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Noninnocence in Metal Complexes: A Dithiolene Dawn

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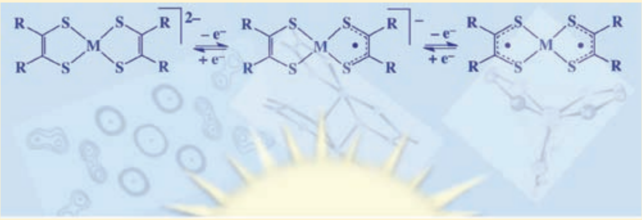
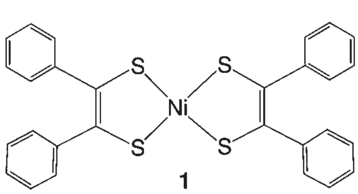


ABSTRACT: Noninnocence in inorganic chemistry traces its roots back half a century to work that was done on metal complexes containing unsaturated dithiolate ligands. In a flurry of activity in the early 1960s by three different research groups, homoleptic bis and tris complexes of these ligands, which came to be known as dithiolenes, were synthesized, and their structural, electrochemical, spectroscopic, and magnetic properties were investigated. The complexes were notable for facile one-electron transfers and intense colors in solution, and conventional oxidation-state descriptions could not account for their electronic structures. The bis complexes were, in general, found to be square-planar, including the first examples of this geometry for paramagnetic complexes and different formal d^n configurations. Several of the neutral and monoanionic tris complexes were found to have trigonal-prismatic coordination, the first time that this geometry had been observed in molecular metal complexes. Electronic structural calculations employing extended Hückel and other semiempirical computational methods revealed extensive ligand—metal mixing in the frontier orbitals of these systems, including the observation of structures in which filled metal-based orbitals were more stable than ligand-based orbitals of the same type, suggesting that the one-electron changes upon oxidation or reduction were occurring on the ligand rather than on the metal center. A summary of this early work is followed with a brief section on the current interpretations of these systems based on more advanced spectroscopic and computational methods. The take home message is that the early work did indeed provide a solid foundation for what was to follow in investigations of metal complexes containing redox-active ligands.

INTRODUCTION

Our story of noninnocence begins in the early 1960s, nearly a half-century ago, with initial reports from three different research groups. The first of these appeared in 1962 from Schrauzer and Mayweg on the synthesis and characterization of compound **1** made from the reaction of NiS_2 with diphenylacetylene.[1] The compound, which was thought to contain two dithiobenzil ligands (**2**) based on chemical characterization, was proposed to have a square-planar structure from magnetic measurements and its behavior in solutions with coordinating solvents. The neutral nature of both complex **1** and the dithiobenzil ligands implied a formal Ni^0 oxidation state, but it was assigned as Ni^{II} to accord with a square-planar geometry, which, in turn, meant that each dithiobenzil ligand was singly (one-electron, $1e^-$) reduced.



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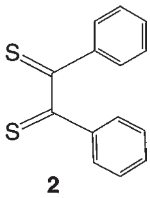

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In 1962 and 1963, initial reports appeared from the group at Columbia University under the direction of one of us (H.B.G.) with the synthesis and characterization of complexes containing the ligands maleonitriledithiolate (mnt^{2-}) and toluenedithiolate (tdt^{2-}).[2,3] Specifically, $M(mnt)_2^{2-}$ complexes (**3**), with coordinated dipositive metal ions $M^{2+} = Ni^{2+}, Pd^{2+}, Pt^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}$, were prepared and found to have virtually identical powder X-ray diffraction patterns indicative of isomorphism and, therefore, essentially the same coordination geometries. On the basis of the propensity of Pt^{2+} and Pd^{2+} complexes to be square-planar, the structures of all of the complexes were assigned to that coordination geometry.[2] In contrast with the developing notion at the time that square-planar coordination was favored in strong ligand fields, the electronic spectra of the $M(mnt)_2^{2-}$ complexes for nickel, cobalt, and copper suggested that mnt^{2-} was indeed a relatively weak field ligand, as did the magnetic susceptibility for the $Co(mnt)_2^{2-}$ species. The second report, less than 1 year later, described nickel, cobalt, copper, and iron complexes of tdt having the formula $M(tdt)_2^-$ (**4**) and their characterization by electronic absorption spectroscopy and magnetic susceptibility, and for the $Ni(tdt)_2^-$ complex, electron paramagnetic resonance (EPR) data.[3] The results of that investigation led to the following conclusion: "the complexes are planar and are composed of M^+ and two dithiolate radical anion moieties. The unpaired electron which each radical anion would possess must be paired with its

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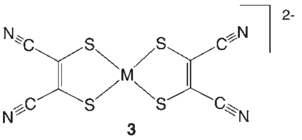
partner in the planar complex in one of the π-molecular orbitals (MOs) of the complex."[3]



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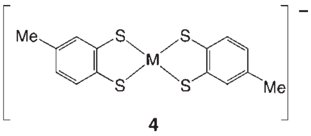
M = Ni, Cu, Co, Pd, Pt



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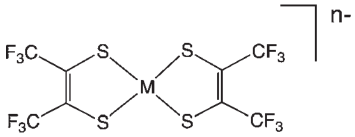
M = Ni, Cu, Co, Fe

The first contribution from the third group appeared in late 1963.[4] The authors—Davison, Edelstein, Holm, and Maki from Harvard University—recognized the two-electron difference between **1** and **3** for M = Ni and suggested that the complexes might exhibit facile redox reactions, specifically 1e$^-$ reduction of **1** and 1e$^-$ oxidation of Ni(mnt)$_2^{2-}$, to generate electronically similar complexes. The complexes shown as **5** were thus prepared and their electron-transfer reactions established by polarography. The R = CF_3 complexes were synthesized using the neutral dithietene $S_2C_2(CF_3)_2$ (**6**) reported by Krespan.[5] Compound **6** was found to react readily with low-valent complexes such as $Ni(CO)_4$, leading to S—S cleavage and chelation of the metal. The observation of 1e$^-$-related complexes **5** extended the number of unusual or unprecedented electronic states, including "the first well-authenticated example of a four-coordinate complex containing nickel in a doublet state and the first four-coordinate *paramagnetic* complexes of palladium and platinum of any description."[4]



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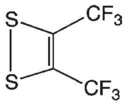
M = Ni, Cu, Co, Pd, Pt

n = 0, 1, 2



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The different sets of complexes with R = Ph, CN, and CF_3 from these reports were distinguished by intense transitions in the visible region of the electronic spectrum and facile 1e$^-$ oxidation or reduction, which suggested low reorganization energies for electron transfer. These early reports pointed to something extraordinary in the bonding and electronic structures of these complexes and others yet to be reported, and it set the stage for a remarkable decade of activity that opened the way for the study of redox noninnocent ligands and the Forum of which this article is part. The ligands became known as dithiolenes, a term introduced by McCleverty in his seminal review in 1968,[6] to underscore their delocalized electronic structures, and they were said to be "redox noninnocent" (Jorgensen earlier had coined the term "redox innocent" for "well-behaved" ligands[7]). Although we loved these ligands, by the end of the 1960s, we knew that they were "guilty" as charged. This article reviews the events that led to that verdict.

It was just at this time that the theoretical models describing inorganic electronic structures were undergoing major changes. Specifically, a hybrid of the MO theory and crystal-field theory called ligand-field theory was taking hold as the method of choice to describe the ground state and electronic excited states of metal complexes.[8−11] Before the 1960s, covalency in these systems was treated in an ad hoc manner that simply was not suitable for structures containing polyatomic ligands. The value of the MO theory for metal complexes was thus just beginning to be appreciated. The particular MO approach being followed was a semiempirical one that relied on spectroscopic data for estimation of the diagonal matrix elements of the Hamiltonian and a simple arithmetic or geometric approximation for off-diagonal elements. Reports appeared that quantitatively accounted for π bonding in metal complexes,[8] including the first papers on the electronic structures of complexes containing metal—oxo multiple bonds.[12] Molecular orbital models for bonding in square-planar complexes,[9] tetrahedral MO_4^{n-} systems,[13] and octahedral metal carbonyl and cyanide complexes,[10] were also published. In each of these cases, the metal—ligand π interactions involved the p or π orbitals of simple mono- or diatomic ligands. During this very active period, dithiolene complexes were examined by these new MO methods, but before much progress could be made in the formulation of electronic structures, it was necessary, or at least advisible, to know the detailed *molecular* structures of the complexes that were being scrutinized computationally.

