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Paramagnetic Cp/Dithiolene Complexes as Molecular Hinges: Interplay of Metal/Ligand Electronic Delocalization and Solid-State Magnetic Behavior

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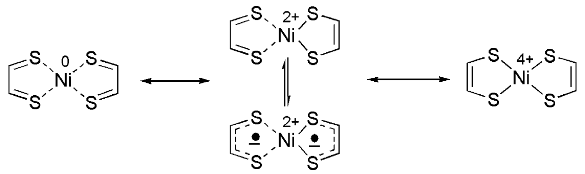
ABSTRACT
Paramagnetic, flexible organometallic dithiolene complexes associating cyclopentadienyl (Cp) and dithiolate (dt) ligands, such as CpM(dt), Cp$_2$M(dt), or CpM(dt)$_2$, are investigated in the solid state through their structural and magnetic properties. The degree of delocalization of the spin density between the metal and the dithiolene fragments in a given complex, its varying molecular geometry and frontier orbitals, and the structures adopted in the solid state are intimately correlated and adapt mutually to each other. A variety of magnetic structures follows, from noninteracting spins to dyads, spin chains, spin ladders, or antiferromagnetic ground state, the detailed properties of which are highly sensitive to “minor” molecular modifications.

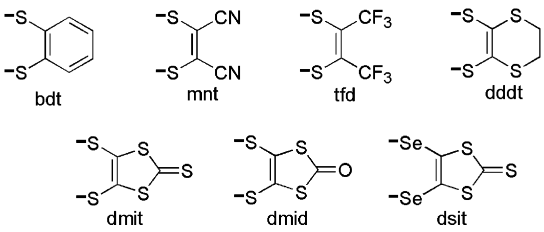
Introduction

The unique nature of the dithiolene complexes has been unraveled in the 1960s by Gray,[1] Schrauzer,[2] and Holm[3] who established the two reversible one-electron electrochemical relationships between a dianionic dithiolene complex Ni(S$_2$C$_2$R$_2$)$_2^{2-}$ and the neutral Ni(S$_2$C$_2$R$_2$)$_2^0$. The high degree of electronic delocalization in these systems can be illustrated (Scheme 1) by the possible resonance structures of a neutral Ni(S$_2$C$_2$R$_2$)$_2^0$: the ligands can be viewed as either neutral “dithioketones” or dinegative “dithiolates” with the metal in formal oxidation states of 0, +2, or +4.[4] Note also that in the intermediate form, the two radical anions must be antiferromagnetically coupled.[5] These *dithiolate* ligands have been described as “noninnocent” and their metal complexes as *dithiolene* complexes. However, as pointed out by McCleverty,[5] the noninnocent character does not just characterize redox-active ligands (such as the dithiolates) but the whole dithiolene complex where “there is a strong mixing between ligand and metal orbitals, such that the assignment of oxidation state to individual metal or ligand components is difficult”.

Scheme 1



Scheme 2



The ability of such “noninnocent” complexes to exist in several clearly defined oxidation states allows for the isolation of the intermediate open-shell *radical* anion complexes such as Ni(mnt)$_2^{-\bullet}$ in which the extensive spin delocalization on the ligands favor magnetic interactions in the solid state with singlet−triplet, ferromagnetic, or antiferromagnetic ground states.[6] Besides, following the discovery by Cassoux and co-workers in 1986 of superconductivity in a mixed-valence salt derived from Ni(dmit)$_2^{-\bullet}$,[7] important synthetic advances toward conducting materials have been reported, such as novel square-planar complexes with various dithiolate ligands or metal centers (Pt, Pd, ...),[8,9] mixed complexes involving two different dithiolate ligands,[10] or dithiolates built directly on a tetrathiafulvalene core.[11,12] During those years, little attention has been directed to *nonplanar* dithiolene complexes, based on the probable assumption that such a geometry would hinder strong enough intermolecular overlaps to allow the formation of conduction bands with sizable dispersion.

This point is still open and probably deserves deeper investigations following earlier reports on paramagnetic tris-dithiolene complexes[13,14] with trigonal prismatic geometry such as Mo(dmit)$_3^{-\bullet}$ or V(dddt)$_3^{\bullet}$ (see Scheme 2 for structures of the dithiolates). Besides these homoleptic tris-dithiolene complexes, other classes of nonplanar complexes have been described that involve both a dithiolate and an organometallic ligand such as η^5-C$_5$H$_5$ (Cp) or η^5-Me$_5$C$_5$ (Cp*) (Scheme 3). Let us mention for example Cp$_2$Ti(bdt), Cp$_2$Nb(dmit), CpCo(mnt) and others which have been the subject of a recent review article.[15]

The capacity of such heteroleptic complexes to sustain *open-shell* species and eventually to promote sizable intermolecular interactions in the solid state has been scarcely addressed in the past and will be the subject of

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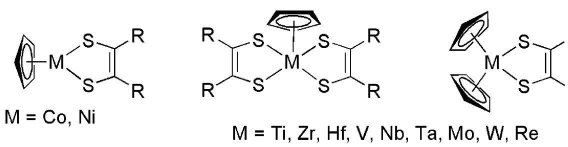
Scheme 3



the present Account, essentially based on our own results over the last 10 years.

