\pi_v$ level, we then assign five electrons to the Re (four in 4e′, one in $3a_1'$) and thus would have a d^5 Re(II) configuration. The d orbital ligand-field splitting then appears to be $xz, yz > z^2 > xy, x^2 - y^2$. In this scheme the two electrons in the $2a_2'$ symmetry orbital of the $3\pi_v$ set give the L_3 ligand unit a charge of -2. Thus in this limiting formulation of [Re(II)]-[L_3^{2-}], the ligand unit possesses considerable radical character.

The other limiting formulation assigns 5e′ as a (d_{xy},$d_{x^2-y^2}$) level and considers 4e′ as being derived from $3\pi_v$. Thus the ground-state configuration is $[4e'(3\pi_v)]^4[2a_2'(3\pi_v)]^2[3a_1'(d_{z^2})]^1$. This is a d^1 Re(VI) configuration and the apparent d orbital splitting is $xz, yz > xy, x^2 - y^2 > z^2$. In accordance with this, the levels derived from $3\pi_v$ ($2a_2'$ and 4e′) are filled, and the ligand unit assumes the configuration L_3^{6-}. In other words, in this limiting formulation the ligands are in classical dianionic form.

The calculation does not clearly favor either limiting formulation, since it appears that the filled 4e′ level is nearly equally divided between metal d and ligand orbitals. This result shows dramatically the inappropriateness of taking the d-electron formulation literally in these complexes. Although the formulation of the ligands as dianions and the metal as Re(VI) has some precedent in past experience, this would obviously be an absurd assignment for a complex such as $V(S_2C_2Ph_2)_3$,[5] which if considered to contain dianionic ligands would call for V(VI). Breaking the $3p^6$ closed shell is not considered to be a likely possibility. The molecular orbital scheme is apparently the only way of realistically designating the ground state and over-all electronic structures of these complexes.

The neutral W and Mo complexes contain one less valence electron, and we expect the highest filled orbitals to be $\ldots(4e')^4(2a_2')^2$, or a ${}^1A_1'$ ground state. We do not expect the molecular orbitals to change greatly on going from Re to W or Mo, and thus the limiting oxidation-state formulations are still [M(II)]-[L_3^{2-}] and [M(VI)][L_3^{6-}], with neither isolated configuration providing a true picture of electronic structure.

We are now in a position to speculate on factors which contribute to the stabilization of the trigonal-prismatic geometry. It is important while doing this to keep in mind that X-ray and other evidence has been presented that establishes square-planar coordination for four-coordinate complexes containing structurally related sulfur-donor ligands.[15,16] These four-coordinate complexes exhibit many unusual properties and oxidation states,[15] and several lines of evidence indicate the complexes are most appropriately formulated as containing radical ligands.[15,26]

From the eight X-ray structural determinations[8,11,27-32] on various complexes containing these bidentate sulfur-donor ligands, it is an interesting and significant result that, independent of the coordination geometry or the central metal, the S–S distance always takes a value close to 3.05 A. We take this relatively short, nominally "nonbonded" S–S distance to indicate that there are interligand bonding forces present in these complexes which are considerably stronger than in classical octahedral, tetrahedral, or planar complexes. It is the compromise between these S–S bonding interactions and the S–S nonbonded repulsions which leads to the ubiquitous 3.05-A separation and to the stability of the nonclassical stuctures. Assuming this argument is sound, we extrapolate it and

(26) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, 87, 3016 (1965).
(27) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 605 (1965).
(28) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, 3, 1500 (1964).
(29) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, 3, 1507 (1964).
(30) C. J. Fritchie, Jr., *Acta Cryst.*, in press.
(31) M. R. Truter, quoted in G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem, Soc.*, 87, 1483 (1965).
(32) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, 4, 1729 (1965).

suggest that eight-coordinate complexes containing these sulfur-donor ligands, in a state of oxidation comparable to $Re(S_2C_2Ph_2)_3$, should exhibit cubic (or approximately cubic) coordination, with each edge of the S_8 cube being 3.0–3.1 A. This requires an M–S distance of 2.6 A, which may possibly be attained using actinide central metals.