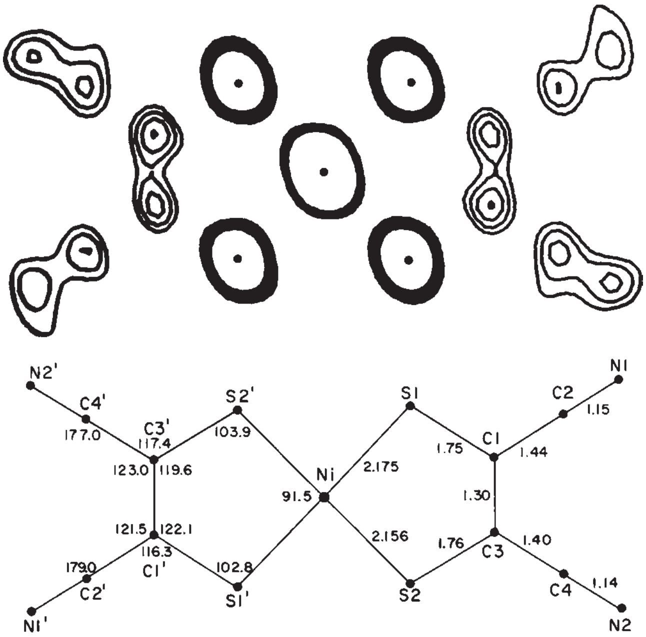


Figure 1. Structure of the Ni(mnt)$_2^{2-}$ anion showing distances and angles. Reproduced with permission from ref 12. Copyright 1962 American Chemical Society.

Structures of Bis(dithiolene) Complexes. While the crystal structure determination of a small molecule is usually a simple and fast process today, such was not the case in 1963 when one of us (R.E.) received crystals of $(Me_4N)_2[Ni(mnt)_2]$ from the other (H.B.G.) and undertook its crystal structure determination with James A. Ibers, then at Brookhaven National Laboratory. The intensity data were collected by film methods, with each diffraction's intensity estimated visually. The result of this first structure determination of a dithiolene complex, reproduced from the initial report, is shown in Figure 1.[14,15] The NiS_4 coordination was rigorously square-planar, and the complex possessed essential D_{2h} symmetry. Note that thermal ellipsoids

Table 1. Structural Studies of Homoleptic Bis- and Tris(dithiolene) Complexes during the 1960s

complex	cation	structural type[a]	ref
$[Ni(mnt)_2]^{2-}$	$(CH_3)_4N^+$	sq. pl.	14
$[Ni(mnt)_2)]^-$	$(C_6H_5)_3(CH_3)P^+$	sq. pl.	23
$[Ni(S_2C_2(CF_3)_2)_2]^-$	$(C_7H_7)^+$	sq. pl.	24
$Ni(S_2C_2Ph_2)_2$		sq. pl.	16
$Ni(S_2C_2(CF_3)_2)_2$	$C_{10}H_6$	sq. pl.	25
$[Co(mnt)_2]^{2-}$	$(n\text{-}C_4H_9)_4N^+$	sq. pl.	19
$[Co(tdt)_2]^-$	$(C_6H_5)_3(CH_3)As^+$	sq. pl.	17
$[Co_2(S_2C_6Cl_4)_4]^{2-}$	$(n\text{-}C_4H_9)_4N^+$	dimer	22
$Co_2(S_2C_2(CF_3)_2)_4$		dimer	20
$[Fe_2(mnt)_4]^{2-}$	$(n\text{-}C_4H_9)_4N^+$	dimer	21
$[Cu(mnt)_2]^-$	$(n\text{-}C_4H_9)_4N^+$	sq. pl.	19
$[Au(S_2C_2(CF_3)_2)_2]^-$	$(C_6H_5)_3PCl^+$	sq. pl.	26
$Re(S_2C_2Ph_2)_3$		trig. pr.	27, 28
$Mo(S_2C_2H_2)_3$		trig. pr.	29
$V(S_2C_2Ph_2)_3$		trig. pr.	30, 31
$[V(mnt)_3]^{2-}$	$(CH_3)_4N^+$	oct.	32

[a] sq. pl. = square-planar coordination; dimer = five-coordinate dimeric structure shown in Figure 2; trig. pr. = trigonal-prismatic coordination; oct. = trigonally distorted octahedral coordination.

are not shown because the *ORTEP* program to present such drawings had not yet been created.

A number of other structure determinations of dithiolene complexes followed during the ensuing few years.[16−32] Table 1 shows the bis(dithiolene) complexes examined structurally, along with their respective counterions. The structure determination of $Ni(S_2C_2Ph_2)_2$[16] confirmed the square-planar coordination proposed initially by Schrauzer,[1] while the structure of $Ni(mnt)_2^-$ exhibited a geometry essentially identical with that seen for the corresponding dianion. The only notable *and significant* differences in metrical parameters between the structures were in the Ni−S distances that were shortest for $Ni(S_2C_2Ph_2)_2$ and longest for $Ni(mnt)_2^{2-}$. For the complex $Co(tdt)_2^-$, the structural result confirmed the planar coordination geometry assumed by one of us (H.B.G.) and Billig.[17] This finding was important because the complex possessed an $S = 1$ ground state. While the conventional oxidation-state assignment for this complex, assuming dithiolate ligands, would be Co^{III}, it already had been assigned as Co^I with two radical-anion ligands based on its isomorphism with other $M(tdt)_2^-$ salts and the EPR results for the nickel analogue.[3,18]

The stabilization of square-planar coordination for iron and cobalt bis(dithiolene) complexes, which did not prove to be completely general, was found to be dependent on ligand π acidity and overall complex charge. For example, while the structure of $Co(mnt)_2^{2-}$ was virtually identical with that of its nickel analogue,[14,19] the neutral $Co(S_2C_2(CF_3)$ complex was found by Enemark and Lipscomb to be dimeric.[20] In this structure, two monomers were linked together by Co−S bonds to give each metal ion a square-pyramidal coordination with the formation of a central Co_2S_2 ring to hold the monomers together, shown schematically in Figure 2. Similar results were found in the structures of $Fe(mnt)_2^-$ [21] and $[Co(Cl_4bdt)_2]^-$,[22] the latter of which contrasted with the monomeric planar structure for the isoelectronic complex $Co(tdt)_2^-$.[17] In all of these dimeric structures, the intermonomer M−S bonds were significantly longer than those within the chelate rings, and each metal ion was displaced from the S_4 plane of the two dithiolenes toward the apical sulfur from the other monomer. The longer M−S intermonomer bonds were also consistent with dissociation of the dimer in solution. For the $Fe(mnt)_2^-$ complex, the structural results explained the difference between the spin state of the complex in solution ($S = {}^3/_2$) and that in the solid state ($S = {}^1/_2$).[18]

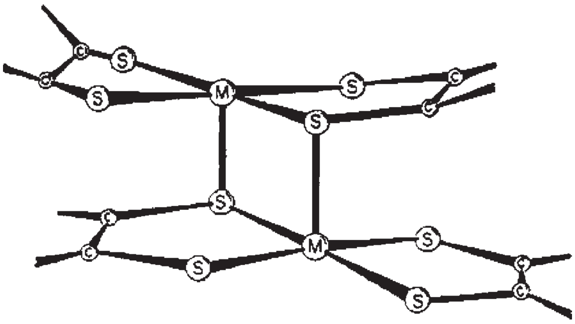


Figure 2. Idealized representation of the structures of dimeric dithiolene complexes of cobalt and iron.

While the structural studies of the 1960s defined the coordination geometries and metrical parameters on which to develop detailed interpretations of bonding, they were lacking in the precision and accuracy subsequently needed to address the partial localization of the delocalized structures. With typical standard deviations for C−C bonds of 0.02−0.03 Å, it was not possible to discern whether the aromatic dithiolene ligands had, in fact, some alternation of bond lengths consistent with quinoidal versus aromatic structure. Only more recent structural work has revealed statistically significant differences in the C−S and C−C bonds that can be used to support rigorous formulations of the bonding in these systems.