The "Older" Heteroleptic and Paramagnetic Dithiolene Complexes

Complexes that combine one cyclopentadienyl (Cp, Cp*) with one dithiolate (dt) ligand are known with Co^{III} metal centers, affording neutral, closed-shell, and diamagnetic 16e complexes such as CpCo(dt). The analogous d^7, formally nickel(III), Ni complexes of general formula CpNi(dt) are also known since 1962. Let us mention CpNi(dmit)[16] or CpNi(tfd), which was described[17] indeed to be paramagnetic with $S = {}^1/_2$. Iron complexes with bdt[18] and tfd[19] ligands associate into dyads such as $[CpFe(bdt)]_2$ or $[CpFe(tfd)]_2$ with a short iron–iron distance suggesting the presence of an Fe–Fe single bond compatible with the diamagnetism observed in $[CpFe(bdt)]_2$.

Another group of complexes is known with the group 4–7 metal centers in their IV oxidation state, either with two cyclopentadienyl and one dithiolate ligands of general formula $Cp_2M^{IV}(dt)$ or with one cyclopentadienyl and two dithiolate ligands of general formula $CpM^{IV}(dt)_2{}^{-1}$, that is, in an anionic form. In these series, the d^1 $Cp_2V(dt)$ and $Cp_2Nb(dt)$ radical complexes were described by Casey,[20] Olk,[21] and Amaudrut[22,23] and their paramagnetic state confirmed by solution electron paramagnetic resonance (EPR). A strong localization of the spin density on the metal was deduced from the large a_0 values and confirmed in the Nb complexes by a Curie-type behavior of the temperature dependence of the magnetic susceptibility.[23,24] Also, a room-temperature magnetic moment of 1.68 μ_B has been reported in the formally W^V, d^1, neutral $CpW(tfd)_2{}^{\bullet}$.[25]

Besides, it should be stressed here that these classes of complexes are also the subject of numerous studies related to their analogy with the so-called molybdenoenzymes (MoCo), which have been shown to incorporate as active site a molybdenum dithiolene complex.[26] Indeed, the conformational modifications accompanying redox changes of the enzymes illustrate the crucial role of the "noninnocent" dithiolene complex in the processes involved in the enzyme's catalytic cycle. Of particular interest is the structure of the intermediate, open-shell, Mo^V oxidation state, only investigated up to now by EPR/electron nuclear double resonance (ENDOR) studies[27] or in model compounds.[28,29]

In the following, we choose to concentrate on specific dithiolate ligands such as $dmit^{2-}$ (1,3-dithiole-2-thione-4,5-dithiolate) and $dddt^{2-}$ (5,6-dihydro-1,4-dithiine-2,3-dithiolate), which are well-known to promote strong intermolecular interactions in the solid state as extensively demonstrated in the conducting and superconducting salts derived from the square-planar Ni, Pt, or Pd complexes.[7-12] In the nonplanar Cp/dt radical complexes described here, these ligands might favor intermolecular overlap interactions provided that the spin density is delocalized on the dithiolene moieties.

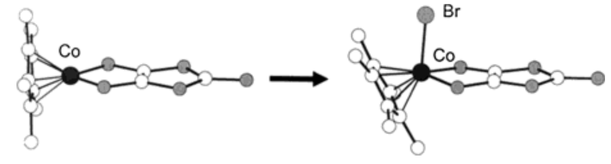
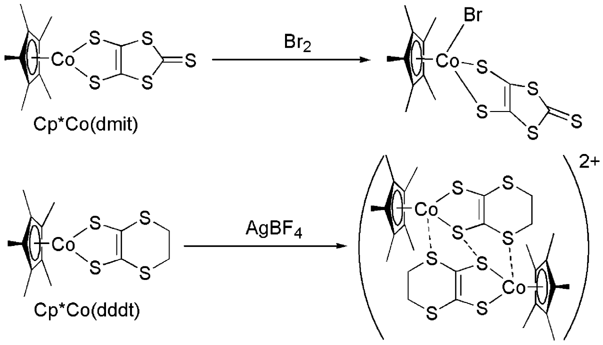


FIGURE 1. Structures of the diamagnetic Cp*Co(dmit) (left) and paramagnetic Cp*Co(dmit)Br (right).

