

SPIN COUPLING INTERACTIONS IN TRANSITION METAL COMPLEXES CONTAINING RADICAL *o*-SEMIQUINONE LIGANDS. A REVIEW

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We dedicate this review to the memory of Professor Antonín A. Vlček.

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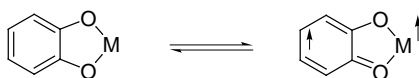
Transition metal complexes of *o*-semiquinone (SQ) ligands have been studied extensively over the past 25 years. A particularly interesting aspect of this coordination chemistry concerns magnetic interactions between paramagnetic metal ions and the radical anionic ligands. In this review we begin with a survey of relatively simple complexes consisting of a paramagnetic metal ion chelated by a single SQ ligand. Recent studies have revealed the importance of SQ-SQ coupling through diamagnetic metals, and complexes of this class are described in the second section of the review. Both interactions combine to account for the often complicated magnetic properties of complexes containing multiple SQ ligands chelated to a paramagnetic metal ion. Research on these complexes is surveyed in the third section with a concluding look toward polymeric SQ complexes. A review with 51 references.

Keywords: Magnetism; Semiquinone; Transition metal; Magnetic exchange; Antiferromagnetic; Ferromagnetic; Quinones; Radicals.

1. INTRODUCTION

Interests in the design of high-spin molecular-based ferromagnets have been directed to combinations of subunits that may be assembled with mu-

tually orthogonal magnetic orbitals¹. Semiquinone (SQ) radical anions have been of great interest in the construction of magnetic materials that are purely organic in composition and in the formation of organotransition metal materials that combine radical ligands with paramagnetic metal ions². Semiquinones have been of utility in the latter class of compounds due to their stability upon coordination, their ease of formation, and, most significantly, the directional character of their magnetic orbital. A further interest in metal-SQ magnetic exchange has developed around the switching properties of quinone complexes that involve shifts in charge distribution *via* valence tautomerism³. Charge transfer within a diamagnetic metal-catecholate complex unit may lead to an easily detectable high-spin paramagnetic metal-SQ species.



*Studies on magnetic interactions between paramagnetic metal ions and radical ligands go back over decades. The earliest and most widely studied class of organic radical ligands are the nitroxyls. A disadvantage of these radicals is that they are not strong ligands, and rotation about the M–O bond leads to ambiguous orbital alignment. Complexes of semiquinones with diamagnetic metals had been investigated in the early 1970's using EPR spectroscopy⁴. Most studies were carried out on solutions. Few SQ complexes were isolated as solids, and the primary focus of interest was on stabilizing a class of “reactive organic radicals” by coordination with a metal ion. In the mid-1970's we reported the formation of binary metal quinone complexes, $[M(Q)_3]$ ($M = V, Cr, Fe$), by treating a neutral metal carbonyl complex with an 1,2-benzoquinone^{5,6}. EPR spectra recorded on the vanadium complex indicated a ligand-based spin for the $S = 1/2$ complex. Temperature-dependent magnetic properties of the Cr and Fe complexes, obtained collaboratively with David Hendrickson, with Mössbauer spectra

+ Glossary of ancillary ligand abbreviations: bpy, 2,2'-bipyridine; CTH, dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; $Me_3[12]N_3$, 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene; NHPy₂, bis(2-pyridyl)amine; py, pyridine; pyz, pyrazine; salen, *N,N'*-bis(salicylidene)-ethylenediamine dianion; saloph, *N,N'*-bis(salicylidene)-1,2-phenylenediamine dianion; salpren, *N,N'*-bis(salicylidene)-1,3-propylenediamine dianion; tmeda, *N,N,N',N'*-tetramethylethylenediamine; Tp, hydrotris(1-pyrazolyl)borate anion; $Tp^{Cum,Me}$, hydrotris-(3-(4-cumenyl)-5-methylpyrazol-1-yl)borate anion; tren, tris(2-aminoethyl)amine.

that indicated high-spin Fe(III) for the $\text{Fe}(\text{Q})_3$ molecules, all pointed to a $\text{M}^{\text{III}}(\text{SQ})_3$ formulation for the molecules containing first-row transition metal ions^{6,7}. This view was further supported by structural features obtained from crystallographic studies⁸. In the context of investigations on SQ magnetic exchange, these compounds provided an entry, but, as multispin systems, they have been the most difficult to interpret with a quantitative model. Rather than structuring this review in a chronological format we will begin with a description of simple $\text{M}^{\uparrow}\text{-SQ}^{\uparrow}$ systems containing one SQ ligand, followed with a review of recent work on metal-mediated SQ-SQ exchange in $\text{SQ}^{\uparrow}\text{-M-SQ}^{\uparrow}$ complexes containing diamagnetic metal ions. Studies on multi-SQ complexes of paramagnetic metal ions will be described in the final section of the review. The structures of commonly used SQ ligands are shown in Fig. 1.