Electronic Structures of the Bis(dithiolene) Complexes. In 1964, shortly after the molecular structure of $Ni(mnt)_2^{2-}$ was determined, the bonding in bis(mnt) complexes was investigated by semiempirical MO theory (the MO energy level ordering is shown as Figure 3).[33] Orbitals were given D_{2h} symmetry designations (the z axis is perpendicular to the molecular plane, with the x axis bisecting each of the ligands and the y axis perpendicular to x and z). The following assignments of the electronic transitions for $Ni(mnt)_2^{n-}$ are consistent with those of other square-planar complexes such as $Ni(CN)_4^{2-}$; the paper discussed the question of the ground-state formulation of these bis(dithiolene) complexes. What follows are the words of Shupack et al.[33] (their reference numbers have been omitted to avoid confusion).

> "We now address ourselves to an important question regarding the new square-planar complexes, which is the formulation of the ground state. The usual method of oxidation states gives M(III) and M(II) for the *mono*-negative and dinegative complexes, respectively. We recently proposed that some of the $M(MNT)_2^-$ and $M(TDT)_2^-$ complexes be considered as composed of M(I) and radical-anion ligands. In this formulation a filled bonding orbital must be mainly localized on the metal, adding an extra pair of electrons to be associated with the metal. Schrauzer and Mayweg had earlier made the suggestion that $Ni(S_2C_2(C_6H_5)_2)_2$ be formulated as Ni(II) and two radical-anion ligands. The following evidence supports the radical-anion formulation for certain of these complexes.

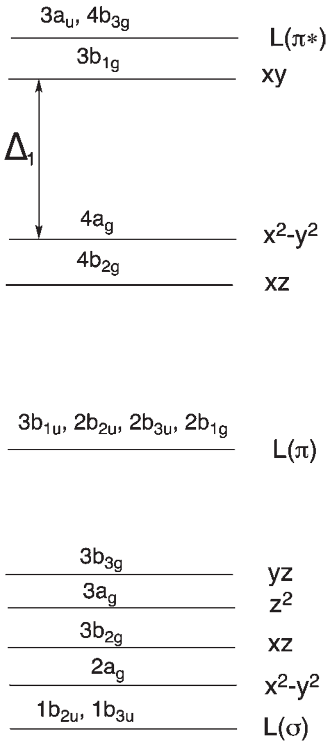


Figure 3. Diagram of the most important MO energies of $Ni(mnt)_2^{2-}$ from ref 33.

1. According to the calculation of the $Ni(MNT)_2^{n-}$ system, the 4b$_{2g}$ and 4a$_g$ orbitals are definitely more "ligand" than "metal," while the 3b$_{2g}$ and 2a$_g$ orbitals, which are bonding, are mainly localized on the metal. This means that square-planar complexes containing MNT^{2-}, in which the 4b$_{2g}$ and 4a$_g$ levels are *not* filled, with the probable electronic structure ...$(4b_{2g})^2$(4a$_g$ empty), contains two MNT radical anions; four "metal" orbitals are filled, 3b$_{2g}$, 3b$_{3g}$, 3a$_g$, and 2a$_g$. The paramagnetic complex $Ni(MNT)_2^{-}$, with the electronic structure ...(4a$_g$), contains one MNT radical anion. All the complexes with the electronic structure ...$(4a_g)^2$ contain MNT^{2-} ligands and can safely be formulated in the usual way. That is, $Ni(MNT)_2^{2-}$ contains Ni(II) and $Cu(MNT)_2^{-}$ contains Cu(III).
2. Recently we have shown that $Co(MNT)_2^{-}$ reacts with certain ligands to give stable five- and six-coordinated complexes. For the reactions with monodentate ligands, it was observed that the five-coordinate adducts are substantially *more stable* than the six-coordinate ones, and, in many cases, the six-coordinate state was not found at all. In addition, the stabilities of the five-coordinate adducts indicate that $Co(MNT)_2^{-}$ follows the Ahrland, Chatt, and Davies type-B behavior, e.g., $Co(MNT)_2(P(C_6H_5)_3)^{-}$ is more stable than $Co(MNT)_2(py)^{-}$. Thus the *chemical* evidence in this case points to a complex in which the metal ion is effectively d^8; certainly the behavior of $Co(MNT)_2^{-}$ is completely different from any usual d^6 Co(III) complex.
3. It has been possible to prepare neutral, six-coordinate complexes of the type $M(TDT)_3$, with M = Ni and Co. These complexes would call for M(VI) in the standard formulation of oxidation state. We believe this is absolutely unreasonable for a complex containing sulfur-donor ligands, and it is very likely that in these cases *at least one filled bonding orbital is mainly localized on the metal.*
4. The hyperfine splitting in the esr spectrum of $Ni(S_2C_2(C_6H_5)_2)_2^{-}$ due to ^{61}Ni $(I - {}^{3}/_{2})$ is only 4.5 ± 1 gauss in DMSO solution. Surely, with this very small metal splitting, the unpaired electron in this case is in an orbital which is delocalized over both the metal and the ligands, but is *predominantly ligand*. The composition of the a$_g$(π*) orbital is consistent with this small splitting. Although the magnetic moment of ^{61}Ni is not accurately known, both values which have been suggested give a normalized hyperfine splitting in $Ni(S_2C_2(C_6H_5)_2)_2^{-}$ which is smaller than the normalized splitting in $Cu(MNT)_2^{2-}$. For the magnetic moment 0.03 nm., the ^{61}Ni splitting is 22.5 gauss/nm.; for 0.09 nm., the splitting is 7.5 gauss/nm. The splitting in $^{63,65}Cu(MNT)_2^{2-}$ in DMF solution is approximately 49 gauss/nm. Thus these experimental results support the MO calculations, which suggest that the unpaired electron in 3b$_{1g}$ in $Cu(MNT)_2^{2-}$ is associated with the metal much more than the unpaired electron in the a$_g$(π*) orbital in $Ni(S_2C_2(C_6H_5)_2)_2^{-}$. In $Ni(MNT)_2^{2-}$, 3b$_{1g}$ is calculated to be 55.7% metal, while the metal character of 4a$_g$ in $Ni(MNT)_2^{-}$ is calculated to be only 26.0%.

> Ideally, therefore, the formulation of oxidation state of the metal should take into consideration the possibility of filled bonding orbitals on the metal. Since in most cases such a procedure is necessarily arbitrary, and since the standard method of assessing oxidation state is almost certainly wrong in many of these complexes, it appears that the general MO formulation of the ground state is preferable."

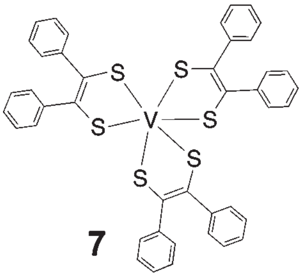
The essence of this study was that the MO calculations revealed a substantial degree of covalency in metal–dithiolene bonding. Most notably, the lower energy 3b$_{2g}$ and 2a$_g$ orbitals in D_{2h} symmetry were primarily metal-based, whereas the higher energy 4a$_g$ and 4b$_{2g}$ that were filled, half-filled, or empty, depending on the complex electron count, were definitely more ligand than metal in character. In subsequent studies done to correlate experimental data from X-ray absorption spectroscopy (XAS) with orbital composition, Solomon and co-workers described this electronic structural situation as "inverted" from the conventional or normal views of bonding in metal complexes.[34] At the time that the Shupack study appeared, controversy arose, partly based on differences in the experimental results [for example, the measured magnetic moment of $Co(mnt)_2^{2-}$] and partly based on spectroscopic analyses. One of the earliest and most notable papers reported single-crystal EPR studies of magnetically dilute ($S = {}^{1}/_{2}$) complexes. Specifically, Maki et al. doped $M(mnt)_2^{2-}$ anions where M = Cu, Co, and Rh into the diamagnetic host of $(TBA)_2[Ni(mnt)_2]$ and $Ni(mnt)_2^{-}$ into the diamagnetic host of $(TBA)[Cu(mnt)_2]$, the structures of which had been determined.[35] For $Cu(mnt)_2^{2-}$, the results were completely consistent with Cu^{II} and a d^9 configuration for the complex. The half-filled MO would have mainly d$_{xy}$ character corresponding to the σ* orbital for metal–dithiolene bonding. For the other paramagnetic complexes, the electron count is 2 less than that for $Cu(mnt)_2^{2-}$, raising the issue of whether they were really d^7 complexes or they were d^9 systems with oxidized dithiolate ligands. A detailed EPR analysis was presented that indicated that these complexes were best viewed as d^7 systems, which required dianionic dithiolate ligands. The ordering of orbitals, while not developed computationally, suggested that, for the $\mathrm{Ni(mnt)_2}^-$ anion, $4b_{2g}$ was higher in energy than $4a_g$ (by ca. 20 000 cm^{-1}) and the assignment of Ni^{III} inferred that $4b_{2g}$ was more metal than ligand in character.[35] However, an extensive π interaction was also envisioned between the d_{xz} orbital and the highest filled ligand π_v function (note that, in this paper, *x* and *y* are interchanged from the paper by Shupack et al. and the orbital label has been changed by us to be consistent with the MO scheme of Figure 3). While no MO ordering was given, the assignment of the singly occupied MO (SOMO) was given as $(b_{2g})^1$, which differed from the $(4a_g)^1$ configuration given by Shupack et al.