Scheme 4



Ligand-Centered Oxidation of Cobalt Complexes

Oxidation of the diamagnetic, Co^{III}, CpCo(dmit) or Cp*Co(dmit) complexes with bromine (Scheme 4) was described by Matsubayashi to afford the 1:1 salts, $[CpCo(dmit)^{+\bullet}][Br^-]$ and $[Cp^*Co(dmit)^{+\bullet}][Br^-]$.[30,31] X-ray crystal structure of $[Cp^*Co(dmit)^{+\bullet}][Br^-]$ revealed that the Br^- anion has entered the coordination sphere of the cobalt (Figure 1), while EPR data and density functional theory (DFT) calculations showed that most of the spin density was localized on the dmit moiety. Each paramagnetic Cp*Co(dmit)Br complex interacts with neighboring molecules through S···S contacts in a uniform chain, as confirmed by the temperature dependence of the magnetic susceptibility, well described with the antiferromagnetic Heisenberg chain model with a large J/k_B value of −46.3 K (32 cm^{-1}).

When the oxidation of Cp*Co(dddt) is performed in the presence of noncoordinating anions such as BF_4^- (Scheme 3), we have shown[32] that the oxidized $[Cp^*Co(dddt)]^{\bullet+}$ species is not stable but dimerizes to afford a diamagnetic, dicationic species $[Cp^*Co(dddt)]_2{}^{2+}$. The outer sulfur atoms of the six-membered ring of the dddt ligand enter the coordination sphere of a neighboring cation (Figure 2) with formation of a $2e^-$ bond: the full spin localization on the dddt moiety leads to its pairing into the bonding combination of the two singly occupied molecular orbitals (SOMOs).

Both examples demonstrate that ligand-centered oxidations provide very good candidates for the elaboration of solid-state materials blessed with electronic properties, since most of the intermolecular interactions needed for

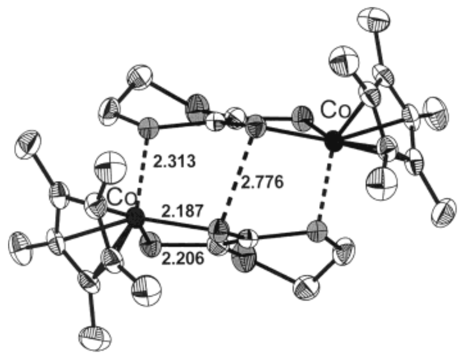


FIGURE 2. ORTEP view of the diamagnetic dyadic $[Cp^*Co(dddt)]_2^{2+}$ moiety in $[Cp^*Co(dddt)][BF_4]$.

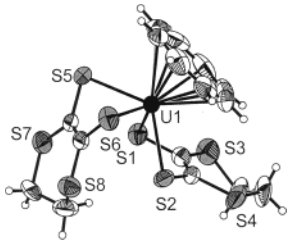


FIGURE 3. ORTEP view of the paramagnetic $U^{(V)}$ dithiolene complex, $[U(cot)(dddt)_2]^{-\bullet}$.

such properties are mediated by the intermolecular dithiolene···dithiolene overlap, provided however that bond formation between the radical species can be avoided.

Metal-Centered Open-Shell Species: Vanadium, Niobium, and Uranium Complexes

In that respect, the opposite situation is found in the d^1 vanadium or niobium complexes $Cp_2V(dt)$ or $Cp_2Nb(dt)$ where the spin density is essentially localized on the metal fragment. The analogous titanium d^0 complexes, $Cp_2Ti(dt)$, reduce at very negative potentials and oxidize irreversibly.[33] However, given the close proximity between the chemistries of titanium and uranium and the possibility to reach U^V and U^{VI} oxidation states, uranium dithiolene complexes have been investigated by Ephritikhine and Arliguie and their redox properties described.[34] While the oxidation of the neutral U^{IV} $Cp^*_2U(dddt)$ complex did not allow the isolation of any radical species, the $AgPF_6$ oxidation of the more electron-rich, dianionic U^{IV} complex, $[U(cot)(dddt)_2]^{2-}$ (cot = η-C_8H_8) afforded the corresponding anionic one-electron oxidation U^V product, $[U(cot)(dddt)_2]^{\bullet-}$, as its Na(18-crown-6)(THF) salt (Figure 3). Bond lengths within the dddt ligands exhibit little changes when compared with those found in the dianionic complex or in $Cp_2Ti(dddt)$, for example, indicating that the oxidation is now essentially centered on the metal, that is, as U^V species. This was further substantiated by the temperature dependence of the magnetic susceptibility of the complex, which exhibits a Curie law characteristic of noninteracting spins.

Between these two extreme behaviors, either a complete metal localization of the spin density associated with a Curie-type susceptibility as in $Cp_2V(dt)$, $Cp_2Nb(dt)$, or $[(cot)U(dt)_2]^-$ or a complete localization of the spin density on the dithiolene moieties with pairing and formation of diamagnetic dyads as in $[Cp^*Co(dddt)]_2[BF_4]_2$, the molybdenum and tungsten complexes described below offer a rich alternative.