2. METAL-SQ MAGNETIC EXCHANGE IN COMPLEXES CONTAINING A SINGLE RADICAL LIGAND

A large number of complexes have been studied that contain a single SQ radical ligand chelated to a paramagnetic metal ion. Complexes ordered by metal d-configuration are listed in Table I. As a general observation, nearly

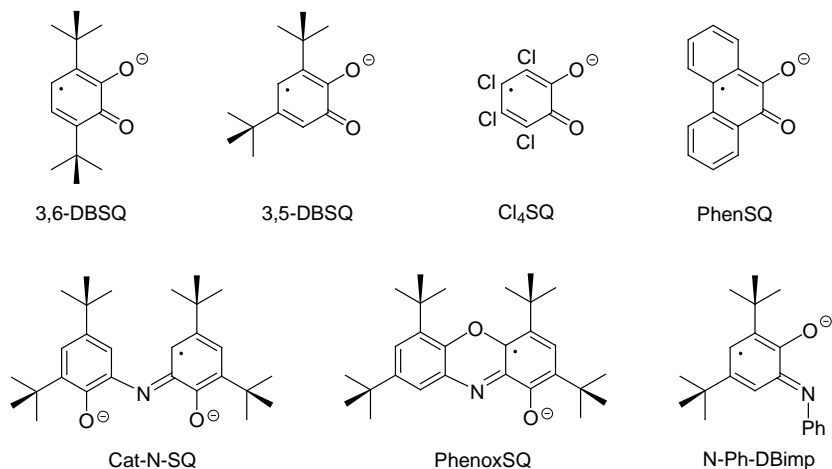


FIG. 1

Commonly used *o*-semiquinone ligands: 3,5-di-*tert*-butyl-1,2-benzosemiquinone (3,5-DBSQ), 3,6-di-*tert*-butyl-1,2-benzosemiquinone (3,6-DBSQ), tetrachloro-1,2-benzosemiquinone (Cl_4SQ), phenanthrenesemiquinone (PhenSQ), 1-hydroxy-2,4,6,8-tetra-*tert*-butylphenoxazin-4a-yl radical (PhenoxSQ), 2-(2-hydroxy-3,5-di-*tert*-butylphenylimino)-4,6-di-*tert*-butylcyclohexa-3,5-dienyl radical (Cat-N-SQ), *N*-phenyl-3,5-di-*tert*-butyliminosesemiquinone (N-Ph-DBimSQ)

all of the entries have magnetic moments near room temperature that reflect strong SQ coupling with the metal. In many cases magnetic moment measurements were extended to low temperature revealing a dependence that may arise from a number of effects including intermolecular exchange, spin-orbit coupling, and the effects of zero-field splitting. At the top of Table I are three Cr^{III}-SQ complexes. Strong antiferromagnetic coupling be-

TABLE I
Magnetic properties of L_nM-SQ complexes containing paramagnetic metal ions

d ⁿ	Complex	μ _{eff} (μ _B) ^a	S	Ref.
d ³	[Cr(tren)(3,6-DBSQ)](PF ₆) ₂	2.9	1	9
	[Cr(CTH)(3,5-DBSQ)] ₂ Cl(PF ₆) ₃	2.9	1	10
	[Cr(bpy)(3,5-DBSQ)(3,5-DBCat)]	2.9	1	11
d ⁴	[Mn(salen)(3,5-DBSQ)]	4.2	3/2	12
	[Mn(4,4'-bpy) ₂ (3,6-DBSQ)(3,6-DBCat)]	4.2	3/2	13
	[Mn(py ₂)(3,6-DBSQ)(3,6-DBCat)] _n	4.2	3/2	14
d ⁵	[Fe(salen)(PhenSQ)]	4.9	2	12
	[Fe(salen)(NapSQ)]	4.9	2	12
	[Fe(salen)(3,5-DBSQ)]	4.9	2	12
	[Fe(bpy)(3,6-DBSQ)(3,6-DBCat)]	5.3	2	15
	[Fe(tmeda)(3,6-DBSQ)(3,6-DBCat)]	5.3	2	15
	[Fe(py) ₂ (3,6-DBSQ)(3,6-DBCat)]	5.2	2	16
	[Fe(Cat-N-BQ)(Cat-N-SQ)]	5.3	2	17
d ⁷	[Co(Tp ^{Cum,Me})(3,6-DBSQ)]	3.9	1	18
d ⁸	[Ni(CTH)(3,5-DBSQ)]PF ₆	4.3	3/2	19
	[Ni(CTH)(Cl ₄ SQ)]PF ₆	4.4	3/2	20
	[Ni(Me ₃ [12]N ₃)(3,5-DBSQ)]ClO ₄	1.9	1/2	21
d ⁹	[Cu(Tp ^{Cum,Me})(3,6-DBSQ)]	3.0	1	18
	[Cu(Me ₃ [12]N ₃)(3,5-DBSQ)]ClO ₄	2.8	1	21
	[Cu(NHPy ₂)(3,5-DBSQ)]ClO ₄	2.7	1	22
	[Cu(py) ₂ (Cat-N-SQ)]	2.8	1	23
f ⁷	[Gd(Tp) ₂ (3,5-DBSQ)]	7.9	3	24

^a Magnetic moment at a temperature near room temperature. Exact temperatures vary for different references.

tween the metal and the radical ligand results in a $S = 1$ spin state for the molecules at room temperature, and a value for μ_{eff} that is close to $2.83\mu_{\text{B}}$ (refs⁹⁻¹¹). A view of the $S = 1$ $[\text{Cr}^{\text{III}}(\text{tren})(3,6\text{-DBSQ})]^{2+}$ ion⁹ is shown in Fig. 2. Semiquinone complexes of high-spin Mn(III) have $S = 3/2$ spin ground states at room temperature including the mixed-charge bis-(quinone) complexes *trans*- $[\text{Mn}(4,4'\text{-bpy})_2(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ and polymeric *trans*- $[\text{Mn}(\text{pyz})(3,6\text{-DBSQ})(3,6\text{-DBCat})]_n$ (Fig. 3). Structural characterization on both SQ-Cat complexes shows axial elongation as a signature of the Jahn–Teller distorted d^4 Mn(III) ion^{13,14}. Bioinorganic interests in Fe–SQ exchange led to a large number of $[\text{Fe}(\text{salen})(\text{SQ})]$ molecules prepared with salen, salpren, and saloph ancillary ligands and a variety of semiquinones^{12,25}. Only the salen complexes are listed in Table I, but magnetic moments at room temperature for the series range from 4.6 to $4.9\mu_{\text{B}}$. A series of mixed-charge ligand complexes, $[\text{Fe}(\text{N–N})(\text{SQ})(\text{Cat})]$ have been studied with various N-donor ancillary ligands and with an assortment of quinone ligands^{15,26}. In general, magnetic moments tend to be slightly higher than that for the $[\text{Fe}(\text{salen})(\text{SQ})]$ species, perhaps due to an additional orbital contribution. But magnetic moments near room temperature are close to the $S = 2$ value and Mössbauer spectra indicate high-spin (hs)-Fe(III) at all temperatures. Magnetic characterization on $[\text{Fe}(\text{bpy})(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ (Fig. 4) points to the importance of other contributions beside Fe–SQ exchange. Magnetic moment begins at a value of $5.64\mu_{\text{B}}$

