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Synthesis and Structure of a Polymeric Complex of Tl(III) Containing Bis(semiquinone) Bridging Ligands

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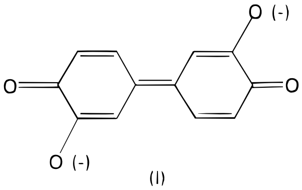
Introduction

Paramagnetic bridging agents have been of use in the synthesis of ferrimagnetic chains. Antiferromagnetic exchange between a $S = {}^1/_2$ radical bridge and a strongly paramagnetic high-spin metal ion may be used to effect parallel spin alignment between bridged metal centers along the length of a linear polymer.[1] Gatteschi has studied chains formed by using the radical nitronyl nitroxide to bridge Mn(hfa)$_2$ units.[2] Kahn has prepared polymers using a bridging Cu(II) complex to link high-spin Mn(II) centers.[3] Interchain ferromagnetic coupling may lead to the formation of materials that behave as a bulk ferromagnet.[1]

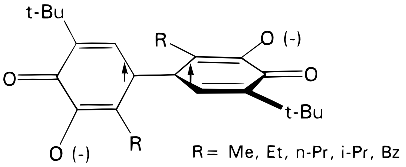
In this report we describe the synthesis of a bridging ligand consisting of linked semiquinones. The radical spin of a semiquinone is contained in a π orbital aligned perpendicular to the plane of the ring. The directionality of spin alignment aids in the rational design of systems that exhibit specific spin−spin coupling interactions. As an example, semiquinone ligands chelated in the basal plane of a square pyramidal complex of Cu(II) interact ferromagnetically with the orthogonal d_σ spin of the metal.[4]



(I)

Bis(semiquinones) (**I**) may be formed by the partial reduction of a bis(benzoquinone). Conjugation between rings results in coplanar alignment and a singlet ground-state electronic structure.[5] Steric interactions that result from bulky functionalization at the ring carbon atoms on either side of the bridge may result in orthogonal alignment of ring planes and a triplet, high-spin ground state.[6]

A recent report on the synthesis of bis(benzoquinones) containing methyl and other alkyl substituents at the 3 and 3′ ring positions of a 4,4′-bis(1,2-benzoquinone) (BQ−BQ) has provided compounds that may serve as precursors to diradical bis(semiquinone) (SQ−SQ) bridges (**II**).[7] Reduction of the rings has required special experimental procedures, however. We now describe the conditions used to form a polymeric thallium complex containing bridging SQ−SQ ligands.



(II)

Experimental Section

Tl(3,6-DBSQ),[8] Tl(Me)$_2$I,[9] and 4,4′-bis(3-methyl-6-*tert*-butyl-1,2-benzoquinone)[7] (BQ−BQ) were prepared according to literature procedures.

Tl(Me)$_2$(3,6-DBSQ). Tl(3,6-DBSQ) (2.12 g, 5 mmol) dissolved in 30 mL of THF was added to Tl(Me)$_2$I (1.81 g, 5 mmol). A precipitate of TlI was removed by filtration, and the filtrate was partially evaporated to give dark blue crystals of Tl(Me)$_2$(3,6-DBSQ) (1.8 g) in 79% yield. Anal. Calcd for $C_{16}H_{26}O_2Tl$: C, 42.3; H, 5.72. Found: C, 41.8; H, 5.92. EPR (THF): $\langle g \rangle = 2.0035$, $A(^{203,205}Tl) = 31.4$ G, $A(H) = 3.3$ G.