Scheme 5

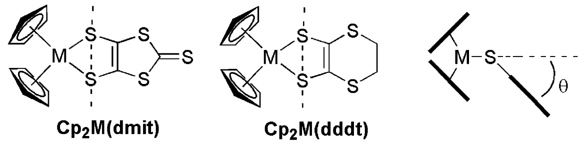


Table 1. Folding Angle (θ) of the MoS_2C_2 Metallacycle in Neutral d^2 $Cp_2Mo(dmit)$ and in Various Salts of d^1 $Cp_2Mo(dmit)^{\bullet+}$

anion	θ (deg)	C−S (Å)	C=C (Å)	ref
neutral complex	4.2(1)	1.745(9)	1.357(12)	44
PF_6^-, AsF_6^-, SbF_6^-	0.0	1.691(8)[a]	1.41(1)[a]	40
$ReO(dmit)_2^-$	5.6(5)	1.688(13)	1.383(16)	42
$TCNQF_4^{\bullet-}$	10.2(1)	1.684(13)	1.43(2)	37
BF_4^-	23.21(5)	1.718(8)	1.360(10)	39
Br^-	30.45(4)	1.712(5)	1.385(6)	39

[a] Values for the AsF_6^- salt.

Variable SOMO in the Flexible d^1 $Cp_2M(dt)^{+\bullet}$ Complexes, M = Mo or W.

The identification by Green[35] of reversible oxidation waves in a d^2, Mo^{IV} $Cp_2Mo(dt)$ complex, prompted us to investigate more closely the corresponding dmit and dddt complexes (Scheme 5), that is, $Cp_2Mo(dmit)$ and $Cp_2Mo(dddt)$.[36] While the latter can be oxidized with 7,7,8,8-tetracyanoquinodimethane (TCNQ) to afford the 1:1 charge-transfer salt, $[Cp_2Mo(dddt)][TCNQ]$, the former with a decreased donor ability could be chemically oxidized only with a stronger acceptor such as $TCNQF_4$ to afford $[Cp_2Mo(dmit)][TCNQF_4]$.[37] Electrocrystallization[38] proved also to be a very efficient tool for the isolation of $Cp_2Mo(dmit)^{\bullet+}$ salts with a variety of anions, be they monatomic (Br^-),[39] tetrahedral (BF_4^-, ClO_4^-),[39] octahedral (PF_6^-, AsF_6^-, SbF_6^-),[40,41] or more complex ($ReO(dmit)_2^-$).[42]

Perhaps the most striking feature of those complexes in their d^1 cation radical state lies in their geometry and particularly the folding angle of the MS_2C_2 metallacycle along the S···S hinge (Scheme 5). As shown in Table 1, folding angles of the d^1 $Cp_2Mo(dmit)^{+\bullet}$ cation extend between 0° (unfolded complexes) and 30°, only by changing the counterion and the crystal structure! Such a folding was originally observed to an even larger extent in the d^0 titanium $Cp_2Ti(dt)$ complexes ($43° \leq \theta \leq 51°$).[33] It finds its origin (Scheme 6) in a mixing of the empty d^0 fragment orbital of the Cp_2Ti moiety with the HOMO of the dithiolene moiety of π character. Indeed, both fragment orbitals have different symmetry in the unfolded, $\theta = 0°$, C_{2v} conformation and cannot interact.[43] Folding allows for orbital mixing and leads to a stabilization of the d^0 system. Accordingly, the d^2 $Cp_2Mo(dt)$ complexes are not expected to exhibit any folding, as experimentally observed. The intermediate situation is therefore of interest and d^1 V or Nb complexes exhibit indeed intermediate folding angles ($20° \leq \theta \leq 30°$).

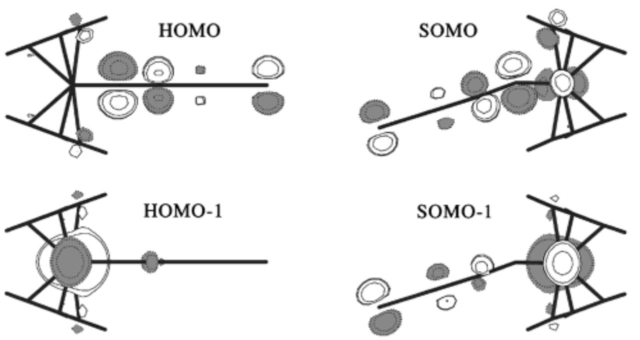
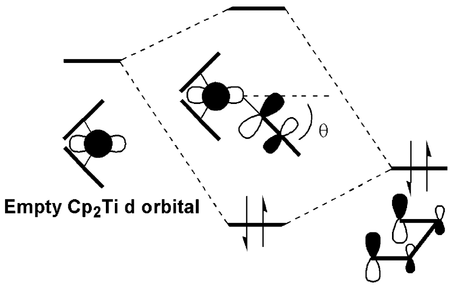


FIGURE 4. Representations of the DFT-calculated HOMO and HOMO − 1 of $Cp_2Mo(dmit)$ (left, $\theta = 0°$) and the SOMO and SOMO − 1 of the $Cp_2W(dsit)^{+\bullet}$ cation (right, $\theta = 30.1°$) in its AsF_6^- salt (taken from ref 44).

