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Review

Trigonal prismatic coordination in tris(dithiolene) complexes: Guilty or just non-innocent?

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Contents

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ABSTRACT

The discovery of trigonal prismatic (TP) coordination in tris(dithiolene) complexes is recounted. The research was stimulated by the efforts of Gray, Schrauzer, Holm and Davison in the 1960s on the chemistry of dithiolene complexes that showed multiple reversible electron transfer processes and challenged conventional oxidation state assignments. The structures of $Re(S_2C_2Ph_2)_3$, $V(S_2C_2Ph_2)_3$ and $Mo(S_2C_2H_2)_3$ were reported at that time. Bonding pictures based on semiempirical molecular orbital calculations were presented and the basis for stability of TP coordination was put forward based on partial oxidation of the unsaturated 1,2-dithiolate ligands. The structures of $M(L)_3{}^n$ complexes for M = Groups 5–7 and $n = 0, -1, -2, -3$ from the Cambridge structural database are tabulated. The results show that for any $M(L)_3$ system as the magnitude of n increases, the coordination geometry twists to intermediate between TP and octahedral. The notion of redox-non-innocence in the dithiolene ligands is revisited through the recent work of Wieghardt including two studies that focus on the molecular and electronic structures of $Re(L)_3{}^n$ and $V(L)_3{}^n$ complexes. New experimental work is briefly summarized and the bonding in these systems is reanalyzed. A comparison is given between the early studies of the 1960s and the experimentally and computationally more complete studies recently published.

1. Prologue

In 1965 the structure of the first trigonal prismatic complex, $Re(S_2C_2Ph_2)_3$ (**1**), was reported [1]. Prior to that report, the only observation of trigonal prismatic (TP) coordination at a metal center was in extended binary solids such as MoS_2 and WS_2 having "softer", more polarizable anions [2]. Shortly after the initial structural report of **1**, several papers appeared addressing the spectroscopic properties and electronic structure of trigonal prismatic complexes exemplified by **1** [3,4]. These papers, which addressed the question of the uniquely observed coordination geometry, indicated the inadequacy of the oxidation state formalism in describing the complex. While **1** was indeed new in terms of trigonal prismatic coordination, it was also a member of the set of dithiolene complexes that commenced to be studied vigorously in the early-1960s [5–24]. Interest and activity in dithiolene complexes was spearheaded principally by three research groups – one by Schrauzer at Munich and the Shell Development Company (before moving to UC-San Diego), the second by Gray at Columbia, and the third by Holm and Davison at Harvard. All of these researchers were drawn to the dithiolate complexes because of the numerous facile reversible electron transfers that the complexes showed, the very different and intense colors that they exhibited, and the prevalent square planar coordination that was found with many metal ions, includ-

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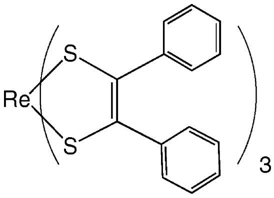
ing those of d^n configuration not usually seen with square planar complexes. The magnetic properties of the complexes also proved of interest to these researchers, as did analyses of EPR spectra that certain members of the set were found to exhibit. The interest in bis(dithiolene) complexes was so keen that Schrauzer, who first synthesized **1**, initially considered it to be a bis(dithiolene) complex with an unprecedented square planar coordination for Re.



1

After a decade of vigorous activity on dithiolene complexes (see the review by McCleverty which coined the term"dithiolene" [25]), vigorous research efforts on these systems subsided, although new complexes continued to be prepared, the relevance of dithiolenes to certain biological systems was realized, especially for Mo and W systems [26–31], luminescence for late metal dithiolate complexes was found [32–34], potential uses such as NIR laser dyes for Ni dithiolene complexes were uncovered [35–38], and new conductive and/or functional materials based on bis(dithiolene) complexes were reported [39,40]. It was, however, the efforts of Wieghardt and his collaborators that kindled a genuine renaissance of interest in dithiolene complexes with the renewed realization that dithiolene ligands were redox active when complexed to metal ions. Wieghardt was able to bring a new armamentarium of methods from theoretical to experimental to bear on the question of the electronic structure of dithiolene complexes. Indeed, these efforts have stimulated interest in complexes of redox active (or at least non-innocent) ligands beyond dithiolenes and have motivated thinking about their use in a variety of venues from catalysis to optoelectronics. In a 2002 article, Ward and McCleverty [41] attempted to define ligand "non-innocence" by beginning with a Jorgensen definition of ligand "innocence" [42], meaning that it allows the metal oxidation state of a complex to be defined. When both ligand and metal frontier orbitals are potentially redox-active and close to each other in energy, then non-innocence can occur. Thus the difficulty with dithiolenes and noninnocence "is not just that the ligands are redox active, but that there is strong mixing between ligand and metal orbitals such that assignment of oxidation states to individual metal and ligand components is difficult [41]."

This review focuses on the tris(dithiolene) complexes from the discovery of **1** to the present. It is in part a personal account because I was involved in the first molecular and electronic structural studies of the systems. It is also personal because this issue of *Coordination Chemical Reviews* celebrates Harry Gray's 75th birthday and his remarkable impact on chemistry. Harry was one of the individuals who really opened up dithiolene chemistry with its excitement and allure. As a student of Harry's, I was drawn into the vortex of dithiolene chemistry that led with some serendipity to the structure of **1**. As much as I write this review to honor Harry, there is another individual to whom this review must be dedicated. Ed Stiefel and I entered graduate school in September 1963 and worked together under Gray's enthusiastic and compelling guidance. While I focused on crystallographic studies with some early molecular orbital calculations thrown in, Ed conducted spectroscopic, electrochemical and magnetic studies putting the flesh of bonding and reactivity on the bones of crystal structure. Ed realized the importance of the new coordination geometry more than anyone and he pursued the study of TP coordination after he started his academic career. After a truly successful career that included many years at Exxon and his final years at Princeton, Ed passed away in 2007. This review is also dedicated to his memory.

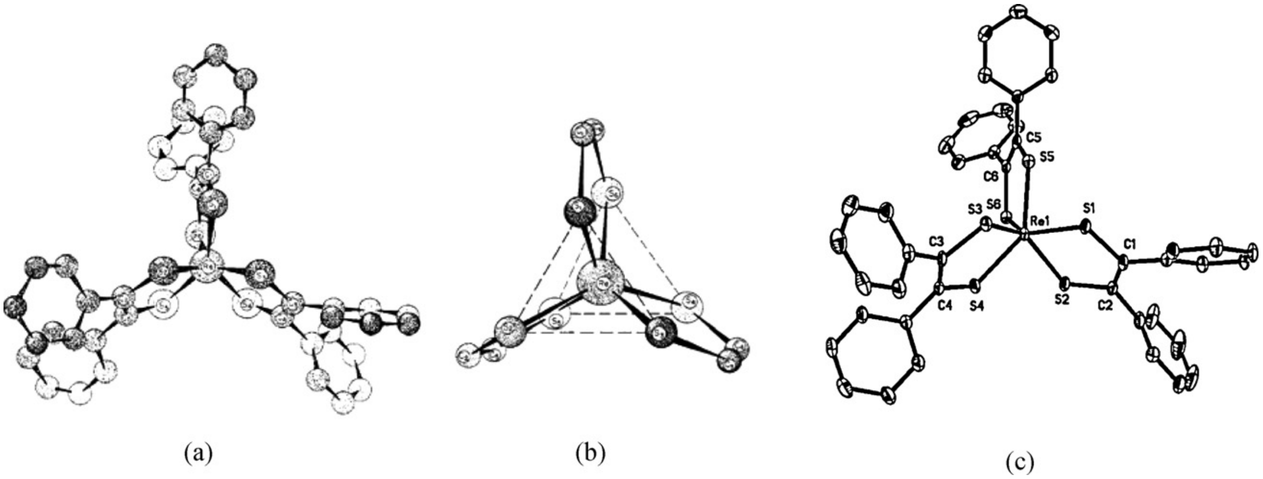
2. The discovery of trigonal prismatic coordination – the structure of $Re(S_2C_2Ph_2)_3$

In July 1964, I returned to Brookhaven National Laboratory to work with Jim Ibers on the crystal structure of $Re(S_2C_2Ph_2)_3$, **1**, and a square planar Co bis(dithiolene), $Co(tdt)_2{}^-$ (tdt = toluene-3,4-dithiolate) that had a formal Co oxidation state of +3. The prior summer we had determined the first structure of a dithiolene complex, namely, $Ni(mnt)_2{}^{2-}$ (mnt = maleonitriledithiolate), as the Et_4N^+ salt [5,43]. The structure had been determined by film methods, as would the structure of $Co(tdt)_2{}^-$ as its $MePh_3As^+$ salt [44]. The crystals of **1** had been prepared by Schrauzer and sent to Gray. Schrauzer's initial formulation of the complex as a bis(dithiolene) had been corrected, but little else was reported about the compound [9].