A strong contributing factor to the stability of trigonal-prismatic coordination may be the effective use of the three valence d orbitals not involved in σ bonding. For example, strong involvement of the sulfur π_h orbitals with the metal d_{z^2} leads to a stable bonding orbital ($2a_1'$), which is occupied in all the complexes. Another possible stabilizing influence for trigonal-prismatic coordination is the large interaction of the $d_{xy},d_{x^2-y^2}$ orbitals with the thoroughly delocalized ligand $3\pi_v$ level. This leads to a particularly stable $4e'$ level, which is occupied in all of these complexes. In this respect it is pertinent to note that ReH_9^{2-} has the structure[33] of a face-centered trigonal prism, with the three face-centered hydrogens strongly σ bonded to the metal, presumably through extensive interaction with the $d_{xy},d_{x^2-y^2}$ orbitals.[33] In the $Re(S_2C_2Ph_2)_3$ trigonal prism the ligand π_v orbitals may play a stabilizing role similar to that of three face-centered hydrogens in ReH_9^{2-}. Further investigations should help elucidate whether or not π_h–d_{z^2} bonding, strong π_v–$d_{xy},d_{x^2-y^2}$ bonding, and interligand conjugation are essential features of trigonal-prismatic coordination.

We will now use the MO scheme to assign the low energy bands in the electronic spectrum of $Re(S_2C_2Ph_2)_3$. We pay particular attention to the characteristic and intense two-band pattern in the visible region. The assignments are given in Table VIII.

Table VIII. Detailed Assignment of the Spectra of $M(S_2C_2Ph_2)_3$ Complexes[a]

Complex	Band[b]	Assignment
$Re(S_2C_2Ph_2)_3$	8,230 (1,090), ν_1	$^2A_1' \rightarrow {}^2E'$ ($3a_1' \rightarrow 5e'$)
	14,050 (24,000), ν_3	$^2A_1' \rightarrow {}^2E'$ ($2a_2' \rightarrow 5e'$)
	[20,800 (sh), ν_4	$^2A_1' \rightarrow {}^2E'$ ($4e' \rightarrow 5e'$)]?
	23,450 (12,300), ν_5	$^2A_1' \rightarrow {}^2E', {}^2A_2''$ ($3e', 2a_2'' \rightarrow 3a_1'$)
$W(S_2C_2Ph_2)_3$	15,180 (27,800), ν_3	$^1A_1' \rightarrow {}^1E'$ ($2a_2' \rightarrow 5e'$)
	[19,000 (sh), ν_4	$^1A_1' \rightarrow {}^1E'$ ($4e' \rightarrow 5e'$)]?
	24,010 (12,700), ν_5	$^1A_1' \rightarrow {}^1E', {}^1A_2''$ ($3e', 2a_2'' \rightarrow 3a_1'$)
$Mo(S_2C_2Ph_2)_3$	14,400 (29,500), ν_3	$^1A_1' \rightarrow {}^1E'$ ($2a_2' \rightarrow 5e'$)
	22,300 (17,700), ν_5	$^1A_1' \rightarrow {}^1E', {}^1A_2''$ ($3e', 2a_2'' \rightarrow 3a_1'$)

[a] Band referred to as ν_2 in Table II can be assigned as $4e' \rightarrow 3a_1'$. [b] Maxima in cm^{-1}; molar extinction coefficients in parentheses.

The first band occurs at 8230 cm^{-1} in $Re(S_2C_2Ph_2)_3$, but this band is absent in $W(S_2C_2Ph_2)_3$ and $Mo(S_2C_2Ph_2)_3$. This band is assigned as the $3a_1' \rightarrow 5e'$ transition, or similar to a "d–d" type band from $d_{z^2} \rightarrow (d_{xy},d_{x^2-y^2})$. The intensity of the band ($\epsilon \sim 1000$) is consistent with this assignment as is the fact that this band is absent in the W and Mo complexes where the $3a_1'$ level is empty.