In another paper from the same authors in the same year,[36] EPR studies were done on paramagnetic ($S = {}^1/_2$) $\mathrm{M(S_2C_2(CF_3))_2}^{n-}$ complexes for M = Ni, Co, Pd, and Pt in both solution and frozen glass. Again, the EPR data were said to be more consistent with a spin-paired d^7 metal configuration, and the dianionic cobalt complex was found to be very similar to $\mathrm{Co(mnt)_2}^{2-}$. However, it was also noted that the EPR data for $\mathrm{Co(S_2C_2(CF_3))_2}^{2-}$ indicated that the unpaired electron was in an orbital of "extensively delocalized character" that was suggested to be of the $b_{2g}-\pi^*$ type. Also worthy of note was an observed diamagnetism and the absence of any EPR signal for the $2e^-$-oxidized complex $\mathrm{Co(S_2C_2(CF_3)_2)_2}$ (formally Co^{IV}). While a suggestion of dimerization with metal−metal bonding was made to explain the diamagnetism, the complex was subsequently characterized crystallographically to dimerize via the formation of Co−S bonds, as described above and illustrated schematically in Figure 2.[20]

Tris(dithiolene) Complexes. Reports appeared beginning in 1964 on six-coordinate tris(dithiolene) complexes. The first of these was by Davison et al. on $\mathrm{M(S_2C_2R_2)_3}^{n-}$ where M = Cr, Mo, W for R = $\mathrm{CF_3}$ and M = V, Cr, Mo for R = CN.[36] This work followed the initial synthesis by King of $\mathrm{Mo(S_2C_2R_2)_3}$ from the reaction of $\mathrm{Mo(CO)_6}$ with dithietene **6**.[37] Davison et al. reasoned that "The existence of electron-transfer reactions in the four-coordinate series of complexes suggested that a similar set of reactions might exist among six-coordinate tris complexes [of these ligands]." Citing King's neutral molybdenum complex and the $\mathrm{Cr(mnt)_3}^{3-}$ complex they had synthesized, they noted that the two complexes differed by three valence electrons, excluding the R substituents. "The ready isolation and considerable stability of both complexes raised the possibility" that the neutral complexes might be reducible and the trianionic complexes oxidizable to give an interesting series of $1e^-$-related tris complexes. This was indeed found to be the case.

In a joint publication by one of us (H.B.G.) and Schrauzer,[38] the existence of the tris(dithiolene) complexes $\mathrm{M(S_2C_2Ph_2)_3}^{n-}$ was reported for M = V, *n* = 0 (**7**), and M = Cr, Mo, *n* = 1. The vanadium and chromium complexes differed by two electrons, and the EPR of each was reported with the conclusion that the SOMO in the chromium complex contained more metal character than the SOMO in the vanadium complex (the HOMO−1 level in the former). Most importantly, the neutral vanadium complex raised important issues regarding the oxidation state of the complexed metal ion as well as that of the dithiolene ligands. The authors wrote the following:

> "The $\mathrm{V(S_2C_2Ph_2)_3}$ complex has special significance in the problem of formulation of the ground states of bis and tris complexes containing bidentate, unsaturated sulfur-donor ligands. The stability of $\mathrm{V(S_2C_2Ph_2)_3}$ makes it clear that the oxidation-state formalism which requires $\mathrm{S_2C_2Ph_2}^{2-}$ and the high oxidation-state metals cannot be applied consistently to these complexes, since the formalism in the V (*n* = 0) case would call for V(VI). It would be unreasonable to suggest that the metal is effectively $3p^5$ in this complex."



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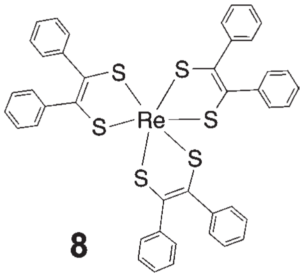

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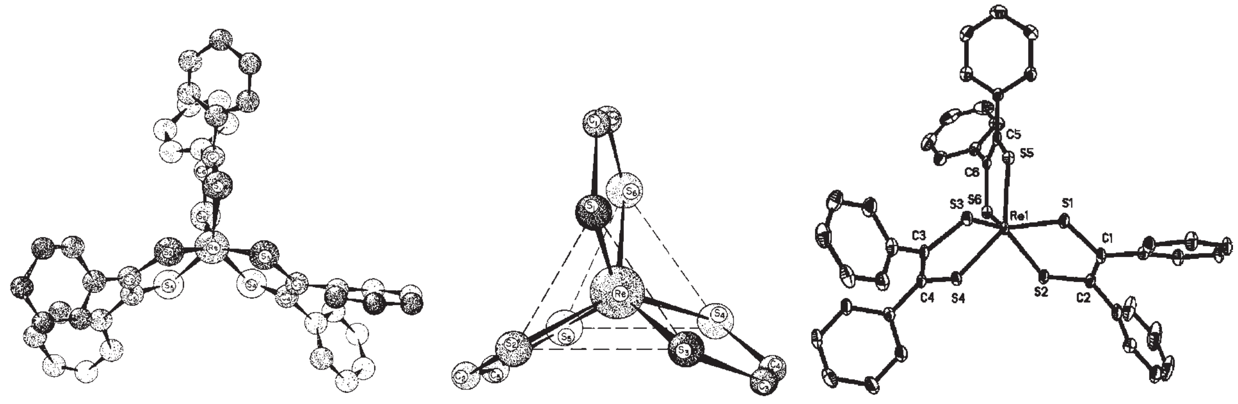
The discussion included the limiting oxidation-state formalisms of the dithiolene ligand as the dianionic *cis*-stilbenedithiolate and the neutral dithiobenzil. The former, if present uniformly in the complex, would necessitate V^{VI}, an impossibly high oxidation state for that element, whereas the latter would dictate V^0, again an unlikely possibility. The situation was akin to the dilemma of the oxidation state assignment for Schrauzer's original nickel complex $\mathrm{Ni(S_2C_2Ph_2)_2}$, which, if considered according to the same ligand oxidation level limits, would correspond to Ni^{IV} or Ni^0.

The history of the tris(dithiolene) complexes and elucidation of their electronic structures has been reviewed recently.[39,40] These complexes offered another surprise in addition to the dilemma of the oxidation-state assignment, and that was the matter of their coordination geometry. In 1965, the structure of the rhenium complex $\mathrm{Re(S_2C_2Ph_2)_3}$ (**8**) was determined at Brookhaven by one of us (R.E.) in collaboration with Ibers using crystals prepared by Schrauzer.[28,41] Unexpectedly, the complex was found to have a trigonal-prismatic (TP) coordination geometry with planar $\mathrm{ReS_2C_2}$ chelate rings and an inner coordination sphere of D_{3h} symmetry. The results of the structure determination are shown as Figure 4a, with the phenyl rings omitted for clarity in Figure 4b. The TP coordination found for **8** was the first to be determined for a molecular complex, although it had been observed in extended solids such as $\mathrm{MoS_2}$ and $\mathrm{WS_2}$.