At Brookhaven Ibers was interested in using a diffractometer to measure the intensity data and this task fell to me to do. The diffractometer was manually controlled with no computer interface so each diffraction had to be located and centered by hand in the detector aperture. Computers at that time were centralized, clunky affairs, not geared to instrument control and definitely pre-PC. Because the diffractions seemed broad, a $\theta/2-\theta$ scan method was abandoned and instead the intensity at positioned peak heights was measured for a fixed amount of time with background counted on each side of the diffraction profile. While this arduous procedure did indeed yield intensity data for the structure shown in Fig. 1a, it was by many crystallographic criteria a poor structure [45,46]. Because of a diffraction overlap problem 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 Re). Ibers wrote and used a group refinement procedure for the phenyl rings. Despite these shortcomings in the data and the hurdles we had to overcome in the refinement, a clearly defined trigonal prismatic coordination geometry was established for **1** as shown in Fig. 1b, albeit with significant variations in the S–C distances (1.62 (4)–1.75 (3) Å) and moderately large esd's in the other metrical parameters.

The structure of **1** was subsequently redetermined in 2006 using a crystal from the same batch that had been given to me 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 [46]. The redetermination with complete anisotropic refinement confirmed in every way the trigonal prismatic coordination of **1** while producing much more accurate and consistent Re–S and S–C bond distances than had been originally reported. The refined structure from this redetermination is shown in Fig. 1c.

Subsequent to the initial structural report of **1** in 1965, Stiefel and Gray characterized the system by spectroscopic, electrochemical and magnetic measurements to confirm that the TP coordination was maintained in solution, and based on these results and similar measurements of other tris(dithiolene) complexes, extended the possibility of TP coordination to closely related systems [3]. For **1**, three reversible reductions and one reversible oxidation were seen, as was a bulk susceptibility of 1.73 B.M. for a doublet ground state, and a broad EPR signal having $\langle g \rangle = 2.015$ suggesting an orbitally non-degenerate ground state. The $Re(tdt)_3$ complex (tdt = toluene-3,4-dithiolate) exhibited an essentially identical EPR spectrum and was also assigned a TP coordination geometry.



(a) (b) (c)

Fig. 1. Diagrams showing (a) the molecular structure of $Re(S_2C_2Ph_2)_3$ (**1**) as originally determined; (b) the inner coordination geometry of **1**; and (c) a thermal ellipsoid plot of the redetermined structure of **1** in 2006. Reproduced by permission from Refs. [1,40,41].

In 1966, Stiefel et al. published a full paper on the electronic structure and spectroscopy of **1** including a molecular orbital description of its TP coordination [47]. For the tris(dithiolene) complexes of Re, W, and Mo with the ligands $S_2C_2Ph_2$ and tdt, the similarity of electronic spectra with two dominant transitions below 30,000 cm^{-1} and reversible electrochemical processes supported the assignment of trigonal prismatic or slightly distorted trigonal prismatic coordination to these complexes. A structure determination by Smith et al., reported at nearly the same time confirmed the TP coordination for the neutral $Mo(S_2C_2H_2)_3$ complex although the chelate rings showed an envelope-type conformation with a fold angle α of ~18° giving the complex overall C_{3h} symmetry [48]. In the 1966 paper by Stiefel et al. [47], the molecular orbital description was based on a semi-empirical approach and revealed in the results the ambiguities that dithiolene complexes possess in terms of conventional oxidation state formalism. An energy level diagram of the orbitals of interest from that paper is shown in Fig. 2 with D_{3h} symmetry labels and the z direction coincident with the trigonal axis. The π_v designation in Fig. 2 refers to the out-of-plane π orbitals of which there are four for each S–C–C–S chelating ligand; $3\pi_v$ refers to the third highest of these orbitals that, if filled, gives ene-dithiolate character to the ligand. The π_h functions are lone pair orbitals in the chelate ring plane for sp^2 hybridized S donors. Both π_v and π_h wavefunctions were made into symmetry adapted linear combinations and handled that way in the calculation.

The paper then goes on to state:

"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 $V(S_2C_2Ph_2)_3$ 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 over-all electronic structures of these complexes [47]."

Additionally, Stiefel et al. proceeded to consider a possible factor that leads to stabilization in these literally unprecedented tris(dithiolene) complexes. Specifically, it was noted that the rectangular sides of the trigonal prism were actually squares with intra-

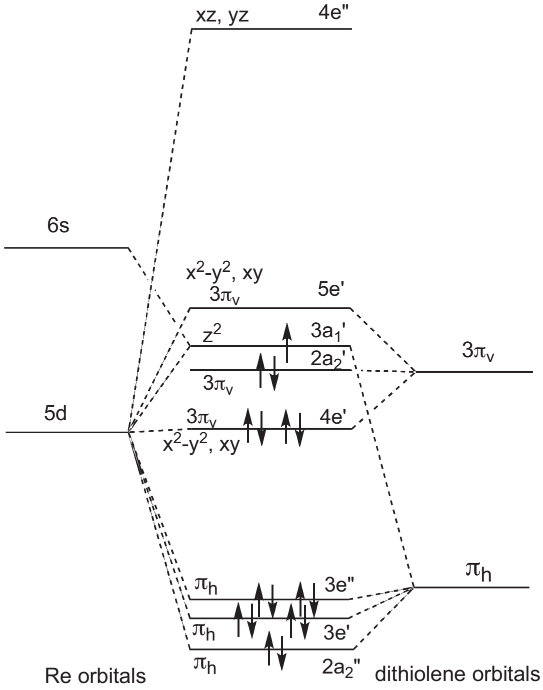


Fig. 2. A diagram showing the orbitals of interest in formulating the ground and lowest excited states of $Re(S_2C_2Ph_2)_3$ (**1**) from Stiefel et al. [42].

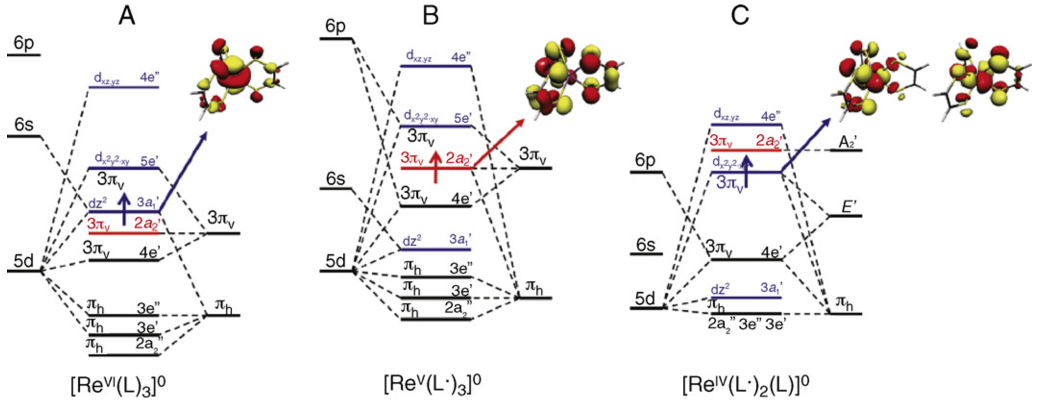


Fig. 3. A diagram from the paper by Sproules et al. showing the different molecular orbital energy level schemes proposed for **1**: (a) from the work of Stiefel et al.; (b) from the study by Al-Mowali and Porte; and (c) from the work by Schrauzer and Mayweg. Reproduced with permission from Ref. [46].

and nearest inter-chelate S···S distances of ~3.05 Å, that while nonbonding are relatively short. It was therefore proposed that weak direct S···S bonding interactions exist and serve to stabilize the TP coordination geometry. 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. Stiefel was the first among the authors to recognize and suggest this possibility, which connects directly to the redox non-innocence of the dithiolenes suggested from studies on the bis(dithiolene)s by Gray, Holm, Schrauzer and their respective collaborators and co-workers.