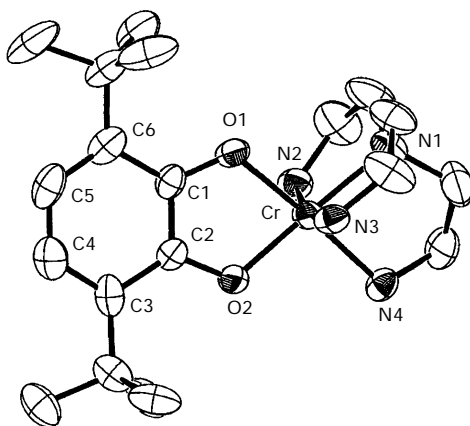


FIG. 2

A view of the $[\text{Cr}(\text{tren})(3,6\text{-DBSQ})]^{2+}$ dication

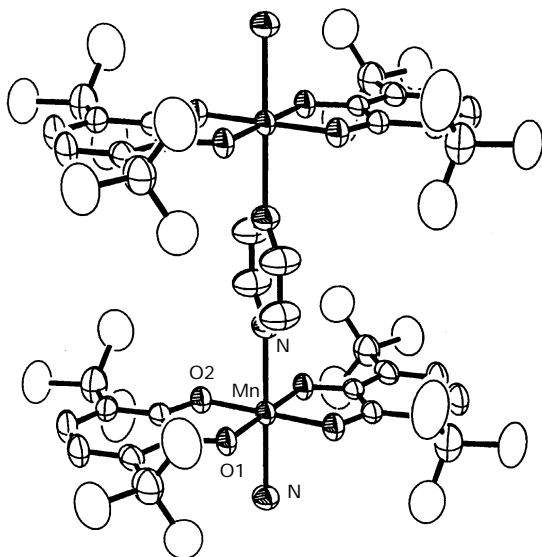


FIG. 3
A view of one unit from the $[\text{Mn}(\text{pyz})(3,6\text{-DBSQ})(3,6\text{-DBCat})]_n$ polymer

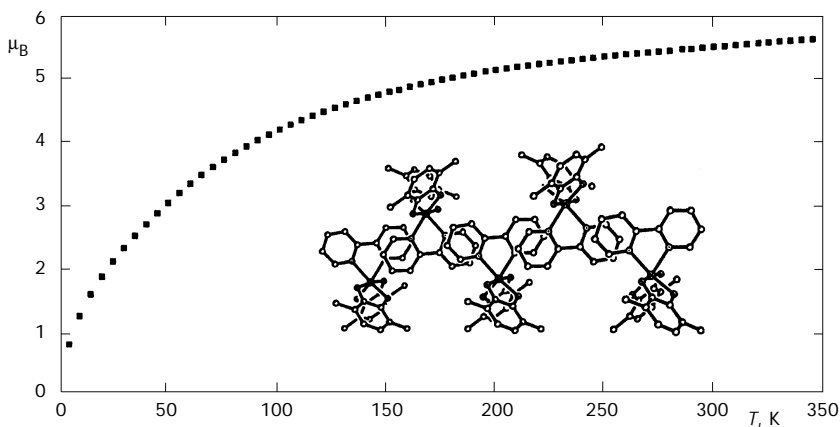


FIG. 4
Temperature dependence of magnetic moment and view of intermolecular stacking for $[\text{Fe}(\text{bpy})(3,6\text{-DBSQ})(3,6\text{-DBCat})]$

at 350 K, slightly above the $S = 2$ value, and drops to a value of $0.81\mu_B$ at 5 K. Mössbauer spectra indicate that the metal remains in the form of hs-Fe(III) to 110 K. In the solid state, molecules are paired in stacks formed by interacting 2,2'-bipyridine ligands. There is only one hs- d^7 complex that we are aware of $[\text{Co}^{\text{II}}(\text{Tp}^{\text{Cum,Me}})(3,6\text{-DBSQ})]$ (ref.¹⁸). Magnetic moment in this case is considerably higher than the $S = 1$ value at 350 K, $4.0\mu_B$, but Co-SQ coupling is clearly antiferromagnetic, with μ_{eff} decreasing to a value of $1.8\mu_B$ at 4.2 K (Fig. 5). Other similar complexes have the diamagnetic low-spin (ls)-Co(III)-Cat charge distribution related by transfer of an electron from the metal to the quinone ligand²⁷.