{[Tl(Me)$_2$(thf)(O$_2$C$_6$H(Me)(*t*-Bu))]$_2$}$_n$. Tl(Me)$_2$(3,6-DBSQ) (2.27 g, 5 mmol) and 4,4′-bis(3-methyl-6-*tert*-butyl-1,2-benzoquinone) (1.77 g, 5 mmol) were dissolved in 50 of mL THF. Partial evaporation of the solvent gave dark violet crystals of {[Tl(Me)$_2$(thf)(O$_2$C$_6$H(Me)(*t*-Bu))]$_2$}$_n$ (3.4 g) in 70% yield. Crystals were washed with THF and dried in a vacuum. Anal. Calcd for $C_{17}H_{27}O_3Tl$: C, 42.2; H, 5.59. Found: C, 41.6; H, 5.63. UV−vis (THF): 524 nm (7800 M^{-1} cm^{-1}), 575 (8000), 806 (10 800). IR (Nujol): 1530 (s), 1515 (s), 1480 (s), 1460 (m), 1440 (m), 1420 (s), 1385 (m), 1325 (s), 1285 (m), 1225 (m), 1165 (m), 1055 (m), 970 (m), 955 (w).

Physical Measurements. Electronic spectra were recorded on a Specord M-40 spectrophotometer, infrared spectra were obtained on a Specord M-80 spectrometer, and EPR spectra were recorded on a Bruker ER 200D-SRC spectrometer.

Structural Characterization on {[Tl(Me)$_2$(thf)(O$_2$C$_6$H(Me)(*t*-Bu))]$_2$}$_n$. A dark violet crystal obtained from THF solution was mounted and aligned on a Siemens SMART diffractometer equipped with a CCD detection system. Crystals were found to form in the orthorhombic crystal system, space group *Pbcn*, in a unit cell of the dimensions listed in Table 1. Nearly a complete sphere of data was collected and averaged to give 5367 independent reflections ($R_{int} = 0.040$). Refinement of the structure converged with $R(F) = 0.044$ and $R_w(F^2) = 0.074$.

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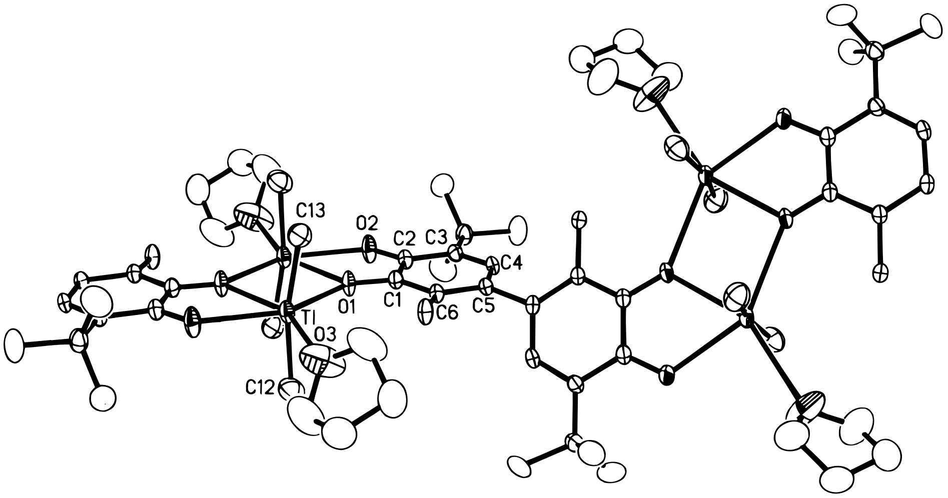

Figure 1. Repeating unit of the $\{[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-Bu}))]_2\}_n$ polymer (50% ellipsoids).