Shortly after the paper by Stiefel et al., detailing the electronic structure of $Re(S_2C_2Ph_2)_3$ and related tris(dithiolene) complexes, Schrauzer and Mayweg [49] published a different molecular orbital scheme based on simple parameterized Hückel molecular orbital theory that for **1** gave the following configuration and ground state: ... $(3a_1')^2\ (4e')^4\ (5e')^1 = {}^2E'$, while in 1975 following a reexamination of the EPR spectra of **1** and $Re(tdt)_3$, Al-Mowali and Porte [50] assigned the electronic configuration and ground state as: ... $(3a_1')^2\ (4e')^4\ (2a_2')^1 = {}^2A_2'$. The basis of Porte's modification of the energy level ordering was that the EPR results for **1** and $Re(tdt)_3$ showed small g-tensor anisotropy, isotropic $\langle g \rangle$ values near 2.002 and no Re hyperfine coupling - features more consistent with a sulfur-containing radical than a system having a large amount of unpaired spin on the Re atom. The three different molecular orbital energy level orderings are shown in Fig. 3 reproduced from a 2009 paper by Sproules et al. [51], that is discussed further below. Also shown in Fig. 3 are the compositions of the respective SOMO's for the neutral Re trigonal prismatic complexes.

3. Trigonal prismatic coordination in 3d metal complexes – the structure of $V(S_2C_2Ph_2)_3$

To probe the notion of redox non-innocence further and examine the electronic structure of neutral tris(dithiolene) complexes of first transition series metals, the complex $V(S_2C_2Ph_2)_3$ (**2**) reported by Schrauzer was resynthesized at Columbia following the procedure described by Davison et al. [19] that involved benzoin condensation with P_4S_{10} followed by halovanadate addition and oxidation. The structure of **2** was determined crystallographically, this time using film methods [52]. Fig. 4 presents a drawing of its structure as originally published [53]. The trigonal prismatic coordination of **1** was also found for **2** 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 intra- and nearest inter-ligand S···S distances of ~3.05 Å are essentially the same despite the different covalent radii of V and Re in a given oxidation state. The ambiguity of oxidation state assignment and the fact that the ligands could not all be dianionic [as it would necessitate V(VI)] indicated clearly the redox involvement of the ligands in an electronic structural description of the TP complex $V(S_2C_2Ph_2)_3$.

Based on isomorphism of the crystals of **2** and its neutral Cr analog, the latter was assigned a trigonal prismatic coordination, and from comparison of the electronic spectra of **2**, $Cr(S_2C_2Ph_2)_3$ and $V(S_2C_2Ph_2)_3^-$, the anionic complex was also suggested to be TP [52]. However, based on electrochemical measurements, it

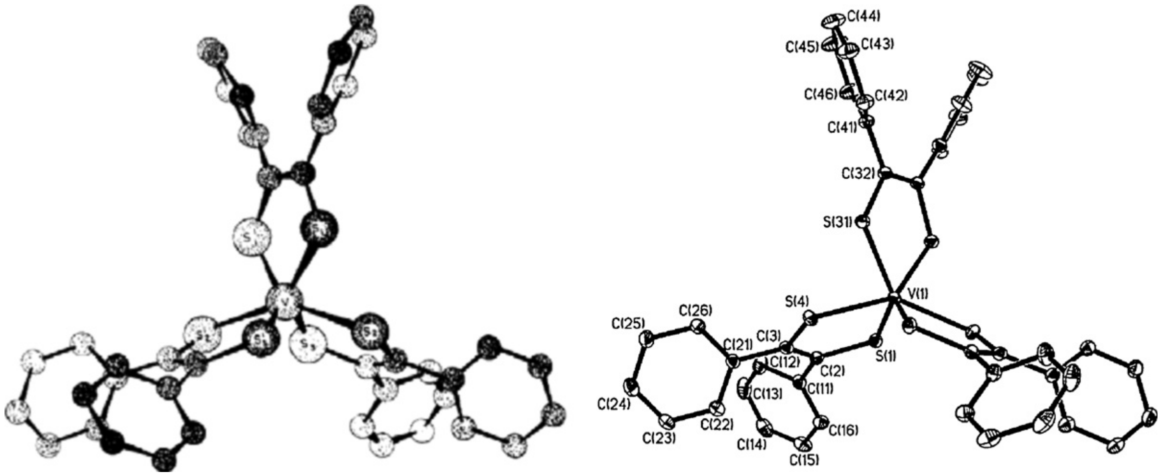


Fig. 4. Structural drawings of $V(S_2C_2Ph_2)_3$ (**2**) as originally determined in 1966 (left) and as redetermined by Sproules et al. in 2010. Reproduced by permission from Refs. [48,49].

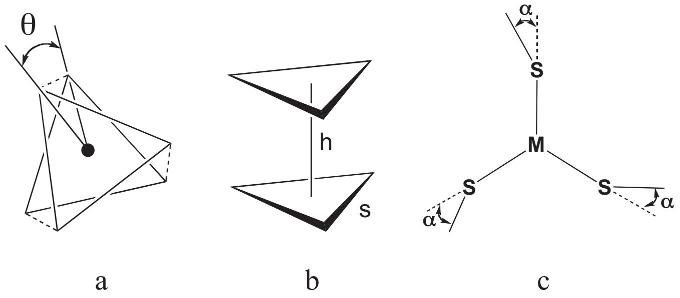


Fig. 5. Structural distortion parameters for trigonal prismatic coordination: (a) the twist angle θ which is 0° for a perfect TP and 60° for an octahedron; (b) the definitions of s and h for the parameter s/h used by Stiefel and Brown [50]; and (c) the chelate ring fold angle α.

was proposed that the more reduced complexes such as $V(tdt)_3{}^{2-}$ may distort towards the octahedral geometry, going from D_{3h} to D_3 by a trigonal twist constrained only by the dithiolene bite angle.

As with **1**, the crystal structure of $V(S_2C_2Ph_2)_3$ has been redetermined using modern crystallographic methods (intensity data from a four-circle diffractometer at 100 K), this time by Sproules and Wieghardt as part of a recent reinvestigation on tris(dithiolene) complexes and their electronic structures that is examined further below [54]. Again, the earlier structural results are 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] and the following statement: “Overall, the agreement of these two structure determinations is exceptional, a testament to the high quality work performed in 1966.”