By most current measures of the quality of a structure determination, the structure of **8** was poor. Intensity data were gathered using a diffractometer that was positioned at individual diffractions manually for a fixed counting time with background counted on each side of the diffraction profile. Because of problems in the collection of individual reflections, some regions of reciprocal space were systematically eliminated, leading to insufficient data for full refinement and rendering anisotropic thermal parameters meaningless, even if they could have been used (they were not except for rhenium). In the least-squares refinements of the structure, the phenyl rings were assumed to have fixed hexagonal (D_{6h}) symmetry. Despite these shortcomings in the data and the hurdles to be overcome in the refinement, a clearly defined TP coordination geometry was established for **8**, albeit with significant variations in the S−C distances [1.62(4)−1.75(3) Å] and moderately large estimated standard deviations (esd's) in the other metrical parameters.



(a) (b) (c)

Figure 4. Diagrams showing (a) the molecular structure of **8** as originally determined, (b) the inner coordination geometry of **8**, and (c) a thermal ellipsoid plot of the redetermined structure of **8** in 2006. Reproduced with permission from refs 28 and 42. Copyright 1966 American Chemical Society and 2006 Blackwell.

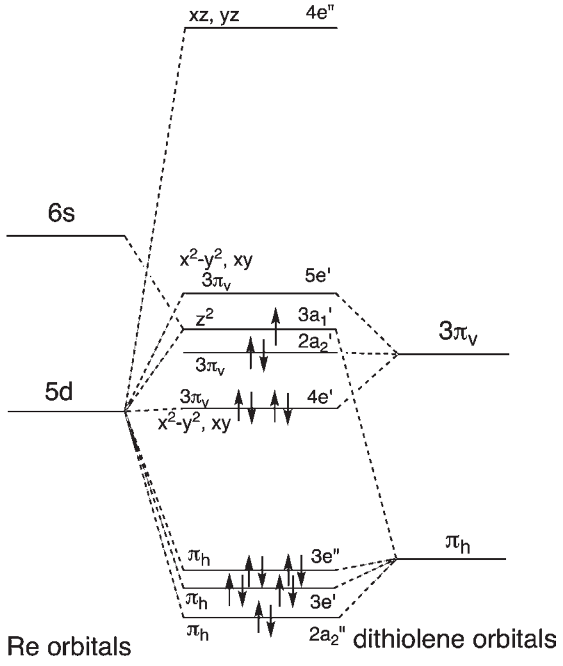


Figure 5. Diagram showing the orbitals of interest in formulating the ground and lowest electronic excited states of **8** from ref 44.

The structure of **8** was subsequently redetermined in 2006 using a crystal from the same batch that had been given to one of us (R.E.) in 1964 (a gap of 42 years!). This time the structure determination employed modern CCD instrumentation at low temperature and the refinement was conducted using modern software for crystal structure refinements.[42] The redetermination with complete anisotropic refinement confirmed in every way the TP coordination of **8** while producing much more accurate and consistent Re−S and S−C bond distances than had been reported originally. The refined structure from this redetermination is shown in Figure 4c.

After the initial structural report of **8** in 1965, the complex was characterized by spectroscopic, electrochemical, and magnetic measurements to confirm that the TP coordination was maintained in solution and, on the basis of these results and similar measurements of other tris(dithiolene) complexes, extended the possibility of that coordination to closely related systems.[43] For **8**, three reversible reductions and one reversible oxidation were seen, as were a magnetic moment of 1.73 μ_B for a spin-doublet ground state and a broad EPR signal having $\langle g \rangle = 2.015$, suggesting an orbitally nondegenerate ground state. The neutral Re(tdt)$_3$ complex exhibited an essentially identical EPR spectrum and was also assigned a TP coordination geometry. In 1966, Stiefel et al. published a full paper on the electronic structure and spectroscopy of **8** and related TP complexes.[44] For the tris(dithiolene) complexes of rhenium, tungsten, and molybdenum with the ligands $S_2C_2Ph_2$ and tdt, the similarity of electronic spectra with two dominant absorptions below 30 000 cm^{-1} and reversible electrochemical processes supported their assignment to TP or slightly distorted TP structures. At nearly the same time, Smith and Schrauzer established TP coordination for the neutral Mo($S_2C_2H_2$)$_3$ complex, although in that structure, the chelate rings showed an envelope-type conformation with a fold angle of ~18°, giving the complex overall C_{3h} symmetry.[29]

In the 1966 paper by Stiefel et al.,[44] the results of a semiempirical MO calculation of the electronic structure of **8** revealed the shortcomings of conventional oxidation-state assignments for the dithiolene complexes. An energy level diagram of the orbitals of interest from that paper is shown in Figure 5 with D_{3h} symmetry labels and the z direction coincident with the trigonal axis. The π_v designation used in Figure 5 was for the out-of-plane π orbitals, of which there were four for each S−C−C−S chelating ligand; $3\pi_v$ corresponded to the third highest of these orbitals that, if filled, gave enedithiolate character to the ligand. The π_h functions were lone-pair orbitals in the chelate ring plane for sp^2-hybridized sulfur donors. Both π_v and π_h wave functions were symmetry-adapted linear combinations in the calculation.

The paper then goes on to state the following:

> "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.

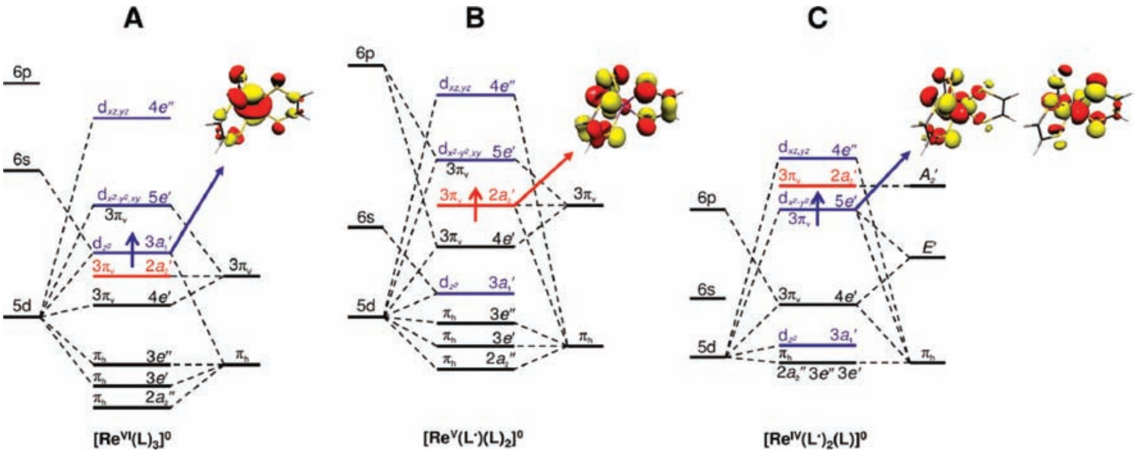


Figure 6. Diagram from the paper by Sproules et al. showing the different MO energy level schemes proposed for **1**: (A) from the work of Stiefel et al.;[44] (B) from the study by Al-Mowali and Porte;[46] (C) from the work by Schrauzer and Mayweg.[45] Reproduced with permission from ref 47. Copyright 2009 American Chemical Society.

> Thus in this limiting formulation of $[\mathrm{Re(II)}][\mathrm{L}_3^{2-}]$, 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 $V(S_2C_2Ph_2)_3$ which if considered to contain dianionic ligands would call for V(VI). Breaking the 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 overall electronic structures of these complexes."

Additionally, Stiefel et al. proceeded to consider a possible factor that led to stabilization in these literally unprecedented tris(dithiolene) complexes.[44] Specifically, it was noted that the rectangular sides of the trigonal prism were actually squares with relatively short intrachelate and nearest interchelate S···S distances of ~3.05 Å. It was therefore proposed that weak direct S···S bonding interactions stabilized TP coordination. Such interactions would not occur for the fully reduced ligand set (i.e., L_3^{6-}) but could exist if the ligands were not in their fully reduced formulation. This proposal connected the unusual TP coordination directly to the redox noninnocence suggested from studies on the bis(dithiolene) complexes.