Scheme 6



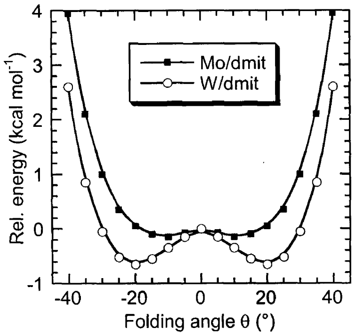
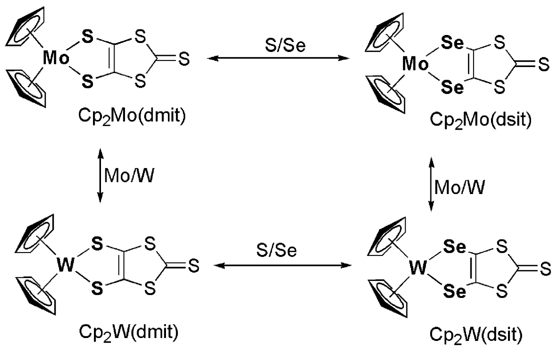


FIGURE 5. Energy profile of the folding process in the d^1 $Cp_2Mo(dmit)^{+\bullet}$ and $Cp_2W(dmit)^{+\bullet}$ complexes.

Table 2. Folding Angle θ (deg) in Various $Cp_2M(dt)$ Complexes in Their Salts

	$TCNQF_4^{\bullet-}$	AsF_6^-
$Cp_2Mo(dmit)^{\bullet+}$	10.2(1)	0.0
$Cp_2Mo(dsit)^{\bullet+}$	27.56(1)	0.0
$Cp_2W(dmit)^{\bullet+}$	27.90(6)	0.0
$Cp_2W(dsit)^{\bullet+}$	32.38(1)	31.1(1)

Scheme 7



The highly variable folding of the $Cp_2Mo(dmit)^{+\bullet}$ complex, with θ between 0° and 30° depending on the counterion, is therefore highly intriguing. It has also important consequences on the SOMO of the d^1 complexes since a larger folding increases the mixing of the Cp_2Mo and dithiolene frontier orbitals and transfers spin density from the dithiolene (where the SOMO is essentially localized when $\theta = 0°$) to the metal (Figure 4). This is also clearly evidenced by the evolution of the bond lengths within the dmit moiety in the different complexes (Table 1). When compared with the neutral $Cp_2Mo(dmit)$ complex, the shortening of the C−S bonds and the lengthening of the C═C double bonds, which are the signature of the oxidation of the dithiolene moiety, are indeed strongest in the unfolded oxidized complexes. We are therefore faced here with donor molecules, the $Cp_2Mo(dt)$ complexes, the SOMO of which in their oxidized state is intimately correlated with their structural environment. DFT calculations were performed to determine the energy profile of this folding process (Figure 5).[44] The d^1 $Cp_2Mo(dmit)$ complex shows a minimum energy at $\theta = 14°$ but with very shallow energy wells (<0.5 kcal mol^{-1}); the folding angle can take values between 0° and 35° without exceeding an energy cost of more than 1 kcal mol^{-1}. As a consequence, the molecular structure of the open-shell species and its solid-state arrangement with a given counterion are intimately correlated and adapt mutually to each other, a very original characteristic of those complexes. It follows that a given complex can exhibit very different SOMOs, depending on the exact geometry (folding angle) it adopts in the crystal structure. This behavior contrasts strongly with that of "classical" square-planar Ni, Pt, and Pd complexes the molecular geometry and frontier orbitals of which are essentially invariant in every solid-state structure they adopt.

Note also that larger folding angles were recurrently observed when moving to heavier elements, either by substituting tungsten for molybdenum or by substituting selenium (in the dsit ligand) for sulfur (in the dmit ligand) as coordinating atoms, as seen for example in their $TCNQF_4^{\bullet-}$ salts (Table 2). This heavy atom effect toward larger θ values was confirmed by the calculations (Figure 5).[44] In that respect, the unfolded, $\theta = 0°$, complex obtained with AsF_6^-, $[Cp_2Mo(dmit)][AsF_6]$, offers an exemplary playground to test this "heavy atom" effect by replacing the molybdenum, the coordinating sulfur atoms, or both by selenium, tungsten, or both (Scheme 7). Electrocrystallizations of $Cp_2Mo(dsit)$, $Cp_2W(dmit)$, and $Cp_2W(dsit)$ were performed in the presence of the same AsF_6^- anion and afforded isostructural salts with the same unfolded, $\theta = 0°$, structure only with $Cp_2Mo(dsit)$ and $Cp_2W(dmit)$, while the "heaviest" $Cp_2W(dsit)$ complex led to a fully different structure with $\theta = 30.1°$.[44]