The electronic structure of **2** was also discussed in a subsequent full report by Eisenberg and Gray 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 $4e' < 3a_1' < 2a_2' < 5e' < 4e''$. 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

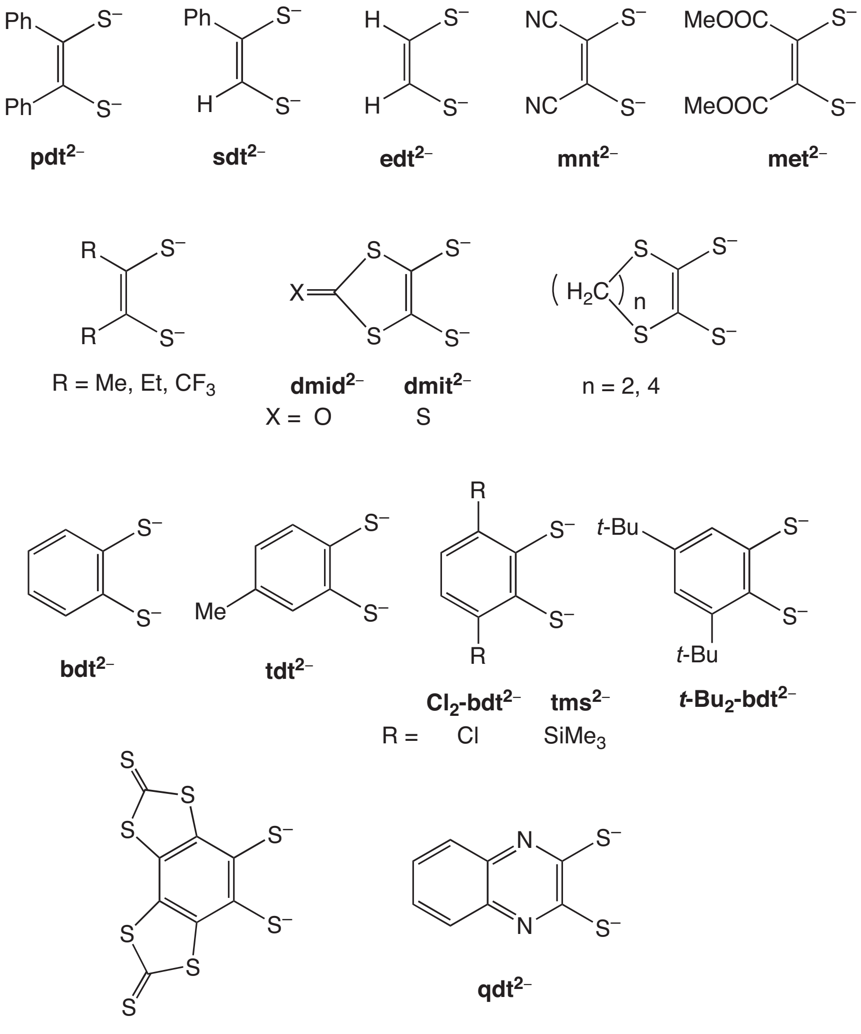


Chart 1. Different dithiolene ligands used in Table 1.

a nearly isotropic g value of 1.99 and a substantial ^{51}V hyperfine splitting of 61.6 gauss [53].”

4. The structures of M(dithiolene)$_3{}^n$ from transition metals in Groups 5–7

Following the groundbreaking discovery of trigonal prismatic coordination from the Gray laboratory, Stiefel continued in his independent studies to examine the scope of TP coordination and how the overall charge, the electron configuration and specific dithiolene would affect the observed coordination geometry of the tris(dithiolene) complexes. He defined two distortion parameters shown in Fig. 5 [55]. The first represents the simple trigonal twist that is quoted most frequently with 0° for TP and 60° for octahedral coordinations, while the second – given by a ratio of s/h – relates to deviation of the sides of the prism from being square. Yet another deviation from perfect D_{3h} symmetry of the trigonal prism is the envelope conformation of the chelate rings initially observed

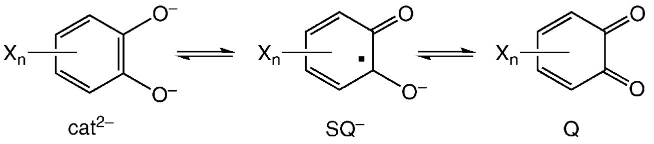
Table 1
Compilation of structural results for M(dithiolene)$_3{}^{n-}$ for M = Groups 5–7 transition metals from the Cambridge Crystallographic Database.

Molecule or anion	Cation	θ	s/h	CSD Refcode	Reference
$V(S_2C_2H_2)_3$		1.6	0.98	NAMPOG	[59]
$V(S_2C_2Ph_2)_3$		4.3	1.00	VDPHSC10	[53]
$V(S_2C_2(SCH_2CH_2S))_3$		15.7	1.02	HAYZEM	[60]
$[V(S_2C_2(SCH_2CH_2S))_3]^-$	$[TTF]^+$	5.0	1.00	HAYZUC	[60]
$[V(S_2C_2(SCH_2CH_2S))_3]^-$	$[NBu_4]^+$	5.6	1.01	GIBNOU	[61]
		1.8	1.00		
$[V(S_2C_2(S(CH_2)_4S))_3]^-$	$[NEt_4]^+$	7.2	1.01	ZOBHIH	[62]
		2.3	0.99		
$[V(S_2C_2(COOMe)_2)_3]^{2-}$	$2[NEt_4]^+$	34.3	1.10	RIXZII	[63]
$[V(dmit)_3]^{2-}$	$2[PMS]^+$	38.2	1.08	KABCAR	[64]
$[V(tdt)_3]^{2-}$	$2[NEt_4]^+$	38.9	1.14	NAMQAT	[59]
$[V(S_2Ph(S_2C{=}S)_2)_3]^{2-}$	$2[PPh_4]^+$	40.6	1.14	JECNEL	[65]
$[Nb(bdt)_3]^-$	$[AsPh_4]^+$	1.4	1.03	BZDTNB10	[66]
$[Ta(bdt)_3]^-$	$[AsPh_4]^+$	30.9	1.13	PABZTA	[67]
$[Cr(t\text{-}Bu_2\text{-}bdt)_3]^-$	$[NBu_4]^+$	39.1	1.11	RINZUK	[68]
$[Cr(mnt)_3]^{2-}$	$2[PPh_4]^+$	45.4	1.12	DUJDAN	[69]
$[Cr(Cl_2\text{-}bdt)_3]^{2-}$	$2[NBu_4]^+$	45.6	1.13	HOZWEZ	[70]
$[Cr(mnt)_3]^{3-}$	$3[PPh_4]^+$	51.5	1.18	DUJCIU	[69]
$Mo(bdt)_3$		0.0	0.99	BZDTMO10	[71]
$Mo(S_2C_2(CF_3)_2)_3$		0.0	1.00	QUQBOT	[72]
$Mo(S_2C_2Et_2)_3$		0.8	1.01	UCEDAI	[73]
		0.5	1.01		
$Mo(t\text{-}Bu_2\text{-}bdt)_3$		1.4	1.01	HIJSID	[74]
$Mo(S_2C_2Me_2)_3$		2.4	1.01	DIZQOS	[75]
$[Mo(S_2C_2Me_2)_3]^-$	$[NEt_4]^+$	1.6	1.02	DIZQUY	[75]
$[Mo(S_2C_8H_4N_2)_3]^-$	$[PPh_4]^+$	14.6	1.02	FOCBUU	[76]
$[Mo(t\text{-}Bu_2\text{-}bdt)_3]^-$	$[NBu_4]^+$	31.7	1.12	HIJSUP	[74]
$[Mo(bdt)_3]^-$	$[NBu_4]^+$	33.5	1.11	ACODAX	[77]
$[Mo(bdt)_3]^-$	$[PPN]^+$	34.8	1.12	MARSEE	[78]
$[Mo(S_2C_2Me_2)_3]^{2-}$	$2[NEt_4]^+$	2.6	1.05	QEPDOE	[79]
$[Mo(Cl_2\text{-}bdt)_3]^{2-}$	$2[NHEt_3]^+$	2.8	1.02	LATSOP	[80]
$[Mo(S_2C_8H_4N_2)_3]^{2-}$	$2[PPh_4]^+$	4.5	1.01	FECJIG	[81]
$[Mo(S_2C_2(COOMe)_2)_3]^{2-}$	$2[PPh_4]^+$	10.6	1.03	CAZLEU	[82]
$[Mo(S_2C_2(CF_3)_2)_3]^{2-}$	$2[NEt_4]^+$	16.1	1.05	QUPZUW	[72]
$[Mo(dmit)_3]^{2-}$	$2[NBu_4]^+$	16.6	1.02	KUWWII10	[83]
$[Mo(bdt)_3]^{2-}$	$2[PPN]^+$	24.9	1.08	MARSAA	[78]
$[Mo(mnt)_3]^{2-}$	$2[AsPh_4]^+$	28.2	1.07	PASMOD10	[58]
$W(bdt)_3$		0.0	1.00	HUKSAH	[84]
$W(S_2C_2Me_2)_3$		0.7	1.01	FORSEL	[85]
$W(t\text{-}Bu_2\text{-}bdt)_3$		1.0	1.01	HIJSOJ	[74]
$W(S_2C_2Ph_2)_3$		3.2	1.02	CUNMIH	[86]
$[W(dmit)_3]^-$	$[Fe(C_5Me_5)_2]^+$	0.8	0.99	LEFHOT	[83]
$[W(S_2C_2Ph_2)_3]^-$	$[NEt_3(CH_2Ph)]^+$	2.2	1.03	CUNBIW	[86]
		14.3	1.04		
$[W(S_2C_2Me_2)_3]^-$	$[NEt_4]^+$	2.8	1.03	QEPDUK	[79]
$[W(t\text{-}Bu_2\text{-}bdt)_3]^-$	$[NBu_4]^+$	31.5	1.11	HIJTAW	[74]
$[W(bdt)_3]^-$	$[PHMe_2Ph]^+$	32.3	1.10	WASGEC	[87]
$[W(bdt)_3]^{2-}$	$2[NEt_4]^+$	1.9	1.02	GEFKOR	[27]
$[W(S_2C_2Me_2)_3]^{2-}$	$2[NEt_4]^+$	2.4	1.04	QEPFAS	[79]
$[W(dmit)_3]^{2-}$	$2[NBu_4]^+$	15.5	1.02	LEFHEJ	[83]
$[W(S_2C_2(CF_3)_2)_3]^{2-}$	$2[NEt_4]^+$	15.8	1.04	QUQBAF	[72]
$[W(bdt)_3]^{2-}$	$2[AsPh_4]^+$	23.1	1.06	YASDOL	[88]
$[W(Cl_2\text{-}bdt)_3]^{2-}$	$2[PPh_4]^+$	23.7	1.05	LATRUU	[80]
$[W(dmid)_3]^{2-}$	$2[PPh_4]^+$	24.9	1.05	SOLKEJ	[89]
$[W(mnt)_3]^{2-}$	$2[AsPh_4]^+$	27.8	1.07	ASCETU	[58]
$[W(bdt)_3]^{2-}$	$2[NMe_4]^+$	29.6	1.09	PARGEU	[90]
$[Mn(bdt)_3]^{2-}$	$2[PPN]^+$	44.7	1.13	WOPGEO	[91]
$[Mn(Cl_2\text{-}bdt)_3]^{2-}$	$2[NEt_4]^+$	47.9	1.18	HOZWID	[70]
$[Mn(mnt)_3]^{2-}$	$2[PPh_4]^+$	49.9	1.14	HOZWOJ	[70]
$[Tc(bdt)_3]^-$	$[AsPh_4]^+$	8.0	1.01	FOPBER	[92]
$[Tc(mnt)_3]^{2-}$	$2[AsPh_4]^+$	38.9	1.10	GOKCUE	[93]
$Re(S_2C_2Ph_2)_3$		3.4	1.01	REPETD10	[45]
$Re(S_2C_2Ph_2)_3$		3.8	1.00	REPETD11	[46]