Shortly after the paper by Stiefel et al. appeared, Schrauzer and Mayweg[45] published a different MO scheme based on a simple parametrized Hückel calculation that for **1** gave the following configuration and ground state: ...$(3a_1')^2\ (4e')^4\ (5e')^1 = {}^2E'$. Then in 1975, following a reexamination of the EPR spectra of **1** and Re(tdt)$_3$, Al-Mowali and Porte[46] assigned the electronic configuration and ground state as ...$(3a_1')^2\ (4e')^4\ (2a_2')^1 = {}^2A_2'$. The basis of Al-Mowali and Porte's modification of the energy level ordering was that the EPR results for **8** and Re(tdt)$_3$ showed $\langle g \rangle$ values near 2.002 and no rhenium hyperfine coupling, features more consistent with a sulfur-containing radical than a system with unpaired spin on the Re atom. The three different MO energy level orderings shown in Figure 6 are reproduced from a 2009 paper by Sproules et al.[47] Also shown in Figure 3 are the compositions of the respective SOMOs for the neutral rhenium TP complexes.

$V(S_2C_2Ph_2)_3$ (7) and Related 3d Metal Complexes. The structure of **7** was determined crystallographically in 1966 using film methods.[30] Figure 7 presents a drawing of the molecular structure as originally published.[31] The TP coordination of the rhenium analogue was also found for **7** with only a very minor trigonal twist distortion. The average bond distances in the structure were found to be as follows: V−S 2.337(4) Å, C−S 1.685(10) Å, and C−C 1.46(2) Å. Overall, the prism dimensions of the two structures as defined by intraligand and nearest interligand S···S distances of ~3.05 Å were essentially the same despite the different covalent radii of vanadium and rhenium in a given oxidation state. The ambiguity of the oxidation-state assignment and the fact that the ligands could not all be dianionic indicated clearly the redox involvement of the ligands in an electronic structural description of **7**.

On the basis of the isomorphism of the crystals of **7** and its neutral chromium analogue, the latter was assigned TP coordination, and from a comparison of the electronic spectra of **7**, $Cr(S_2C_2Ph_2)_3$, and **7**$^-$, the anionic complex was also suggested to be TP, but on the basis of electrochemical measurements, it was proposed that the more reduced complexes such as V(tdt)$_3^{2-}$ would distort toward the octahedral geometry, going from D_{3h} to D_3 by a trigonal twist constrained only by the dithiolene bite angle.[30]

As with its rhenium analogue, the molecular structure of **7** was redetermined using modern crystallographic methods (intensity data from a four-circle diffractometer at 100 K), this time by

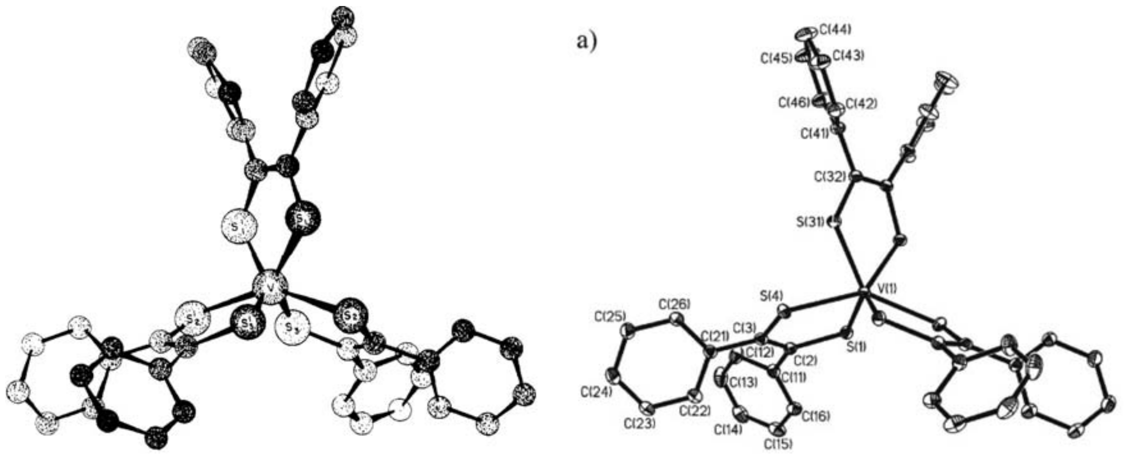


Figure 7. Structural drawings of 7 as originally determined in 1966 (left) and as redetermined by Sproules et al. in 2010. Reproduced with permission from refs 31 and 48. Copyright 1967 and 2010 American Chemical Society.

Sproules and Wieghardt as part of a recent reinvestigation on tris(dithiolene) complexes and their electronic structures.[48] Again, the earlier structural results were confirmed, but with more accurate bond distances and angles [average V−S of 2.3440(3) Å, C−S of 1.702(1) Å, and average olefinic C−C distance of 1.399(2) Å].

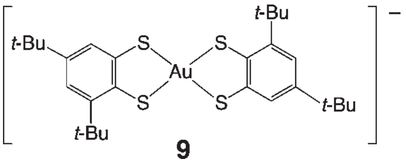
The electronic structure of **7** was also discussed briefly in a subsequent full report by us[31] that included the following comments:

> "In suggesting a modification of the $Re(S_2C_2Ph_2)_3$ molecular orbital ordering [for the V analog], we take cognizance of the fact that antibonding levels of d symmetry and character are more stable in first-row complexes than in analogous second- and third-row situations .... Thus, it is reasonable to suggest that an inversion of the $2a_2'$-$3a_1'$ order occurs in going to the first-row $M(S_2C_2R_2)_3$ systems such that we have $4e' < 3a_1' < 2a_2' < 5e' < 4\ e''$. The proposed ground state is therefore $...(4e')^4\ (3a_1')^1 = {}^2A_1$. This means that if the $4e'$ level is assigned to the ligand (as is traditional), the complex is formally a d^1 complex of V(IV) and $[(S_2C_2Ph_2)_3{}^{4-}]$ and the ligand system is fully oxidized by two electrons from its classical tris dithiolate state ... it is clear that the ligand system is at least partially oxidized and the $4e'$ level [noted above as having significant metal and ligand character] is strongly delocalized over the MS_2C_2 chelate ring.
>
> It is also worth noting that the assignment of the unpaired electron to $3a_1'$ ($s + z^2$) is not in conflict with the esr data which show a nearly isotropic g value of 1.99 and a substantial ^{51}V hyperfine splitting of 61.6 gauss."

Dithiolene Redux: Epilogue. By the end of the 1960s, the key protagonists in this surge of interest in dithiolene complexes had moved on to other chemical challenges such as (1) nitrogen fixation and cobaloxime complexes as B_{12} models (Schrauzer), (2) biological electron transfer, metalloenzyme electronic structure, and metal complex photochemistry (H.B.G.), and (3) iron−sulfur clusters for electron transfer in biology and modeling the iron−molybdenum cofactor (FeMoco) in nitrogenase (Holm). Holm did return to dithiolene chemistry after it was found that molydopterin units of oxo transferase enzymes were indeed molybdenum dithiolene moieties,[49−51] and H.B.G., working with Bill Connick, investigated the photochemistry of platinum dithiolene[52] following seminal research by R.E. and co-workers on luminescent heteroleptic dithiolene complexes of the platinum group elements.[53−55] Work on dithiolene complexes is still actively pursued with focus on pterin enzyme models[51,56−58] and applications such as laser Q switches (nickel dithiolenes) and anisotropically conducting materials.[59−61]