(33) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 3, 558 (1964).

The 14,050-cm^{-1} band is assigned to the $2a_2'(3\pi_v) \rightarrow 5e'(3\pi_v, d_{xy},d_{x^2-y^2})$ transition and the 23,450-cm^{-1} band to the $3e'(\pi_h),2a_2''(\pi_h) \rightarrow 3a_1'(d_{z^2})$ transitions. It should be noted that $5e'$ has considerable ligand $3\pi_v$ character, and $3a_1'$ has a substantial component of π_h. Thus, although somewhat L $\rightarrow$ M in character, both transitions are between levels which have large sulfur-orbital components and are expected to be strongly allowed for electric-dipole radiation. This is consistent with the observed large intensities of these two bands, $\epsilon \sim 24{,}000$ and 12,300, respectively. The nature of the orbitals between which the transitions occur is such that we would not expect the transition energies in a series of neutral $M(S_2C_2Ph_2)_3$ complexes to change considerably with small changes in the atomic number of the central metal. The small changes which do occur in going from Re to W are, however, consistent with the L $\rightarrow$ M type assignments. In the W complex we have one less electron and one less positive charge on the central metal nucleus. This destabilizes the W d orbitals with respect to Re and therefore also is expected to lead to a destabilization of any orbital derived from them. Thus, in going from Re to W, we expect both $3a_1'$ (derived from d_{z^2}) and $5e'$ (derived from $d_{xy},d_{x^2-y^2}$) to increase in energy (be destabilized), whereas $2a_2'$ (entirely ligand $3\pi_v$) and $3e'$ and $2a_2''$ (mainly ligand π_h) remain approximately at the same position in both complexes. Thus the two strongly allowed bands should increase in energy in going from $Re(S_2C_2Ph_2)_3$ to $W(S_2C_2Ph_2)_3$. This is indeed the case; the band maxima in $W(S_2C_2Ph_2)_3$ for the $2a_2' \rightarrow 5e'$ and $2a_2'',3e' \rightarrow 3a_1'$ transitions are at 15,170 and 24,010 cm^{-1}, respectively.[34]

The observed bands in the spectra of the $M(tdt)_3$ complexes are governed by the same trends and are given analogous assignments. The bands in the $M(tdt)_3$ complexes are always at higher energy than the corresponding bands in the $M(S_2C_2Ph_2)_3$ complexes. This indicates that the π_v-ligand levels in question are slightly more stable in tdt than in $S_2C_2Ph_2$. This is reasonable, because the six-membered benzene ring would further delocalize and stabilize these π_v orbitals. We note that the polarographic data show that it is always easier to reduce a given $M(tdt)_3$ complex than the corresponding $M(S_2C_2Ph_2)_3$ complex. Thus the combined data point to more stable ligand levels in tdt than in $S_2C_2Ph_2$.

We can now correlate the detailed polarographic results, as given in Table III, with the molecular orbital levels. The $n = +1 \rightarrow n = 0$ wave is found only in the Re complexes. This is consistent with our model in which the Re complexes have one electron in the relatively high-lying $3a_1'$ orbital, whereas this orbital is empty in the W and Mo complexes. This electron can be removed relatively easily in the Re complexes and thus they show a single one-electron oxidation wave.

The $n = 0 \rightarrow n = -1$ reduction wave occurs in all of the complexes and can be compared for complexes of the same ligand with different metals. It is to be

(34) Several shoulders which appear in the electronic spectra (Table II) can all be satisfactorily accommodated using the above scheme. Owing to the approximate nature of our treatment at this stage, we are emphasizing only those assignments which account for the gross features of the electronic spectra. Thus the suggested assignments for the lower intensity electronic bands, indicated by the presence of shoulders, are necessarily quite tentative.

noted that the variation of this wave with metal is within only 0.2 v. The Re values are least negative, meaning that the Re complex is most easily reduced. This result is consistent with the electron entering the $3a_1'$ level in each case. As discussed above (and illustrated by the spectra), this level should be more stable in Re than in W, and thus we expect it to be easier to put an electron into the $3a_1'$ orbital in the Re complex.[35]

The potential of the $n = -1 \rightarrow n = -2$ wave is quite negative for the Re complexes. There is a change of -1.5 v for the Re complexes, but a change in only -0.6 v for the W or Mo complexes (compared to the voltage of the $n = 0 \rightarrow n = -1$ wave). This is consistent with the electron going into the higher lying (by 8000 cm^{-1} from the spectra) $5e'$ level for the Re complexes and into the $3a_1'$ level for W and Re.