by Smith et al. in the form of a fold angle α that is also shown in Fig. 5. In subsequent studies, Stiefel reported a number of structure determinations that indeed confirmed his intuition that as the negative charge on the complex increased, the twist angle became larger [56–58]. Table 1, prepared with the help of William Brennessel, the crystallographic specialist at the University of Rochester, provides a tabulation of all of the structural results for the tris complexes M(dithiolene)$_3^{n-}$ for M = Groups 5–7 transition metals obtained from the Cambridge Crystallographic Database. Chart 1 shows the different dithiolene ligands used in these complexes and their abbreviations. Please note that different abbreviations and different representations have been used often for the same ligand – for example, $S_2C_2Ph_2$ and pdt.

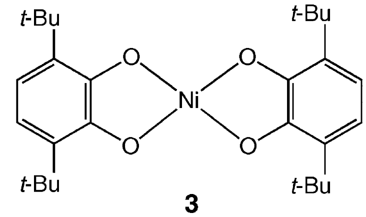
5. Redox-active Ligands Redux

Nearly a decade ago, the concept of dithiolenes as redox-active ligands was revisited by Karl Wieghardt and his collaborators using state-of-the-art theory and newer, more accurate experimental methods to probe the electronic structures of bis(dithiolene) and related complexes. The questions of metal oxidation state and ligand charge had continued from the early days of dithiolene chemistry with notions of unpaired electron spin residing on the ligands and antiferromagnetic coupling of ligand odd electrons to rationalize observed diamagnetism. Analogous complexes with O as the donor atom had been reported, and they, like the dithiolene systems, exhibited reversible electron transfer reactions that seemed to challenge the conventional thinking of solely metal-based redox behavior. For the ML_2 bis complexes that received the most attention, metal-based electron transfers would lead to unusual or unprecedented d^n configurations in a square planar coordination geometry if the ligands were assumed to maintain their classical dianion formulation. On the other hand, pyrocatechols were known to have easily reversible oxidation chemistry to semiquinones (SQ) and orthoquinones (Q) as shown in equation 1 that in turn would be compatible with more limited and conventional d^n configurations for square planar coordination.



(1)

Over an extended period beginning in the late-1970s, Pierpont [94–103] had conducted investigations of complexes of pyrocatechol and orthoquinone ligands, that have been termed dioxolenes, to probe exactly what was oxidized or reduced when an electron was transferred from or to the complex. In one such study, Ni($O_2C_6H_2$-3,6-*t*-Bu_2)$_2$ (**3**), that formally contains Ni(IV) with dianionic catecholate ligands, was found to have a square planar coordination geometry and be diamagnetic, both of which were inconsistent with a d^6 configuration [102]. The Ni oxidation state was therefore assigned as Ni(II) consistent with the coordination geometry, while each of the ligands was considered to be a semiquinone monoanion (SQ$^-$) with the two unpaired spins antiferromagnetically coupled to explain the diamagnetism. However, for other Ni(II) bis(dioxolene) complexes such as the Ni($O_2C_6H_2$-3,5-*t*-Bu_2)$_2$ isomer, aggregation led to clusters having NiO_6 octahedra or insoluble polymers exhibiting paramagnetism more consistent with octahedral Ni(II).



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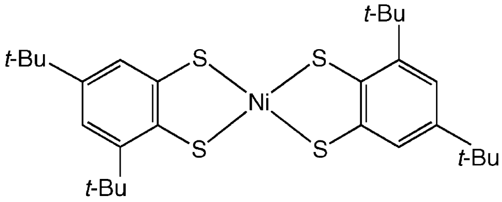

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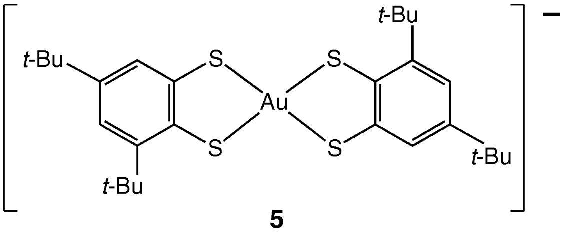
A different situation was found for the dithiolene analog Ni($S_2C_6H_2$-3,5-*t*-Bu_2)$_2$ (**4**) by Sellman who formed the mono- and dianions of this complex and was able to characterize crystallographically all three species [104]. Increases in the Ni–S distances in going from neutral **4** to its mono- and dianions (2.124 Å → 2.144 Å → 2.175 Å) were not matched by significant changes in the S–C and C–C distances, and the EPR spectrum of the monoanion prepared with enriched ^{61}Ni exhibited a strong hyperfine coupling indicative of metal orbital involvement in the SOMO. Sellman considered that for this system the redox processes were not ligand based but rather part of the "NiS_4" moiety alone, and that in terms of formal metal oxidation state changes, the Ni 2p$_{3/2}$ binding energies for the neutral and dianionic complexes were more consistent with IV and II, respectively.