With the shift from hs- d^7 to d^8 all d_π metal spins are paired, the remaining metal spins reside in d_σ orbitals. Since the SQ spin is contained in an orbital of π symmetry, the nature of the coupling interaction with the metal changes. This is clear for the octahedral SQ complexes of Ni(II) that have values for magnetic moment at room temperature near the $S = 3/2$ value. This spin state arises from ferromagnetic Ni-SQ exchange. The $S = 1/2$ value reported for $[\text{Ni}(\text{Me}_3[12]\text{N}_3)(3,5\text{-DBSQ})]\text{ClO}_4$ is strongly antiferromagnetic and anomalous²¹. It may result from changes in orbital symmetry associated with the five-coordinate structure, or a dimeric structure of the type found commonly²⁷ for complexes of 3,5-DBSQ. Five-coordinate complexes of Cu(II) are found to have $S = 1$ values for magnetic moment arising from strong ferromagnetic exchange. Recent characterization on the f^7 gadolinium(III) complex $[\text{Ga}(\text{Tp})_2(3,5\text{-DBSQ})]$ has shown that the complex has an

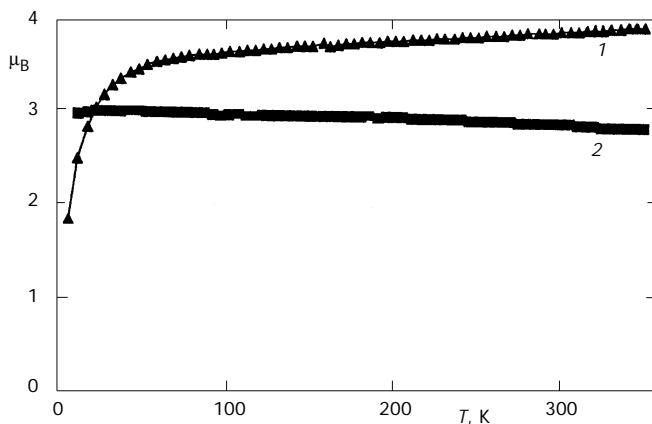


FIG. 5

Temperature dependence of magnetic moment for $[\text{Co}(\text{Tp}^{\text{Cum,Me}})(3,6\text{-DBSQ})]$ (1) and $[\text{Cu}(\text{Tp}^{\text{Cum,Me}})(3,6\text{-DBSQ})]$ (2)

$S = 3$ spin ground state arising from weak antiferromagnetic Ga-SQ exchange²⁴ ($J = -5.5 \text{ cm}^{-1}$).

2.1. Conclusions

- M-SQ magnetic exchange is generally strong for paramagnetic metal ions of the first transition series.
- The nature of exchange is dependent on spin alignment. M-SQ interactions for metal ions containing d_π spins are antiferromagnetic, d_σ -SQ interactions tend to be ferromagnetic.
- Magnetic measurements extended to low temperature often drop below the magnetic moment expected for strong M-SQ exchange due to secondary effects that might include zero-field splitting, spin-orbit coupling, and intermolecular exchange interactions.

3. COUPLING BETWEEN SQ LIGANDS THROUGH A DIAMAGNETIC METAL ION

Analyses of temperature-dependent changes in magnetism for SQ complexes of paramagnetic metal ions have focused primarily on M-SQ exchange. In more recent investigations it has been shown that the coordinated metal ion can propagate SQ-SQ coupling, and the interaction is often quite strong. Further interests have been directed at the dependence of exchange on the nature of metal orbitals interacting with SQ spin²⁸. Table II contains a list of complexes containing diamagnetic metal ions that provide a "bridge" between radical SQ ligands. There are several examples of $[\text{RuL}_2(\text{SQ})_2]$ complexes prepared with PPh_3 , CO, and α -diimine ligands^{27,29}. They are all diamagnetic and show sharp NMR spectra. Metal-mediated coupling between SQ ligands is clearly very strong for this series. Members of the $[\text{M}(\text{DBSQ})_2]$ series with Ni, Pd, and Pt and both 3,5-DBSQ and 3,6-DBSQ have been investigated³⁰. Square planar $[\text{Ni}(3,6\text{-DBSQ})_2]$ and $[\text{Pd}(3,5\text{-DBSQ})_2]$ are nominally diamagnetic at room temperature, but they both show residual paramagnetism with broadened and shifted ^1H NMR resonances. $[\text{Pt}(3,5\text{-DBSQ})_2]$ is completely diamagnetic and shows sharp NMR signals. Out-of-plane d_π orbitals appear to be quite effective at promoting SQ exchange. Magnetic characterization on $[\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2]$ and $[\text{Co}(3,6\text{-DBSQ})_3]$ (Figs 6, 7) showed temperature-dependent behavior, indicating antiferromagnetic coupling between radical ligands³¹. Related complexes of main group metal ions, Ga(III), Al(III), and Sn(IV), show the effects of ferromagnetic exchange between SQ ligands, pointing to a difference in coupling mechanism. The difference, antiferromagnetic vs ferro-

magnetic, has been viewed as arising from differences in symmetry of the metal orbital promoting exchange (d vs p)^{28,34}. Recent magnetic characterization on [Co(H-Ph-Dbimp)₃], obtained as the C₁ structural isomer, has shown that exchange between the imidophenolate radical ligands is ferromagnetic³⁵. Two coupling constants were used in the analysis, but the result is clearly different from the more symmetrical [Co(3,6-DBSQ)₃] molecule. Dei and Gatteschi have studied a series of octahedral complexes prepared with the Cat-N-SQ radical ligand³³. In each case, planar tridentate radical ligands are aligned in orthogonal planes and the exchange interaction is predictably ferromagnetic.

3.1. Conclusions

– Metal-mediated SQ–SQ magnetic exchange can be relatively strong and observable in variable temperature magnetic measurements.