An interesting extension is also offered with the *ansa*-metallocene dithiolene complexes (Figure 6) such as $Me_2C(\eta^5\text{-}C_5H_4)_2Mo(dmit)$ or $Me_2C(\eta^5\text{-}C_5H_4)_2W(dmit)$.[45] The *ansa* substitution not only rigidifies the structure but also brings closer together the two Cp rings. Despite the

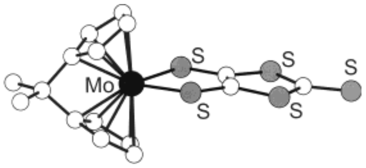


FIGURE 6. The *ansa*-metallocene dithiolene complex $Me_2C(\eta^5\text{-}C_5H_4)_2Mo(dmit)$ in its oxidized form, as observed in the X-ray crystal structure of $[Me_2C(\eta^5\text{-}C_5H_4)_2Mo(dmit)]_2[TCNQF_4]$.

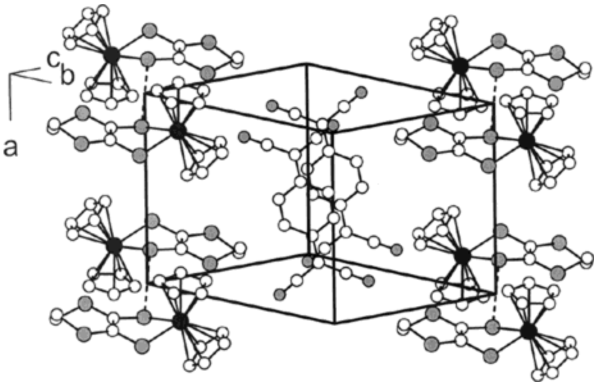
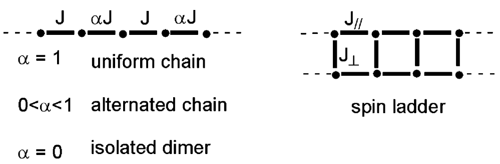


FIGURE 7. A view of the solid-state arrangement of $[Cp_2Mo(dddt)]$-$[TCNQ]$ showing the $[TCNQ]_2{}^{2-}$ dyad at the center of the unit cell and $[Cp_2Mo(dddt)]^{+\bullet}$ dyads interacting weakly with each other in an alternated chain running along *a*.

Scheme 8



presence of the electron-donating Me_2C substituent, the complexes oxidize at 0.1 V higher than the corresponding unsubstituted complexes. Both Mo and W neutral molecules are essentially unfolded ($\theta_{Mo} = 0.68°$, $\theta_W = 0.29°$) as expected for d^2 complexes, while the oxidized molecules, as $TCNQF_4$ salts, experience only a weak folding ($\theta_{Mo} = 7.35°$, $\theta_W = 6.99°$).

Solid-State Structural and Magnetic Properties.

The varying degrees of delocalization of the spin density on the dithiolene fragments, together with the solid-state organization adopted by these $Cp_2M(dt)^{+\bullet}$ radical cations in their crystalline salts, are expected to generate different solid-state magnetic behaviors, since they control the strength and extent of intermolecular dt···dt and dt···Cp interactions. As shown below, two characteristic structural motifs have been identified, either dyadic entities more or less strongly coupled or extended three-dimensional structures.

In the isostructural $[Cp_2Mo(dddt)][TCNQ]$[36] and $[Cp_2W(dddt)][TCNQ]$ salts,[46] the cationic $Cp_2M(dddt)^{\bullet+}$ species are indeed organized into dyads with short S···S contacts (Figure 7). These dyadic entities are not isolated from each other but interact with neighboring ones along *a* to give rise to an alternated chain system (Scheme 8, $0 < \alpha < 1$, each dot represents a spin carrier, each bold line an interaction) with the following characteristics, $J_{Mo}/k = -26$ K (18 cm^{-1}), $\alpha_{Mo} = 0.0-0.2$, $J_W/k = -16$ K (11 cm^{-1}), $\alpha_W = 0.5-0.6$ where J and αJ characterize the interactions between radicals along the chain.[47] The negative values obtained for J and αJ confirm the antiferromagnetic nature of the interactions, due to direct exchange interaction between SOMOs.

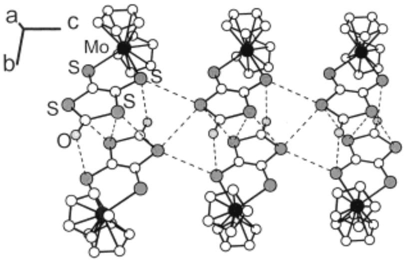


FIGURE 8. The ladder-like stacking of $[Cp_2Mo(dmid)]^{+\bullet}$ species along *c* in $[Cp_2Mo(dmid)][TCNQF_4]$.