In the context of this overly simplified and under-referenced background, Wieghardt addressed the challenge posed by the Ni bis chelate complexes of dithiolene, dioxolene and structurally similar diimine ligands, as well as mixed OS, NS and ON analogs, of the identities of the frontier orbitals from and to which electrons were transferred in these systems. For the diamagnetic complexes, the question considered was exactly the same as the one raised by Gray and Holm more than 35 years earlier – do the neutral complexes really contain Ni(IV) or are they complexes of Ni(II) with partially oxidized ligands having spins that were antiferromagnetically coupled? The latter are considered as "singlet diradical" systems with the spins weakly antiferromagnetically coupled. In 2002, a paper by Bachler et al. [105] tackles this question using Density Functional Theory and complete self-consistent field computations using the broken symmetry formalism introduced by Noodleman [106–108]. In this analysis, a new index for the diradical character was proposed based on symmetry breaking that led to the conclusion that Ni(*o*-catcholate)$_2$ complexes had the *largest* amount of singlet diradical character and Ni(benzenedithiolate)$_2$ had the *smallest* amount of singlet diradical character, based in part on the *relative* stability of the semiquinone or partially oxidized form of the ligand that in turn relates to the ability of the O, N and S 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."

In a subsequent study from the Wieghardt laboratory, it was pointed out that while bond distances and angles from crystallographic studies could in principle indicate ligand oxidation level, the expected metrical differences – most notably in S–C, O–C, N–C and ring C–C distances – would only be significant for the most accurately determined crystal structures – a quality definitely not true for many of the earlier dithiolene structures [109]. Instead, the question of ligand redox level and metal formal oxidation state could be better addressed experimentally using spectroscopic methods such as electronic, EPR and Mössbauer spectroscopies. This was done for the Au(III) complex anion **5** and its one electron oxidation product. From the absence of ^{197}Au hyperfine in the EPR of the neutral S = ½ complex, the near identity of the Mössbauer spectra from **5** and its one-electron 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 **5** – and a dithiobenzosemiquinone ligand (in addition to the remaining di-*t*-butylbenzenedithiolate).



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6. The wisdom of Solomon

In the biblical story of two mothers claiming a single baby, Solomon the King threatened to divide the infant in two until the real mother pleaded for the baby's life. The less traumatic but still profound division of a bond, specifically its electron density, *based on meaningful experiment* led to a modern Solomon's judgment that should be introduced at this point. Specifically, in 2002 Solomon, along with Hodgson and Hedman, and in collaboration with Holm, examined $[Ni(S_2C_2Me_2)_2]^{n-}$ for $n = 0, 1, 2$ using sulfur K-edge X-ray absorption spectroscopy (XAS) along with DFT calculations to determine Ni-dithiolene covalency, ligand oxidation level and therefore Ni oxidation state [110]. The S pre-edge features were found not to differ substantially for the three redox-related Ni bis(dithiolene) species in distinct contrast to what was observed for ferrous/ferric tetrathiolates. For the $[Ni(S_2C_2Me_2)_2]^{n-}$ complexes, the authors write, "the shift in the rising-edge position gives ... the increase of Z_{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_{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* [110]." (my italics)

The DFT calculations showed that the frontier orbitals for $[Ni(S_2C_2Me_2)_2]^{n-}$ $n = -2, -1, 0$ possess substantial dithiolene composition. The HOMO in the dianion that becomes the LUMO in the neutral complex is an orbital of b_{2g} symmetry that is mainly composed of the out-of-phase combination of the dithiolene $3\pi_v$ functions - that is, the $+--+\pi$ function. The bonding was said to be "inverted" meaning that the frontier orbitals have greater ligand than metal character and that a decrease in 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 [110]. 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.*, sulfur K-edge XAS and DFT calculations – to examine the electronic structures of Mo tris(dithiolene) complexes [111]. According to the authors, for the $[Mo(S_2C_2Me_2)_3]^{n-}$ complexes where $n = -2, -1, 0$, "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. 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_{eff} increases, that is, the dianion and monoanion undergo ligand-based oxidation." The authors write further, "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) [111]". Both the neutral and monoanionic complexes were found crystallographically to be trigonal prismatic, although the fold angle differed between the two structures (α of 15.8° and 4.0°, respectively) [75].

The S K-edge data were also compared to those of another Mo tris(dithiolene) series, $[Mo(t\text{-}Bu_2\text{-}bdt)_3]^{n-}$ $n = 0, -1$, collected by Kapre et al. [74]. The neutral complex $[Mo(t\text{-}Bu_2\text{-}bdt)_3]$, which possesses TP coordination, has a S K-edge spectrum similar to that of $[Mo(S_2C_2Me_2)_3]$, 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 $[Mo(S_2C_2Me_2)_3]^{1-}$. The Solomon group considered the difference between the S K-edge data of $[Mo(t\text{-}Bu_2\text{-}bdt)_3]^{1-}$ and $[Mo(S_2C_2Me_2)_3]^{1-}$ to be the result of configurational interaction in the twisted D_3 structure for the former. Interestingly, the bonding model for the $[Mo(t\text{-}Bu_2\text{-}bdt)_3]^{n-}$ $n = 0, -1$ complexes differed from that put forth by the Solomon group. Kapre et al. assigned an unchanging oxidation state of Mo^{V} (d^1) to the complexes which meant for the neutral complex one dithiolene radical ligand antiferromagnetically coupled to the d^1 electron [74], whereas Solomon and co-workers assigned an unchanging Mo^{IV} oxidation state and a doubly oxidized ligand set (L_3^{4-}) in the neutral TP complex [111].

7. Trigonal prismatic coordination and tris(dithiolenes) – a re-examination

The studies described above from the Wieghardt and Solomon laboratories set the context for the recent papers by Sproules et al. [51,54,70] that address directly the electronic structures of trigonal prismatic tris(dithiolene) complexes and their redox-related analogs. In the first of these, neutral Re and redox related tris(dithiolene) complexes were examined for the aryldithiolate ligands bdt, tdt, Cl_2-bdt and tms shown in Chart 1 [51]. The molecular structure of $Re(tms)_3^-$ as its $C_8H_{16}N^+$ salt was shown crystallographically to be trigonal prismatic, while the neutral complexes $Re(bdt)_3$ and $Re(tms)_3$ yielded optimized trigonal prismatic structures. The more reduced members of the set $Re(dithiolene)_3^{n-}$ for $n = 2, 3$, as well as some of the monoanions, were calculated to be intermediate between TP and octahedral coordinations. 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, two important sets of studies were done for these systems. The first involved EPR studies for the neutral complexes which confirmed the earlier observations of Porte. 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 $I = 5/2$) were 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 assignment of their electronic configuration as $\ldots(3a_1')^2\ (4e')^4\ (2a_2')^1$ with a $^2A_2'$ ground state. Sproules et al. concluded: "Therefore, we can definitively affirm the electronic structure of these neutral [trigonal prismatic] tris(dithiolene)rhenium complexes as $[\mathrm{Re^V(L^\bullet)(L)_2}]$"[51].

The redox related $\mathrm{Re(bdt)_3}^{2-}$ complex also has an S = ½ ground state and exhibits an EPR signal greatly different from that of the neutral, structurally established TP complex. The EPR spectrum of the dianion clearly shows ^{187}Re hyperfine and it is concluded that this dianion (and others with the different aryldithiolene ligands) corresponds to Re(IV) with three fully reduced dithiolene ligands – *i.e.*, $[\mathrm{Re^{IV}(L^{2-})_3}]^{2-}$. The optimized structure calculated for $\mathrm{Re(bdt)^{2-}}$ has a twist angle θ of 33.5° putting it almost exactly midway between TP and octahedral coordinations.