TABLE II
SQ–SQ magnetic exchange through a diamagnetic metal ion

Complex	J^a , cm ⁻¹	Ref.
[Ru(CO) ₂ (3,6-DBSQ) ₂]	strong, antiferromagnetic ^b	29
[M(3,6-DBSQ) ₂], M = Ni, Pd, Pt	strong, antiferromagnetic ^b	30
[Zn(tmeda)(3,6-DBSQ) ₂]	-33.7	31
[Sn(3,6-DBSQ) ₂ (3,6-DBCat)]	6.2	32
[Ti(Cat-N-SQ) ₂]	23	33
[Ge(Cat-N-SQ) ₂]	14	33
[Sn(Cat-N-SQ) ₂]	12	33
[Ga(3,6-DBSQ) ₃]	6.2	31
[Al(3,6-DBSQ) ₃]	8.6	31
[Ga(3,5-DBSQ) ₃]	7.8	34
[Co(3,6-DBSQ) ₃]	-39.1	31
[Co(N-Ph-DBimp) ₃]	9.1, 59.5 ^c	35

^a $H = -2J(S_1S_2)$ for [ML_n(SQ)₂], $H = -2J(S_1S_2 + S_1S_3 + S_2S_3)$ for [M(SQ)₃]. ^b Diamagnetic. ^c $H = -2J(S_1S_2 + S_2S_3) - 2J_{13}(S_1S_3)$.

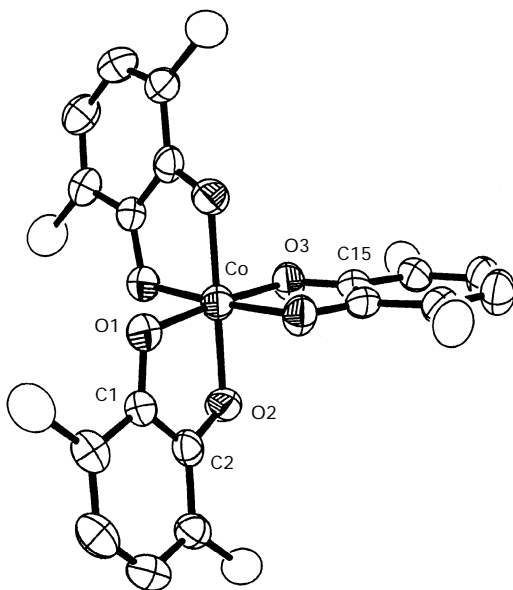


FIG. 6
Structural features of $[\text{Co}(3,6\text{-DBSQ})_3]$ and isostructural $[\text{Ga}(3,6\text{-DBSQ})_3]$

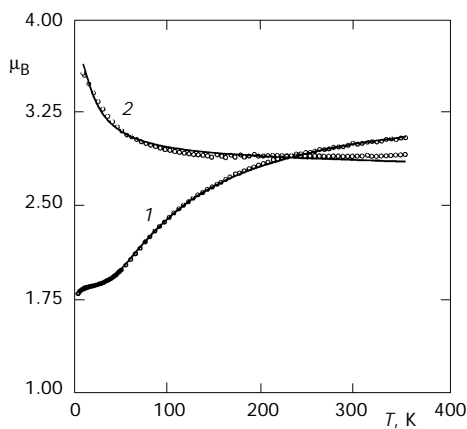


FIG. 7
Temperature dependence of magnetic moment for $[\text{Co}(3,6\text{-DBSQ})_3]$ (1) and $[\text{Ga}(3,6\text{-DBSQ})_3]$ (2)

– Coplanar radicals couple antiferromagnetically and orthogonal radical planes result in ferromagnetic exchange. Chelated octahedral complexes exhibit magnetic properties that result from subtle differences in ligand orbital alignment, and from the symmetry of metal orbitals propagating interrational exchange.

4. COMPLEXES CONTAINING PARAMAGNETIC METAL IONS AND MULTIPLE RADICAL LIGANDS

A large number of complexes containing multiple radical SQ ligands chelated with paramagnetic metal ions have been studied. A selection of complexes is listed in Table III. Crystallographic data available for nearly all of these compounds provides clear definition of crystal and molecular structure. Insights gained from M–SQ exchange in the simple compounds described in the first section of the review, and the importance of SQ–SQ exchange emphasized in the second section, aid in understanding the magnetic properties of these more complicated systems. Exchange in simple Cr^{III}–SQ complexes was found to be strong and antiferromagnetic. This carries over to members of the [Cr^{III}(SQ)₃] series which all have singlet spin ground states due to strong coupling between the $S = 3/2$ metal ion and the three $S = 1/2$ ligands⁷. The related d³ metal complex of Mn(IV), [Mn(3,6-DBSQ)₂(3,6-DBCat)], exhibits temperature dependence associated with weaker radical coupling with the metal³⁶. Magnetic moment reaches a value close to the $S = 1/2$ moment at low temperature. Here two radical ligands are coupled with the $S = 3/2$ metal. Related complexes of iron, members of the [Fe^{III}(SQ)₃] series, would be expected to have $S = 1$ spin ground states due to strong exchange with the three d_π spins. This appears true for [Fe(3,5-DBSQ)₃], but a strong contribution from SQ–SQ exchange was required to obtain a satisfactory fit to the data of [Fe(3,6-DBSQ)₃] (refs^{7,38}). Low temperature data for all members of the series but [Fe(3,5-DBSQ)₃] fall below the $S = 1$ value. This may be ascribed to intermolecular effects. Structural data on [Fe(PhenSQ)₃] shows solid-state stacking of the planar radical ligands of adjacent complex molecules, a feature that seems to appear generally for complexes of PhenSQ (Fig. 8). The phenoxazinyl radical complex [FeCl(PhenoxSQ)₂] has the strongly coupled $S = 3/2$ moment at room temperature which decreases slightly with decreasing temperature. Surrounding *tert*-butyl groups serve to isolate molecules in the solid state³⁹. Consequently, this decrease in moment seems associated with intramolecular orbital effects. The strongly temperature-dependent magnetic properties of

the methoxy-bridged $[\text{Fe}(\mu\text{-OMe})(3,6\text{-DBSQ})_2]_2$ dimer were satisfactorily modeled with two interacting $S = 3/2$ $\text{Fe}(\text{SQ})_2$ centres³⁸.