The $n = -2 \rightarrow n = -3$ wave occurs in the Re and Mo complexes but not in the W complexes (below 3.0 v). This wave in each case is interpreted as due to an electron entering $5e'$, and its absence in the W complexes indicates a high energy $5e'$ level in this case. This result may be compared to the position of the $2a_2' \rightarrow 5e'$ transition, which is considerably higher energy in the W complexes than in either Mo or Re systems.

Thus it appears that the polarographic and electronic spectral results may be correlated quite satisfactorily using the proposed model of molecular orbitals. When taken together the theoretical and experimental results allow us to present a reasonable description of the electronic structures of these unusual and interesting complexes.

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(35) This argument assumes that interelectronic-repulsion effects are very small. This is reasonable since we are dealing with molecular orbitals which are thoroughly delocalized over the ReS_6 framework. Furthermore, interelectronic-repulsion parameters for Re are small relative to 3d and 4d series metals, as are the parameters for sulfur compared to lighter donor atoms.

Hydrogen-Bonding Interaction of Chloroform with Metal Complexes. Chloroform Nuclear Magnetic Resonance Contact Shifts

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Abstract: The complexes $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PMI_3]$ (M = Co(II), Ni(II), and Zn(II)) have been found to interact *via* hydrogen bonding with chloroform. In the $CDCl_3$ solutions of the complexes, the interaction is accompanied by the appearance of a broad, well-resolved, intense infrared band at 2224 cm^{-1}. The decrease in intensity of the unperturbed chloroform C–H stretching overtone vibration in the presence of the complexes indicates that 4.5 ± 0.5 chloroform molecules are interacting with the complexes. The direct interaction is further manifested in the large upfield contact shifts observed for the chloroform resonance in the presence of both the nickel and cobalt complexes. It is shown that the nmr results are consistent only with a strong dominance of the contact contribution over the pseudo-contact contribution. The calculated chloroform contact shift is found to be +233 or +186 cps for the four- or five-coordinate cases, respectively. Possible distributions of the bonded chloroform molecules are suggested on the basis of the available data. Finally, these contact shifts provide additional evidence, probably the best available to date, to indicate that the hydrogen-bonding interaction is at least partially covalent.

A part of our present interest in nuclear magnetic resonance contact shifts[2] deals with the paramagnetic ion–solvent interaction. We have found evidence for such interactions by means of shifts in the solvent nmr frequency on dissolution of a paramagnetic solute. The complexes found most suitable for this work were tetra-*n*-butylammonium triiodo(triphenylphosphine)cobaltate(II) and -nickelate(II), prepared originally by Cotton, *et al.*,[3,4] and more recently studied by La Mar.[5–8] These complexes were chosen for study for two principal reasons: (1) their solubility properties are such that a wide range of concentrations can be studied; and (2) the *g*-value anisotropies are such that

(1) Abstracted in part from the Ph.D. Thesis of M. F. Rettig, University of Illinois, 1967; National Science Foundation Graduate Fellow, 1963 to present.

(2) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, 27, 314 (1957).

(3) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, 83, 1780 (1961).

(4) F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *ibid.*, 83, 344 (1961).

(5) G. N. La Mar, *J. Chem. Phys.*, 41, 2992 (1964).

(6) G. N. La Mar, *ibid.*, 43, 235 (1965).

(7) G. N. La Mar, *ibid.*, 43, 1085 (1965).

(8) G. N. La Mar, *J. Am. Chem. Soc.*, 87, 3567 (1965).