X-ray Absorption Spectroscopy (XAS) provided the second set of results that were used in the analysis of the $\mathrm{Re(dithiolene)_3}^{n-}$ systems. While the Re $\mathrm{L_1}$-edge spectra for $\mathrm{Re(bdt)_3}$ and its monoanion were consistent with Re(V), the S K-edge XAS results were compatible with "an extra hole in the dithiolene ligands" and therefore the $[\mathrm{Re^V(L^\bullet)(L)_2}]$ formulation. In the DFT calculations that were done as a major part of this study, the molecular orbital energies change as a function of electron occupancy and the trigonal twist angle θ. This is shown in Fig. 6 which is reproduced from the paper by Sproules et al. In this figure, one can also see qualitatively the relative compositions of the different frontier orbitals (while the symmetry changes from D_{3h} to D_3 as θ increases from 0°, the labeling in D_{3h} was maintained)[51].

Sproules et al. conclude, "The most salient feature of this study is the observation that the neutral $[\mathrm{Re(L)_3}]$ (S = ½) and the monocation $[\mathrm{Re(L)_3}]^+$ (S = 0) contain both a trigonal prismatic $\mathrm{ReS_6}$ polyhedron and a central Re(V) ion (d^2, $S_{\mathrm{Re}} = 0$) with two electrons in the $5d_{z^2}$ metal orbital, namely $(3a_1')^2$ in D_{3h} symmetry. The unpaired electron in neutral $\mathrm{Re(bdt)_3}$ occupies a pure ligand MO, $(2a_2')^1$. Thus, both the neutral and monocationic forms [of $\mathrm{Re(L)_3}$] possess oxidized forms of the ligands (formally one and two ligand holes, respectively) [51]." The assignment of the SOMO in the neutral $\mathrm{Re(L)_3}$ complexes was thus the same as that reported by Al-Mowali and Porte [50].

The second study by Sproules et al. turned attention to the V complex **2**, its analogs with other dithiolene ligands and redox related members of the series $\mathrm{V(L)_3}^n$ where n = +1, 0, −1, −2, −3, −4 [54]. The particular dithiolene ligands examined in the study include pdt, sdt, edt, mnt, bdt and tdt (see Chart 1). For no ligand was the entire redox series studied experimentally, but computationally the $\mathrm{V(L)_3}$ complexes were studied for different redox members of the series using broken symmetry (BS) DFT calculations that employed the B3LYP functional for structure optimization and electronic properties. As noted above, the structure of **2** was confirmed using modern crystallographic methods as TP with nearly D_{3h} symmetry (ignoring the phenyl rings) and an average twist angle θ of *ca.* 4°. A number of related complex anions were also characterized crystallographically including monoanions $\mathrm{V(pdt)_3}^-$ and $\mathrm{V(bdt)_3}^-$ and the dianion $\mathrm{V(mnt)_3}^{2-}$. While both monoanions were also found to be trigonal prismatic, the $\mathrm{VS_2C_2}$ chelate rings deviated from planarity with an envelope type conformation and average fold angles α of 23.4 and 23.6°, respectively. In contrast, the $\mathrm{V(mnt)_3}^{2-}$ anion showed significant twisting towards octahedral coordination (average θ of ∼38° and approximate D_3 symmetry) that had been reported earlier in several other structure determinations (not included in Table 1 because of the absence of reported positional parameters), including one by Stiefel et al. [56], that differed in the counter-ion.

The EPR spectra for both neutral and dianionic $\mathrm{V(L)_3}$ complexes were employed in the assignment of the SOMO for these complexes. 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 $\sim 58 \times 10^{-4}\,\mathrm{cm^{-1}}$ for ^{51}V (I = 7/2). The observations were interpreted to mean that the *same* orbital was the SOMO in the $2e^-$ separated forms $\mathrm{V(L)_3}$ and $\mathrm{V(L)_3}^{2-}$ and that the SOMO was the V orbital of a_1' symmetry. This meant that the V 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.*, $\mathrm{(L)_3}^{4-}$.

In order for the SOMO of $\mathrm{V(L)_3}$ and $\mathrm{V(L)_3}^{2-}$ to be the same, a molecular orbital 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 that was mainly V d_{z^2} in character and the exclusively thiolate-based $2a_2'$ function. The V K-edge XAS data for the $\mathrm{V(L)_3}^n$ systems indicated that the V oxidation state was the same for the oxidation levels n = 0, −1, −2 in support of the proposed inversion. Consistent with this conclusion were the nearly identical V–S bond distances that were determined structurally for the neutral, mono- and dianionic $\mathrm{V(L)_3}^n$ structures.

The notion of a molecular orbital level inversion in going from neutral to dianionic tris(dithiolene) complexes of V was actually put forward by Kwik and Stiefel [112] when a single crystal EPR study

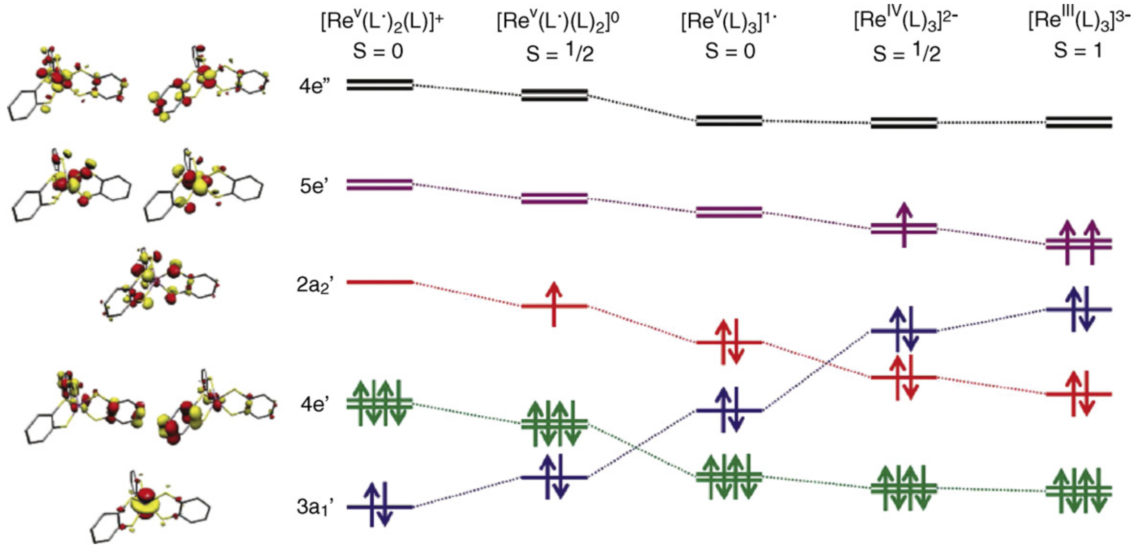

Fig. 6. Diagrams showing the molecular orbital energy level orderings for $\mathrm{Re(bdt)_3}^n$. Reproduced by permission from Ref. [46].