We have seen a renaissance in research on dithiolene complexes and their analogues in the past 15 years. Several investigators, most notably Wieghardt and his team, have introduced new methods of characterization, measurement, computation, and analysis in reinvestigations of some of the classic systems. This work was launched initially to examine electronic structures but increasingly has focused on interpretations of the reaction chemistry and catalysis. A 2002 paper by Bachler, Olbrich, Neese, and Wieghardt[62] tackled the question of ligand noninnocence through density functional theory (DFT) and complete self-consistent-field computations using Noodleman's broken-symmetry (BS) formalism. In this analysis, a new index for the diradical character was proposed based on symmetry breaking and led to the conclusion that nickel bis(*o*-catcholate) complexes had the *largest* and nickel bis(benzenedithiolate) complexes the *smallest* amount of singlet diradical character, based, in part, on the *relative* stability of the partially oxidized form of the ligand, which, in turn, relates to the stability of the O-, S-, and N-donor atoms to form partial double bonds with ring C atoms. Most importantly, the authors wrote "the diradical character of all complexes suggests the presence of Ni(II) central atoms."[62]

In a subsequent studies from the Wieghardt laboratory, the question of the ligand redox level and metal formal oxidation state was addressed experimentally using electronic, EPR, and Mössbauer spectroscopies and computational methods. Particularly revealing was the work on the gold(III) complex anion **9** and its $1e^-$ oxidation product.[63] From the absence of ^{197}Au hyperfine in the EPR of the neutral $S = {}^1/_2$ complex, the near identity of the Mössbauer spectra of **9** and its $1e^-$ oxidation product, and the presence of an intervalence charge transfer between dithiolene ligands, it was concluded that the *neutral* complex contained Au^{III}, as did **9**, and a dithiobenzosemiquinone ligand (in addition to the remaining di-*tert*-butylbenzenedithiolate).



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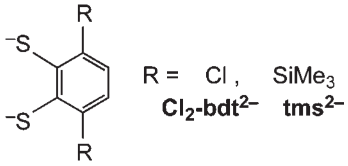
Further computational work by Ray et al.[64] was carried out on $[M(bdt)_2]^{n-}$ complexes (n = 0−2; M = Ni, Pd, Pt, Cu, Au) in conjunction with highly accurate crystal structure determinations on representative complexes and electronic and EPR spectroscopic investigations. While the spin-unrestricted calculations were done for the $[Au(bdt)_2]^{n-}$ system, the bonding scheme was said not to change qualitatively for nickel, palladium, and platinum. For all of these complexes, the metal was said to have a d^8 configuration with an overall complex charge dependent on the net ligand charge. This meant that, for the paramagnetic complex $[Ni(bdt)_2]^-$ with a spin-doublet ground state, the metal ion was Ni^{II} and the ligands were bdt^{2-} and bdt^-. On the basis of the calculated orbital energies, the ground state for $[Ni(bdt)_2]^-$ was assigned as $^2B_{2g}$, which, on a symmetry basis, was the same as that proposed in 1964 by Maki et al.[35] but, on an electron distribution basis, was more consistent with the results of Shupack et al.[33] The change from $[Ni(bdt)]^{2-}$ to the paramagnetic monoanion occurred not at the metal ion but at the ligand.

Another powerful experimental approach to the determination of ligand redox levels was taken by Holm in 2002 in collaboration with Solomon, Hodgson, and Hedman for the complexes $[Ni(S_2C_2Me_2)_2]^{n-}$ for n = 0−2.[34] Specifically, XAS measurements including S K-edge and metal L-edge pre-edge features were employed to determine the nickel dithiolene covalency, ligand oxidation level, and therefore nickel oxidation state. The sulfur features were found not to differ substantially for the three redox-related nickel bis(dithiolene) species, in distinct contrast to what had been observed for model ferrous/ferric tetrathiolates. For the $[Ni(S_2C_2Me_2)_2]^{n-}$ complexes, the authors wrote "the shift in the rising-edge position gives ... the increase of $Z_{\rm eff}$ for S to be only 0.4 eV between the di- and monoanionic complexes and approximately the same between the monoanionic and neutral complexes. The constant energy position of the pre-edge features requires a similarly constant compensation of the d manifold. The smaller change in the d-manifold of the Ni dithiolenes (0.4 eV) compared to that of the thiolate complexes (1.5 eV) indicates a smaller change in $Z_{\rm eff}$ on the metal atom, arguing for larger ligand characters in the Ni dithiolene complexes. In addition, this indicates that oxidation of the Ni dithiolene complexes (from $-2 \rightarrow -1 \rightarrow 0$) *mainly occurs on the ligand*."[34] (our italics)

The DFT calculations showed that the frontier orbitals for $[Ni(S_2C_2Me_2)_2]^{n-}$, $n = -2, -1, 0$, possess substantial dithiolene character. The highest occupied MO (HOMO) in the dianion that becomes the lowest unoccupied MO (LUMO) in the neutral complex is an orbital of b_{2g} symmetry, which is mainly composed of an out-of-phase combination of the dithiolene $3\pi_v$ functions, that is, the $+ - - +$ π function. As mentioned above, the bonding was said to be "inverted", meaning that the frontier orbitals have greater ligand than metal character and that a decrease in the ligand character would lead to a more covalent bond rather than a less covalent bond that would result from the same change in "normal" metal−ligand bonding. Experimentally, the "inverted" bonding model was supported by high intensities of the S pre-edge features that quantify the S 3p character in the valence orbitals as greater than 50%.

In 2008, the same principal investigators applied similar methods, i.e., S K-edge XAS and DFT calculations, in an investigation of the electronic structures of molybdenum tris(dithiolene) complexes.[65] According to the authors, for the $[Mo(S_2C_2Me_2)_3]^{n-}$ complexes (n = −2, −1, and 0), "The pre-edge features (of the S K-edge spectra) ... have approximately the same energy through the series, which is in contrast to the ~1.0 eV decrease in the pre-edge observed upon oxidation of a ferrous tetrathiolate [model]. Specifically, in going from $[Mo(S_2C_2Me_2)_3]^{2-}$ to $[Mo(S_2C_2Me_2)_3]^{1-}$, there is no change in energy of the pre-edge ..., and in going from $[Mo(S_2C_2Me_2)_3]^{1-}$ to $[Mo(S_2C_2Me_2)_3]$, the energy of this pre-edge increases by 0.23 eV. A fraction of this increase can be attributed to an increase in ligand field strength ..., so the remaining ~0.1 eV increase in pre-edge energy indicates that the sulfur $Z_{\rm eff}$ increases, that is, the dianion and monoanion undergo ligand-based oxidation." The authors further stated that "Therefore, the formally Mo^V and Mo^{VI} complexes [*i.e.*, $[Mo(S_2C_2Me_2)_3]^{1-}$ and $[Mo(S_2C_2Me_2)_3]$] have the same number of electrons in the d manifold as the Mo^{IV} complex ($[Mo(S_2C_2Me_2)_3]^{2-}$) (*i.e.*, d^2 configurations)."[34] Both the neutral and monoanionic complexes were found crystallographically to be TP, albeit with envelope conformations for the chelate rings to give an overall C_{3h} coordination sphere. The S K-edge data were also compared to those of another molybdenum tris(dithiolene) series, $[Mo(t\text{-}Bu_2\text{-}bdt)_3]^{n-}$ (n = 0 and −1), collected by Kapre et al.[66] The neutral complex $[Mo(t\text{-}Bu_2\text{-}bdt)_3]$, which possessed TP coordination, had a S K-edge spectrum similar to that of $[Mo(S_2C_2Me_2)_2]$, while the corresponding anion, which was found crystallographically to have a twist angle of 31.7°, exhibited significant differences in its S K-edge spectrum from that of $[Mo(S_2C_2Me_2)_2]^-$.

The studies described above from the Wieghardt and Solomon laboratories set the table for the more recent papers by Sproules et al. that have shed new light on the electronic structures of TP tris(dithiolene) complexes and their redox-related analogues. In the first of these papers, neutral rhenium and redox-related tris(dithiolene) complexes were examined for the aryldithiolate ligands bdt, tdt, Cl_2-bdt, and tms.[47] The molecular structure of $Re(tms)_3^-$ as its $C_8H_{16}N^+$ salt was shown crystallographically to be TP, while the neutral complexes $Re(bdt)_3$ and $Re(tms)_3$ yielded optimized TP structures computationally. The more reduced $Re(dithiolene)_3^{n-}$ (n = 2 and 3) complexes, as well as some of the monoanions, were calculated to be intermediate between TP and octahedral coordination. Spin-unrestricted DFT calculations with the inclusion of scalar relativistic effects were used for geometry optimizations and analyses of spin distributions in the complexes.