Table 3. Magnetic Properties of the Spin-Ladder Systems

compound	$\lvert J_\perp \rvert/k$	$\lvert J_\parallel \rvert/k$	ref
$[Cp_2Mo(dmid)][TCNQF_4]$	106.8 K (74.2 cm^{-1})	40.7 K (28.3 cm^{-1})	37
$[Cp_2W(dmid)][TCNQF_4]$	23.4 K (16.3 cm^{-1})	15.6 K (10.8 cm^{-1})	37
$[Cp_2W(dsit)][AsF_6]$	165 K (114.7 cm^{-1})	90 K (62.5 cm^{-1})	44

We note also that $|J_{Mo}| > |J_W|$, a first illustration of an increased metal localization in the tungsten complexes. The same effect is observed in the $TCNQF_4{}^{\bullet-}$ salts[37] of $Cp_2Mo(dsit)$ and $Cp_2W(dsit)$ where a uniform chain model (Scheme 8, $\alpha = 1$) with $J/k = -147$ K (102 cm^{-1}) best applies for the molybdenum salt while the more pronounced susceptibility maximum observed in $[Cp_2W(dsit)]$-$[TCNQF_4]$ reflects a higher degree of interaction between dyads, well-fitted with the alternated chain model with $J_W/k = -113$ K (78.5 cm^{-1}) and $\alpha = 0.5$, with again $|J_{Mo}| > |J_W|$.

The first examples of molecular spin ladders[48] were found in $TCNQF_4{}^{\bullet-}$ salts[37] of $Cp_2Mo(dmid)$ and $Cp_2W(dmid)$ (Figure 8), as well as in $[Cp_2W(dsit)][AsF_6]$.[44] In the salts, the dyadic entities formed by two organometallic cations stack on top of each other to afford a ladder-like system. Such magnetic systems are characterized by two interaction paths, $J_\perp$ within the rungs and $J_\parallel$ along the arms (Scheme 8); they have been recently the subject of much interest in solid-state physics as a result of the increased importance of the quantum-mechanical effects operating with them.[49] The magnetic characteristics of the spin ladders described here are collected in Table 3. They illustrate again the stronger intermolecular interactions observed in the molybdenum salts due to their SOMOs being more concentrated on the dithiolene moiety. We note also that $|J_\perp|$ is systematically larger than $|J_\parallel|$, a confirmation of the strong tendency of these cation radicals to associate into dyads, the elementary building block for further associations in the solid state, either in an alternated chain or in a ladder system.

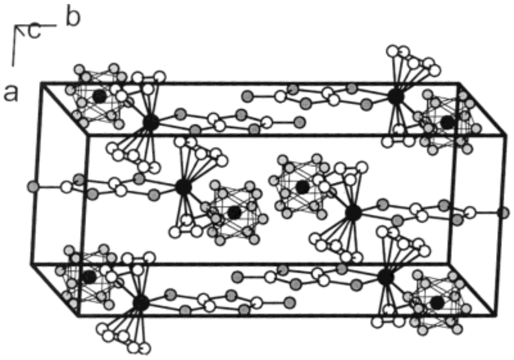


FIGURE 9. View of the unit cell of [Cp_2Mo(dmit)][AsF_6].

Table 4. Magnetic Properties of the [$Cp_2M(dmit)^{+\bullet}$][X] Salts, M = Mo or W and X = PF_6^-, AsF_6^-, or SbF_6^-

compound	$\theta_{Curie-Weiss}$ (K)	$T_{Néel}$ (K)
[Cp_2Mo(dmit)][**P**F_6]	−37	11.5
[Cp_2Mo(dmit)][**As**F_6]	−21	9.5
[Cp_2Mo(dmit)][**Sb**F_6]	−14	7.5
[Cp_2**W**(dmit)][AsF_6]	−3.4	3.5

The only exception to dyad formation is found in [Cp_2Mo(dmit)][AsF_6].[40] In this salt (Figure 9), each cation, in a surprising unfolded ($\theta = 0°$) conformation, is surrounded by 10 neighbors, affording a truly three-dimensional set of intermolecular interactions. This peculiar structural organization with a unfolded cation was maintained when the AsF_6^- anion was replaced by the smaller PF_6^- or larger SbF_6^- [40,41] or molybdenum was replaced by tungsten, that is, with Cp_2W(dmit).[44] In these salts, a Curie−Weiss behavior at the higher temperatures and a transition to an antiferromagnetic ground state (AF) below $T_{Néel}$ confirm the presence of strong 3D antiferromagnetic interactions and their increase with the smaller anions, in accordance with the unit cell contraction (Table 4).

The Neutral d^1 Cp*M(dt)$_2^\bullet$ Complexes, M = Mo or W.