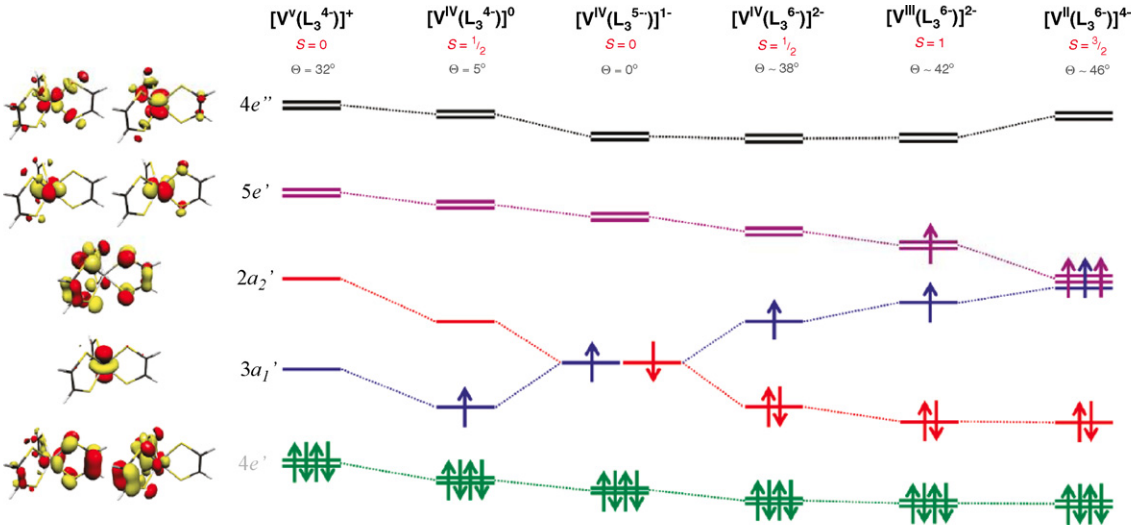

Fig. 7. The orbital energy level orderings for $V(S_2C_2Ph_2)_3$ (**2**) and the related redox derivatives from +1 to −4. Reproduced by permission from Sproules et al. [49].

of $V(mnt)_3{}^{2-}$ doped into $[AsPh_4]_2[Mo(mnt)_3]$ was conducted. The results "were totally consistent with the unpaired electron being in a nondegenerate molecular orbital which is substantially d_{z^2} on the metal ion. The ground state for the $V(mnt)_3{}^{2-}$ ion is thus described as $^2A_1$." These authors note that both neutral and dianionic V complexes as well as related S = ½ systems have extremely small observed g tensor anisotropy. "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) [112]."

In the study by Sproules et al., the final experimental measurements to provide insight into the electronic structural description of the $V(L)_3{}^n$ complexes were sulfur K-edge X-ray absorption spectra that revealed a pre-edge feature for neutral **2** and its redox-related monoanion 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 that does not exist for dianions as indicated in equation 2 from Sproules et al. [54].

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

The results of the DFT calculations from Sproules et al., are shown in Fig. 7 for the entire series $V(L)_3{}^n$ for $n = +1, 0, -1, -2, -3$. The optimized geometries agree well with experimental values. For $n = +1, 0, -1$, the coordination geometry is trigonal prismatic ($\theta = 0°$) whereas for $n = -2, -3$, it is trigonally distorted towards octahedral ($\theta > 30°$ with $\theta_{oct} = 60°$). In Fig. 7, however, D_{3h} symmetry labeling was maintained throughout the diagram for correlating how molecular orbital energy levels change. For the neutral $V(L)_3$ complexes exemplified by **2**, the energy level ordering in terms of increasing energy is: $4e' < 3a_1' < 2a_2' < 5e' < 4e''$. While the 4e′ level is extensively delocalized over V and dithiolene, it has greater ligand character and is therefore designated as dithiolene-based for oxidation state assignment. As the system is increasingly reduced, the proposed level inversion that is needed to maintain the V oxidation state as fixed in Eq. (2) involves the metal-based $3a_1'$ orbital and the ligand-localized $2a_2'$ function composed mainly of S orbitals. Interestingly, this means that for the *diamagnetic* $V(L)_3{}^-$ monoanion, two electrons in different orbitals are antiferromagnetically coupled to produce the observed result. For the dianions (and beyond), the ligands are fully reduced – *i.e.*, $(L)_3{}^{6-}$ – and the complexes are twisted toward octahedral. While the complex charge clearly affects the coordination geometry, the chelate fold angle α that is significant for the monoanions appears relatively unimportant in the calculations.

For complex **2**, the electronic configuration is thus $(4e')^4$ $(3a_1')^1$ with a $^2A_1'$ ground state. The V oxidation state is +IV and the ligands are oxidized by 2 e^- from the dithiolate formulation to $(L)_3{}^{4-}$. EPR, magnetic and XAS data are all consistent with this formulation. The unpaired electron is in the mainly V $3d_{z^2}$ orbital and "the three bidentate ligands accommodate 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 Gray and myself [53] (but with 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 as first suggested by Stiefel et al. [47,113].

8. Concluding thoughts

"*Whatever goes around, comes around.*" In the recent literature, increased attention has been given to the chemistry of complexes containing redox-active ligands. Multiple metal oxidation states are now complemented by frontier ligand orbitals that also can undergo electron transfer processes. This was, of course, recognized some time ago in biological systems with ligands like porphyrins and catecholates. However, among non-biological systems, the dithiolene complexes exemplify the notion of metal complexes possessing redox-active ligands. The early studies of the dithiolene complexes – both bis and tris – by Gray, Schrauzer, Holm and their respective collaborators focused initially on their synthesis, characterization and determination of molecular and electronic structures. Current interest in these complexes and others having similarly capable ligands is now expanding with the help of better experimental and computational methods to their reaction chemistry particularly for multi-electron transformations and catalysis. What went around in the 1960s has indeed come around in a more useful, insightful and compelling way.

A touch of irony. When I first started my scientific journey with dithiolenes, we discussed the meaning of oxidation states and their inadequacies in describing different complexes. It is therefore with a touch of irony that I note that we are still formalistically in the same pickle. In the extensive and insightful work by Sproules et al., the $4e'$ levels were found to be extensively delocalized over the metal *and* ligands (we had found the same result) yet were assigned to either the ligand or the metal for the purpose of assigning a formal metal oxidation state. (Indeed, it was the delocalization of the $4e'$ orbitals and the fact that they were not purely ligand in character that stimulated the idea that in $Re(S_2C_2Ph_2)_3$ the ligands were partially oxidized.) While we made a giant step forward to recognize redox active ligands, we still have difficulty with truly delocalized orbitals where the relative % composition may change significantly (but not in discrete electron units) upon ligand modification and overall complex charge. If the $4e'$ level changes from 60% metal to 40% metal, the change wreaks havoc with oxidation state designations if the electrons are assigned to *either* one or other major component of the orbital. However, while a Mulliken population analysis can be done, it lacks the quick simplicity that the formalism has.

A special moment. Since this is an article dedicated to Harry Gray as part of a volume in his honor, I am allowed some final personal reflections. I first met Harry when he was 28 years old and I was just shy of 20. His enthusiasm and spirit were enthralling – he did say we would win a Nobel prize and invited me straight away to a party at his apartment. It was for me a transformative moment (the party sounded really good!). More importantly, I was able to embark on research in a most interesting and fundamentally challenging area. We were revisiting and revising established models of bonding. And serendipity was with us in the trigonal prismatic structure of $Re(S_2C_2Ph_2)_3$.

With the knowledge that Karl Wieghardt, with his profound insight, and his collaborators with their new experimental capabilities and computational methods were now re-examining compounds that we had studied four decades earlier, I kept asking myself as I wrote this article, “So how did we do?” How did Team Gray really do? (There was no Gray Nation or Harry’s Army back then, just a Gray team – that is today a lot grayer). The answer thankfully is, “Damn good!” The crystallography yielded correct structures, although with larger standard deviations on metrical parameters than are routinely obtained today. While the assignment of the ground state and orbital ordering of the Re complex **1** was incorrect because of the relative positions of the $3a_1'$ and $2a_2'$ orbitals, the corresponding assignment for the V complex **2** was spot on. More profoundly, the notion of ligand orbitals as part of the frontier orbitals of a metal complex and the idea that some of these orbitals may be extensively delocalized over the entire complex broke new ground. My profound respect goes to Harry Gray (my mentor), Ed Stiefel (my colleague), Dick Holm, Alan Davison and Gerhard Schrauzer (our friendly competitors) for really uncovering this field, and to Karl Wieghardt (as well as others like Cort Pierpont (*my* former student) and the late Dieter Sellman) who showed that what we uncovered is in fact a more fertile field than I originally realized.

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