Table 1. Crystallographic Data for $\{[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-Bu}))]_2\}_n$

formula	$C_{17}H_{27}O_3Tl$
fw	483.8
space group	*Pbcn*
a (Å)	12.7022(2)
b (Å)	12.6197(1)
c (Å)	23.0110(1)
vol (Å^3)	3688.62(7)
Z	8
T (K)	166
λ(MoKα), Å	0.710 73
D_{calcd} (g cm^{-3})	1.742
μ (mm^{-1})	8.764
R, R_w	0.028, 0.065[a]

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Results and Discussion

Dinuclear complexes of Ru have been prepared with bis(semiquinone)[10] and bis(benzoquinonediimine)[11] bridging ligands in studies on metal ion communication through an extended redox-active bridge. In the absence of structural characterization little is known about the relative orientation of rings in the bridge, but it is presumed that they are coplanar. Ring functionalization, in the present case (**II**), has been used to constrain the angle between rings to a value close to 90°. Structural characterization on 4,4′-bis(3-methyl-6-*tert*-butyl-1,2-benzoquinone) (BQ−BQ) has shown that rings of the unreduced bis(benzoquinone) are nearly orthogonal with a dihedral angle of 82.9° between ring planes.[7] Thallium complexes of semiquinones have proven to be useful precursors to semiquinone complexes of transition metal ions. However, the simple procedures that form Tl(SQ) species are not the best routes to the Tl complexes of SQ−SQ. An approach that has proven to be successful involves using the 3,6-DBSQ ligand of $Tl(Me)_2$(3,6-DBSQ) as a reducing agent (eq 1). The procedure described in the Experimental Section gives $[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-Bu}))]_2$ using relatively simple procedures.

$$\text{BQ}-\text{BQ} + 2\ \text{Tl(Me)}_2\text{(3,6-DBSQ)} \rightarrow \text{(Me)}_2\text{Tl(SQ}-\text{SQ)Tl(Me)}_2 + 2\ \text{3,6-DBBQ} \quad (1)$$

Table 2. Selected Bond Lengths (Å) for $\{[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-Bu}))]_2\}_n$

Tl−C12	2.128(5)	C2−O2	1.267(4)
Tl−C13	2.129(4)	C1−C2	1.502(5)
Tl−O1	2.467(2)	C2−C3	1.455(4)
Tl−O1′	2.745(3)	C3−C4	1.364(5)
Tl−O2	2.487(3)	C4−C5	1.448(5)
Tl−O3	2.862(3)	C5−C6	1.403(4)
Tl−Tl′	4.001(1)	C6−C1	1.407(4)
C1−O1	1.300(4)	C5−C5′	1.465(6)

Crystallographic characterization on $[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-Bu}))]_2$ has shown that in the solid state the complex is polymeric. A view of one unit is given in Figure 1; selected bond lengths and angles are given in Table 2. The polymer consists of alternating $Tl_2Me_4(thf)_2$ and $O_2C_6H(Me)(t\text{-Bu})-(t\text{-Bu})(Me)HC_6O_2$ (SQ−SQ) subunits. The Tl(III) ions are located about a crystallographic inversion center. They have a distorted octahedral coordination geometry consisting of axial methyl groups with the oxygens of a chelated semiquinone in the equatorial plane. The remaining two equatorial sites are occupied by a weakly coordinated thf ligand, with a Tl−O(3) length of 2.862(3) Å, and a bridging oxygen from the SQ ligand chelated to the adjacent Tl ion. This length is also long (2.745(3) Å) relative to the two Tl−O lengths of 2.467(2) and 2.487(3) Å within the SQ chelate ring. The Tl−Tl separation within the $Tl_2Me_4(thf)_2$ unit is 4.001(1) Å. Carbon atom C5 of the semiquinone ring is close to a crystallographic 2-fold axis that relates the two halves of the bis(semiquinone) ligand. The dihedral angle between planes of adjacent rings is 51.5°, a value that is less than the dihedral angle of the parent bis(benzoquinone). The length between carbon atoms joining the two rings (C5−C5′) is 1.465(6) Å, slightly shorter than the value for biphenyl (1.49 Å) but considerably longer than the double-bond value that would be expected for strong conjugation between radical rings (**I**). Carbon−carbon bond lengths within the independent SQ ring show evidence for a resonance contribution from the electronic structure shown above (**II**). The C1−C2 and C4−C5 lengths are the longest of the ring, and the C3−C4 and C5−C6 lengths are the shortest, a pattern that appears for simple SQ ligands.[4] Therefore, the features of the two halves of the bis(semiquinone) ligand resemble isolated SQ ligands with little electronic coupling between rings. In agreement with these structural features, the electronic spectrum of the polymer dissolved in THF consists of transitions at 524 and 806 nm that appear commonly for semiquinone complexes.[12]