The move to octahedral $\text{Ni}(\text{II})$ with an $S = 1$, d^8_o configuration should lead to a change in the nature of radical exchange. Exchange in the simple Ni-SQ complexes is ferromagnetic, and it might be expected that an octahedral $\text{Ni}(\text{SQ})_2$ species would have a $S = 2$ spin ground state. Three complexes of this type have been reported. $[\text{Ni}(\text{bpy})(3,5\text{-DBSQ})_2]$ and $[\text{Ni}(3,6\text{-DBBQ})-$

TABLE III
Magnetic data for complexes of paramagnetic metal ions with multiple semiquinone ligands

Complex	μ_{eff} (≈ 300 K)	μ_{eff} (≈ 5 K)	Ref.
$[\text{Cr}(3,5\text{-DBSQ})_3]$	diamagnetic		7
$[\text{Cr}(\text{PhenSQ})_3]$	1.2	0.3	7
$[\text{Cr}(\text{Cl}_4\text{SQ})_3]$	1.1	0.4	7
$[\text{Mn}^{\text{IV}}(3,6\text{-DBSQ})_2(3,6\text{-DBCat})]$	3.7	1.7	36
$[\text{Mn}^{\text{II}}(3,5\text{-DBSQ})_2]_4$	5.1	5.6	37
$[\text{Fe}(3,5\text{-DBSQ})_3]$	3.0	2.8	7
$[\text{Fe}(3,6\text{-DBSQ})_3]$	4.7	2.2	38
$[\text{Fe}(\text{PhenSQ})_3]$	3.4	1.5	7
$[\text{Fe}(\text{Cl}_4\text{SQ})_3]$	3.9	2.1	7
$[\text{Fe}(\mu\text{-OMe})(3,6\text{-DBSQ})_2]_2$	3.0	1.0	38
$[\text{FeCl}(\text{PhenoxSQ})_2]$	3.8	2.9	39
$[\text{Fe}(3,5\text{-DBSQ})(3,5\text{-DBCat})]_4$	3.0	0.3	40
$[\text{Co}(\text{py})_2(\text{PhenSQ})_2]$	5.4	1.8	41
$[\text{Co}(3,5\text{-DBSQ})_2]_4$	4.6	2.3	41
$[\text{Ni}(3,5\text{-DBSQ})_2]_4$	4.3	2.8	41
$[\text{Ni}(\text{bpy})(3,5\text{-DBSQ})_2]$	4.3	3.9	41
$[\text{Ni}(3,6\text{-DBBQ})(3,6\text{-DBSQ})_2]$	4.6	4.4	30a
$[\text{Ni}(\text{py})_2(\text{PhenSQ})_2]$	4.2	2.6	41
$[\text{Ni}(\text{PhenoxSQ})_2]$	diamagnetic		39
$[\text{Cu}(3,6\text{-DBSQ})_2]$	2.8	1.9	42
$[\text{Cu}(2,5\text{-DBSQ})_2]_2$	2.6	0.8	22
$[\text{Cu}(\text{PhenoxSQ})_2]$	2.5	1.5	43

(3,6-DBSQ)₂] have high temperature magnetic moments (Table III) that are slightly below the $S = 2$ value ($4.90\mu_B$), but above the ($S = 1 + 2 \times S = 1/2$, $\mu_{\text{eff}} = 3.74\mu_B$) value for a decoupled system^{30a,41}. The 9,10-phenanthrene-semiquinone complex *cis*-[Ni(py)₂(PhenSQ)₂] shows a drop in μ_{eff} with decreasing temperature, and the structure determination shows⁴¹ strong pairing between PhenSQ ligands of adjacent molecules (Fig. 9). This undoubtedly leads to a significant antiferromagnetic intermolecular component to the coupling mechanism. The [Ni(Me₃[12]N₃)(Cl₄Q)₂] molecule seems from its structure to be best described as [Ni^{II}(Me₃[12]N₃)(Cl₄Cat)-(Cl₄BQ)], similar in quinone-ligand structure and charge distribution to [Cu(tmeda)(PhenBQ)(PhenCat)] (refs^{44,45}). The phenoxazinylate radical complex of Ni(II) is tetrahedral in structure (Fig. 10). Assuming that the metal is high-spin, metal-radical exchange is quite strong leading to diamagnetism at room temperature³⁹. Related complexes of Cu(II) are of particular interest as relatively simple spin systems that exhibit complicated behavior. Abakumov reported⁴² square-planar [Cu(3,6-DBSQ)₂] and mea-

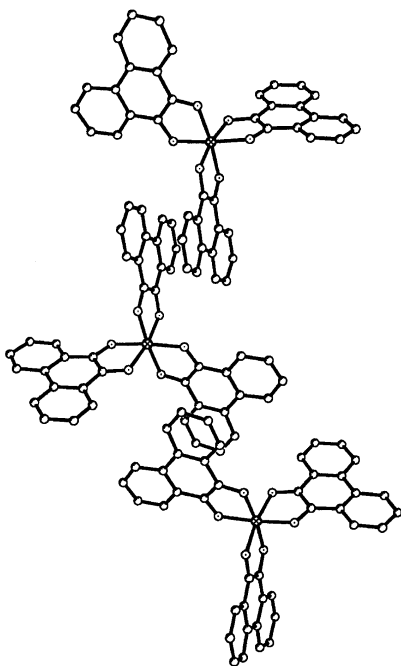


FIG. 8
Intermolecular stacking interactions in the crystal structure of [Cr(PhenSQ)₃]