Experimentally, there were two particularly important investigations of these systems. The first involved analyses of EPR spectra of the neutral complexes that confirmed the earlier observations of Porte.[46] Specifically, $Re(bdt)_3$ was found to exhibit a narrow signal consistent with a SOMO having pure ligand character. Anisotropy of the **g** tensor due to metal-based electron spin and hyperfine couplings from ^{185}Re and ^{187}Re (both $I = {}^5/_2$) was not observed. The EPR spectra and simulation parameters derived therefrom for $Re(bdt)_3$, $Re(Cl_2\text{-}bdt)_3$, and $Re(tms)_3$ were essentially identical, leading to the assignment of their electronic configuration as $...(3a_1')^2(4e')^4(2a_2')^1$ with a $^2A_2'$ ground state and a majority of unpaired spin on the dithiolene ligands. Sproules et al. concluded that "Therefore, we can definitively affirm the electronic structure of these neutral (trigonal prismatic) tris(dithiolene)rhenium complexes as $[Re^V(L^\bullet)(L)_2]$."[47]

XAS measurements provided the second set of results that were used in the analysis of the $Re(dithiolene)_3{}^{n-}$ systems. The Re L_1-edge spectra for $Re(bdt)_3$ and its monoanion were consistent with Re^V, while the S K-edge XAS data were compatible with "an extra hole in the dithiolene ligands". Both results were therefore consistent with the $[Re^V(L^\bullet)(L)_2]$ formulation. Sproules et al. concluded that "The most salient feature of this study is the observation that the neutral $[Re(L)_3]$ ($S = {}^1/_2$) and the monocation $[Re(L)_3]^+$ ($S = 0$) contain both a TP ReS_6 polyhedron and a central Re^V ion (d^2, $S_{Re} = 0$) with two electrons in $5d_{z^2}$, namely, $(3a_1')^2$ in D_{3h} symmetry. The unpaired electron in neutral $Re(bdt)_3$ occupies a pure ligand MO, $(2a_2')^1$. ... Both the neutral and monocationic forms [of $Re(L)_3$] possess oxidized forms of the ligands (formally one and two ligand holes, respectively).[47]" The assignment of the SOMO in the neutral $Re(L)_3$ complexes was thus the same as that reported by Al-Mowali and Porte.[46]

The second study by Sproules et al.[48] was focused on the vanadium complex **7**, its analogues with other dithiolene ligands, and redox-related members of the series $V(L)_3{}^n$ (n = +1, 0, −1, −2, −3, and −4). The entire redox series was not established experimentally for any given dithiolene ligand, but computationally the $V(L)_3$ complexes were studied for different redox members of the series using BS DFT calculations for structure optimization and electronic properties. Crystallographically, **7**, its monoanion, and $V(bdt)_3{}^-$ were found to have TP coordination, while the dianion $V(mnt)_3{}^{2-}$ showed significant twisting toward octahedral coordination (average twist angle of ~38° and approximate D_3 symmetry). EPR spectra for both neutral and dianionic $V(L)_3$ complexes were employed in the SOMO assignments. Despite the $2e^-$ difference between the neutral and dianionic species, their EPR spectra were essentially identical, exhibiting an isotropic g value of ca. 1.98 and an isotropic hyperfine coupling of $\sim 58 \times 10^{-4}$ cm^{-1} for ^{51}V ($I = {}^7/_2$). The observations were interpreted to mean that the *same* orbital was the SOMO in the $2e^-$ separated forms $V(L)_3$ and $V(L)_3{}^{2-}$ and that the SOMO was the V $3d_{z^2}$ orbital of a_1' symmetry. This finding, in turn, established that the vanadium oxidation state was IV+, assuming that the HOMO−1, HOMO−2, and HOMO−3 levels were ligand-based and that the dithiolate ligands were collectively partially oxidized, i.e., $(L)_3{}^{4-}$.

In order for the SOMO of $V(L)_3$ and $V(L)_3{}^{2-}$ to be the same, a MO energy level inversion must occur, consistent with other spectroscopic and electronic properties and the calculated electronic structures. The two orbitals in question for the inversion were the $3a_1'$ MO, which was mainly V d_{z^2} in character, and the exclusively thiolate-based $2a_2'$ function. The V K-edge XAS data for the $V(L)_3{}^n$ systems indicated that the vanadium oxidation state was the same for the oxidation levels n = 0, −1, and −2 in support of the proposed inversion. Consistent with this conclusion were the nearly identical V−S bond distances that were determined for the neutral and mono- and dianionic $V(L)_3{}^n$ structures. The notion of a MO level inversion in going from neutral to dianionic tris(dithiolene) complexes of vanadium had actually been put forward by Kwik and Stiefel in 1973 based on a single-crystal EPR study of $V(mnt)_3{}^{2-}$ doped into $[AsPh_4]_2[Mo(mnt)_3]$.[67] The results "were totally consistent with the unpaired electron being in a nondegenerate MO which is substantially d_{z^2} on the metal ion.... For the V complexes, this requires a reversal of metal and ligand levels in going from the dianionic to the neutral species. In other words, the dianion has a roughly $l^2\,d^1$ configuration [l = ligand] while the neutral complex has a roughly $d^1\,l^0$ configuration. This type of reversal does not seem unusual as increasing positive charge will often stabilize metal levels more than ligand levels (*i.e.,* the metal will always bear a larger part of the net positive charge no matter where the electrons are removed from)."[67]

Experimental measurements to provide additional insight into the electronic structural description of the $V(L)_3{}^n$ complexes were S K-edge XAS spectra that revealed a pre-edge feature for **7** and its redox-related monoanion but not seen for any of the $V(L)_3{}^{2-}$ anions examined. This feature was taken as evidence of *partial ligand oxidation* from the fully reduced dithiolate level as indicated in eq 2 from Sproules et al.[48]

$$[V^{IV}(L_3{}^{4-})]^0 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [V^{IV}(L_3{}^{5-})]^{1-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [V^{IV}(L_3{}^{6-})]^{2-} \qquad (2)$$

DFT calculations by Sproules et al.[48] gave the energy level ordering for **7** as $4e' < 3a_1' < 2a_2' < 5e' < 4e''$. While the $4e'$ level was extensively delocalized over vanadium and dithiolene, it had greater ligand character and was therefore designated as dithiolene-based for the oxidation-state assignment. As the system was increasingly reduced, the proposed level inversion needed to maintain the vanadium oxidation state as fixed in eq 2 involved the metal-based $3a_1'$ orbital and the ligand-localized $2a_2'$ function composed mainly of sulfur orbitals. Interestingly, this meant that, for the *diamagnetic* $V(L)_3{}^-$ monoanion, two electrons in different orbitals would be antiferromagnetically coupled to produce the observed result. For the dianions (and beyond), the ligands were fully reduced, i.e., $(L)_3{}^{6-}$, and the complexes were twisted toward octahedral.

For **7**, the electronic configuration was thus $(4e')^4(3a_1')^1$ with a $^2A_1'$ ground state. The vanadium oxidation state was IV+, and the ligands were oxidized by $2e^-$ from the dithiolate formulation to $(L)_3{}^{4-}$. EPR, magnetic, and XAS data were all consistent with this formulation. The unpaired electron would be in a mainly V $3d_{z^2}$ orbital, and the three bidentate ligands accommodated two oxidative holes in the empty $2a_2'$ ligand orbital (which is the LUMO of the neutral species). It is extraordinarily gratifying that *this is exactly the same ordering put forth in 1967* by us,[31] albeit based on more complete experimental data and more extensive computational analysis, and the results overall support fully the idea that TP coordination depends on partial ligand oxidation from the classical dithiolate formulation. In this context, partial ligand oxidation also led to square-planar coordination for what initially appeared to be extraordinary or unprecedented metal d^n configurations.

The dithiolene dawn of 50 years ago was a period of fervent activity in which new and improving structural and spectroscopic methods were being applied, conventional formalisms were being challenged, and new bonding models were being formulated. We hope you agree that this story sets an interesting context for current and future research on the chemistry of dithiolenes, other redox-active ligands, and their complexes.

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