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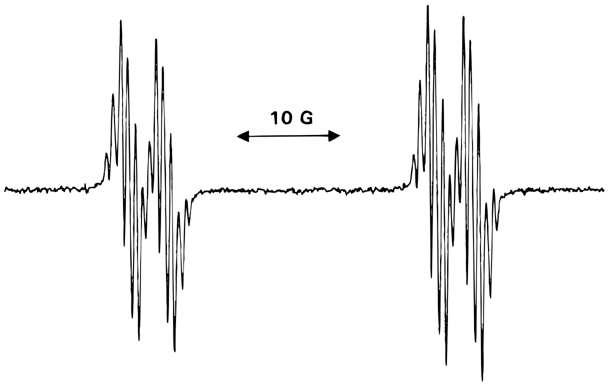

Figure 2. EPR spectrum of $Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-}Bu)-C_6H(Me)(t\text{-}Bu)O_2$ $[TlMe_2(SQ-BQ)]$ formed by the addition of BQ−BQ to a THF solution of $\{[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-}Bu))]_2\}_n$.

While electronic coupling between SQ rings of $\{[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-}Bu))]_2\}_n$ is small, exchange coupling between radical centers is strong. The polymer is diamagnetic over the temperature range 20−340 K. There are two possible mechanisms for spin coupling. Metal-mediated interligand exchange between SQ groups through the $Tl_2Me_4(thf)_2$ bridge is a possibility, but direct exchange seems most likely with the large deviation of the dihedral angle between rings from 90°. In THF solution $[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-}Bu))]_2$ is EPR silent, but over time, two radical spectra appear. The $S = {}^1/_2$ products may result from disproportionation of the SQ−SQ ligand to give BQ−SQ and SQ−Cat products. The addition of 4,4′-bis(3-methyl-6-*tert*-butyl-1,2-benzoquinone) (BQ−BQ) to a THF solution of $[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-}Bu))]_2$ results in one-electron oxidation of the SQ−SQ ligand to give a single radical product. The EPR spectrum of this product, shown in Figure 2, is centered about a g value of 2.0039. It consists of two well-separated resonances that arise from coupling of 28 G to the $^{203,205}Tl$ ($I = {}^1/_2$) nuclei. Each of these resonances is split into two multiplets by coupling to a single ring hydrogen of 3.1 G, and each of these is split further by coupling to six protons of two methyl groups of 0.6 G. The methyl groups responsible for this splitting are presumably the ring substituents, since coupling to alkyl groups of TlR_2(3,6-DBSQ), R= Me, Et, does not appear in the EPR spectrum of the coordinated semiquinone ligand.[13] The spectrum of free BQ−SQ fails to appear with the spectrum of the partially oxidized product. Therefore, electron transfer occurs with the transfer of $TlMe_2^+$ to the reduced BQ−BQ (eq 2).

$$\mathrm{BQ{-}BQ} + \mathrm{TlMe_2(SQ{-}SQ)TlMe_2} \rightarrow 2\ \mathrm{TlMe_2(SQ{-}BQ)} \qquad (2)$$

Conclusions

Features of a complex prepared with a bis(semiquinone) ligand have been described for the first time. The diamagnetism of $\{[Tl(Me)_2(thf)(O_2C_6H(Me)(t\text{-}Bu))]_2\}_n$ and the contracted angle between semiquinone rings indicate that substitution with alkyl groups larger than methyl at the 3-positions of the semiquinone rings will be required to maintain orthogonality between radical regions of the SQ−SQ ligand.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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