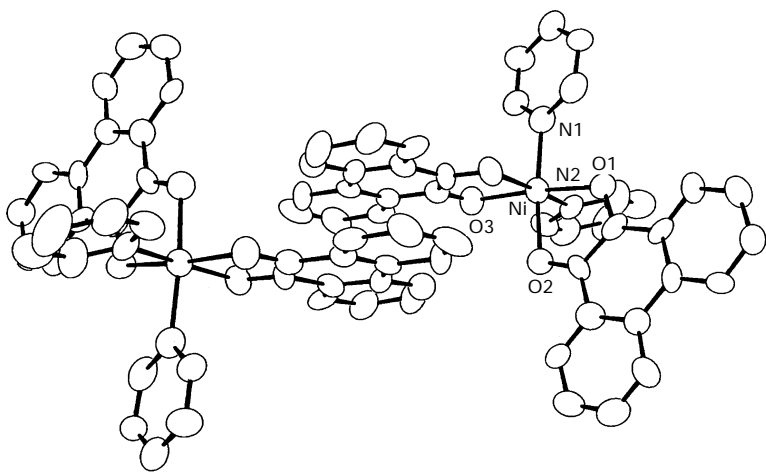


FIG. 9
Intermolecular stacking between *cis*-[Ni(py)₂(PhenSQ)₂] complex molecules

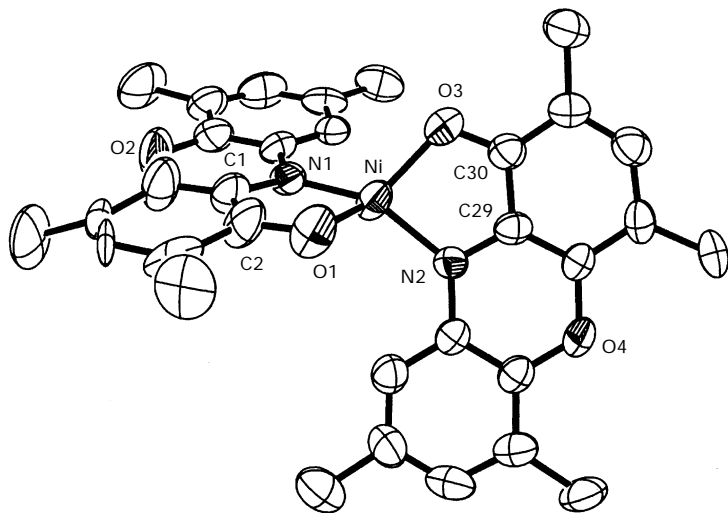


FIG. 10
View of [Ni(PhenoxSQ)₂]. The dihedral angle between PhenoxSQ planes is 72°

sured magnetic properties to 100 K. Based on $[\text{Ni}(\text{3,6-DBSQ})_2]$, SQ-SQ exchange should be strong and antiferromagnetic. Observations on simple $[\text{CuL}_n(\text{SQ})]$ systems indicate that radical coupling with the in-plane metal spin should be ferromagnetic. The magnetic moment of $[\text{Cu}(\text{3,6-DBSQ})_2]$ at high temperature is close to the value of $3.0\mu_{\text{B}}$ expected for three noninteracting $S = 1/2$ centres, counter to expectation, and drops to 1.9 at 100 K due to the effects of competing SQ-SQ ($J_{\text{SQ-SQ}} = -179 \text{ cm}^{-1}$) and Cu-SQ ($J_{\text{Cu-SQ}} = +100 \text{ cm}^{-1}$) exchange interactions. The related complex containing 3,5-DBSQ is dimeric with planar metal centres bridged by SQ oxygens of adjacent $\text{Cu}(\text{3,5-DBSQ})_2$ units²². Metal ions are five-coordinate and the tetragonal plane of the units is slightly folded. Magnetic moment for this compound drops below the $S = 1/2$ value at low temperature due to antiferromagnetic exchange between planar units through the bridge. This is not unexpected from the magnetic properties of the $[\text{Cu}(\text{bpy})-(\text{3,5-DBCat})]_2$ dimer of similar structure⁴⁶. The phenoxazinylate complex of Cu(II), the analog of $[\text{Ni}(\text{PhenoxSQ})_2]$, has a “crushed tetrahedral” structure⁴³. The net effect of exchange between the three spin centres is antiferromagnetic with magnetic moment dropping from $2.5\mu_{\text{B}}$ at 300 K to $1.5\mu_{\text{B}}$ at 4.2 K.