Considering the competition between the 1D and 3D extension of antiferromagnetic interactions in the salts of $Cp_2M(dt)^{\bullet+}$, it was thought that complexes incorporating *two* dithiolate for *one* cyclopentadienyl ligands would stabilize 3D structures through a larger number of dithiolene···dithiolene intermolecular interactions. We have found indeed (Figure 10) that the d^2 anionic, Mo^{IV} Cp*Mo(dmit)$_2^-$ anionic complex, can be successfully electrocrystallized to afford a one-electron oxidation product, that is, the neutral Cp*Mo(dmit)$_2^\bullet$ radical.[50] In this complex, as well as in the analogous tungsten derivative,[51] the oxidation process affects the dithiolene moieties where the SOMO is essentially localized, while the MS_2C_2 metallacycles change folding upon oxidation, as already observed in the Cp_2M(dt) series. Both Mo and W neutral radicals exhibit a 3D set of intermolecular interactions (Figure 11), and the temperature dependence of the spin susceptibility is of a Curie−Weiss type [$\chi = C/(T - \theta)$] with $\theta_{Mo} = -38$ K and $\theta_W = -20$ K. They both order antiferromagnetically below $T_{Néel}$ at 8 K (Mo) or 4.5 K (W), confirming the three-dimensional set of intermolecular interactions. Here again, the Mo complex exhibits stronger intermolecular interactions, reflected by higher θ and $T_{Néel}$ values, indicating a stronger localization of the spin density on the dithiolene moiety, also confirmed by DFT calculations[51] on these Cp*M(dmit)$_2^{-,\bullet}$ (M = Mo, W) series. The spin density is indeed almost exclusively located on the dmit and Cp* ligands with essentially no contribution of the Mo atom in [Cp*Mo(dmit)$_2$]$^\bullet$, while 15% of the spin density is located on the W atom in [Cp*W(dmit)$_2$]$^\bullet$.[52]

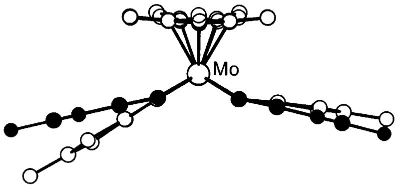


FIGURE 10. Evolution of the folding of the metallacycles deduced from the X-ray crystal structures in the d^2 [Cp*Mo(dmit)$_2$]$^-$ (dithiolene ligands in black) and the d^1 [Cp*Mo(dmit)$_2$]$^\bullet$ (dithiolene ligands in white) complexes.

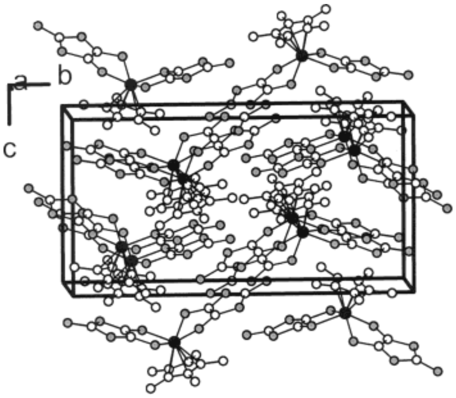


FIGURE 11. View of the unit cell of [Cp*Mo(dmit)$_2$]$^\bullet$.

Conclusion

Besides the metal-centered, noninteracting radical species such as Cp_2Nb(dt) or (cot)U(dddt)$_2^-$, the different radical complexes described above exhibit a very delicate balance of spin delocalization between the metallic and dithiolene fragments. These radical complexes the varying SOMO of which is intimately correlated with the crystal structure they adopt, illustrate also perfectly the characteristic structural and magnetic behaviors encountered with such radical molecular systems, either a *delocalized* interaction between open-shell species, which extends in the whole solid in a 1D (the uniform spin chain of Cp*Co(dmit)Br or [Cp_2Mo(dsit)][$TCNQF_4$]), 2D, or 3D organization ([Cp_2Mo(dmit)][AsF_6] and analogues with antiferromagnetic ground state), or a *localized*, dimerized state where two radicals associate through a 2e$^-$ bond. The magnetic behavior of those dyadic entities will then depend (i) on the strength of the interaction, very strong in [Cp*Co(dddt)]$_2$[BF_4]$_2$ and weaker in other examples with an activated singlet−triplet state, and (ii) on the degree and geometry of interaction of those dyads with neighbors within alternated chains or spin ladders. Because of their highly adaptable geometry, these nonplanar radical dithiolene complexes have demonstrated here their ability to interact in the solid state to give rise to ordered magnetic states. It is therefore expected that more delocalized dithiolate ligands, mixed-valence systems based on such complexes, or both could also offer opportunities as single-component conducting systems.[11,53,54]

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$$\mathbf{H} = -J\sum_{i=1}^{n-1}\mathbf{S}_i\cdot\mathbf{S}_{i+1}$$

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