A series of compounds listed in Table III that deserve special consideration, are the tetramers^{37,41} $[\text{M}^{\text{II}}(\text{3,5-DBSQ})_2]_4$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$). These are particularly complicated systems due to the high-spin state of the metal and the potential for M-SQ, SQ-SQ, and M-M exchange interactions. The related complex of iron, $[\text{Fe}^{\text{III}}(\text{3,5-DBSQ})(\text{3,5-DBCat})]_4$, has a different charge distribution⁴⁰. Magnetic properties emphasize the importance of coupling between $\text{Fe}^{\text{III}}(\text{3,5-DBSQ})(\text{3,5-DBCat})$ units with the drop in magnetic moment with decreasing temperature to near diamagnetism at 4.2 K. In this respect, magnetic behavior resembles $[\text{Fe}(\mu\text{-OMe})(\text{3,6-DBSQ})_2]_2$ with strong antiferromagnetic Fe-SQ exchange, and residual temperature-dependent behavior associated with the interaction between Fe centres. The Mn analog, $[\text{Mn}(\text{3,5-DBSQ})_2]_4$, also with an $S = 5/2$ metal centre, but with an additional SQ ligand, exhibits magnetic properties that appear to arise from competing ferromagnetic and antiferromagnetic interactions³⁷. Magnetic moment (per metal ion) begins at high temperature with a value that exceeds the $S = 3/2$ value for a spin coupled $\text{Mn}^{\text{II}}(\text{SQ})_2$ unit, and *increases* slightly with decreasing temperature. The magnetic behavior of $[\text{Co}^{\text{II}}(\text{3,5-DBSQ})_2]_4$ and $[\text{Ni}^{\text{II}}(\text{3,5-DBSQ})_2]_4$ has been fit to simple $\text{M}(\text{SQ})_2$ models, but it is likely that exchange coupling within the tetrameric structure is far more complicated.

5. FUTURE DIRECTIONS TOWARD POLYMERIC HIGH-SPIN M-SQ ARRAYS

Interests in materials that may exhibit cooperative magnetic effects have turned to high-spin polymeric materials. The directional nature of SQ spin, orthogonal to the plane of coordination with a chelated metal ion, facilitates design of ferromagnetic polymers, but practical synthetic routes must be developed. Kitagawa⁴⁷ has succeeded in forming two-dimensional polymers based on chloranilate (Cl_4SQ) bridges (Fig. 11). Dei and Gatteschi⁴⁸ have investigated binuclear complexes containing dihydroxysemiquinone (DHSQ) bridging ligands. These two reports point to the promise of two- or three-dimensional polymers formed with DHSQ bridges between paramagnetic metal centres. Shultz⁴⁹ is developing the coordination chemistry of quinonemethide-semiquinone bridging ligands. SQ units couple ferromagnetically at the meta positions of an aromatic bridge, and the addition of oxidohydroxy functionality on the bridging ring leads to interesting switching effects. Abakumov has taken the approach of synthesizing bis(semiquinone) ligands functionalized to direct the rings in orthogonal planes to give a triplet ground state^{50,51}. The diamagnetism of

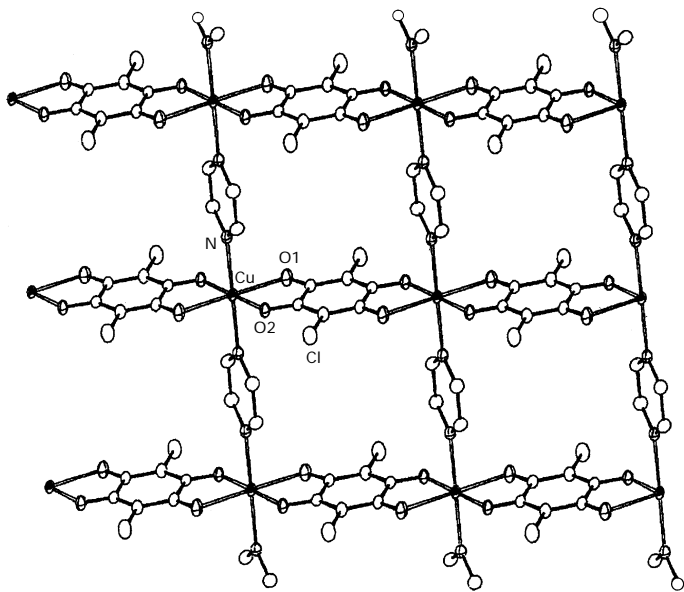


FIG. 11

View of the two-dimensional $[\text{Cu}(\text{pyz})(\text{chloranilate})]_n$ polymer

$[\text{Me}_2\text{Tl}(\text{SQ}^{\text{Bu,Me}}-\text{SQ}^{\text{Bu,Me}})]_n$ with a 51.5° dihedral angle between ring planes (Fig. 12) indicates that deviations from orthogonality will lead to spin pairing. These are all promising steps toward high-spin polymeric organo-transition metal materials based on the combined magnetic properties of radical semiquinone ligands and paramagnetic metal ions.

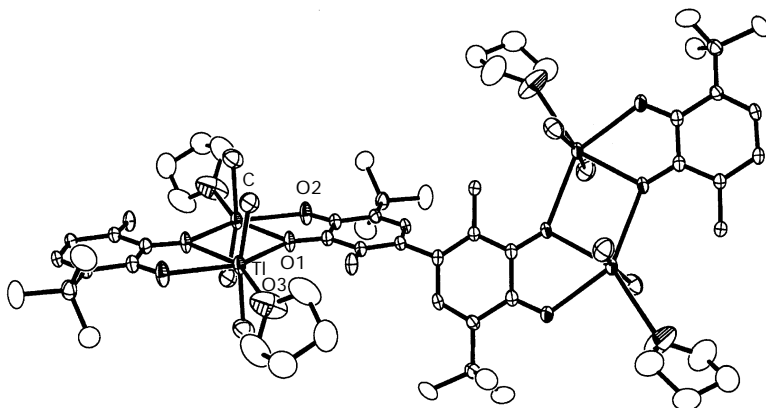


FIG. 12

View of the $[\text{Tl}(\text{Me})_2(\text{thf})(\text{SQ}^{\text{Bu,Me}}-\text{SQ}^{\text{Bu,Me}})]_n$ ($\text{SQ}^{\text{Bu,Me}}$ = 3-methyl-6-*tert*-butyl-1,2-benzo-semiquinone-4-yl) polymer. The dihedral angle between planes of SQ rings is 51.5°

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