New Semiquinone/Catecholate Complexes That Exhibit Valence Tautomerism. Synthesis and Characterization of $Mn^{III}(thf)_2(3,6\text{-}DBSQ)(3,6\text{-}DBCat)$ and Observations on the $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)/Mn^{III}(3,6\text{-}DBSQ)_3$ Equilibrium in the Solid State

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Irradiation of a THF solution containing $Mn_2(CO)_{10}$ and 3,6-di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ) gave dark green crystals of $Mn(thf)_2(3,6\text{-}DBQ)_2$. Structural characterization has shown that the inner coordination geometry about the metal has the axially elongated trans structure that appears characteristically for d^4 Mn(III). *trans*-$Mn^{III}(thf)_2(3,6\text{-}DBSQ)(3,6\text{-}DBCat)$ has a solid-state electronic spectrum that resembles spectra of related Mn(III) complexes containing nitrogen-donor ligands. Crystallographically imposed *mmm* symmetry averages structural differences between the SQ (semiquinonate) and Cat (catecholate) ligands. When the related reaction between $Mn_2(CO)_{10}$ and 3,6-DBBQ was carried out in the presence of 2,2′-bithiophene, $Mn(3,6\text{-}DBQ)_3$ was obtained. Crystallographic characterization has shown that the molecule is octahedral with relatively short Mn−O bond lengths (1.863(5)−1.927(5) Å), and without the structural distortion that might be indicative of Mn(III). This result, with the spectral and magnetic properties of the complex, points to the $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$ charge distribution at room temperature in the solid state. An intense transition at 2300 nm has been assigned as an intervalence transfer (IT) band between SQ and Cat ligands of the Mn(IV) redox isomer. This band decreases in intensity with increasing temperature. Similar behavior has been observed for $Mn^{IV}(N\text{-}N)(DBCat)_2$ species as an indication of valence tautomerism. In this case the equilibrium is between $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$ and $Mn^{III}(3,6\text{-}DBSQ)_3$ redox isomers.

Introduction

Valence tautomerism has been observed to occur for a series of transition metal complexes containing semiquinonate (SQ) and catecholate (Cat) ligands chelated to Co and Mn.[1,2] Equilibria between Co^{III} and Co^{II} redox isomers (eq 1) have

$$Co^{III}(N\text{-}N)(SQ)(Cat) \rightleftharpoons Co^{II}(N\text{-}N)(SQ)_2 \qquad (1)$$

been observed by monitoring temperature-dependent changes in the electronic spectrum and magnetism that occur with the shift from low-spin Co^{III} to high-spin Co^{II}.[1] Three redox isomers are possible for the complexes of Mn, and equilibria occur in two steps (eqs 2 and 3).[2,3] Tautomeric equilibria have been

$$Mn^{IV}(N\text{-}N)(Cat)_2 \rightleftharpoons Mn^{III}(N\text{-}N)(SQ)(Cat) \qquad (2)$$

$$Mn^{III}(N\text{-}N)(SQ)(Cat) \rightleftharpoons Mn^{II}(N\text{-}N)(SQ)_2 \qquad (3)$$

observed for a relatively narrow collection of complexes prepared with SQ and Cat ligands derived from 3,5- and 3,6-di-*tert*-butyl-1,2-benzoquinone, and with nitrogen-donor ancillary ligands (N-N) occupying the remaining cis or trans octahedral coordination sites.[4] Temperature-dependent spectral changes have been reported for planar d^8 metal complexes containing quinone ligands, but the effect seems related to intermolecular interactions that occur in solution and that appear in solid-state structures.[5,6] Quinone complexes of copper have been observed to form as $L_2Cu^{II}(Cat)$ and $L_2Cu^{I}(SQ)$ redox isomers, but no system has been shown to interconvert between redox isomers under equilibrium conditions.[7] This is due, in part, to different structural preferences of the metal ions and the large barrier to intramolecular electron transfer for planar Cu(II) and tetrahedral Cu(I). Even quinone complexes of iron that are related to the Mn and Co complexes described above fail to undergo similar shifts in charge distribution.[8]

The synthetic procedure used to form members of the $M(N\text{-}N)(DBQ)_2$, M = Co, Mn series, where DBQ is used to refer to a di-*tert*-butylquinone ligand of unspecified charge, has involved the reaction between a neutral metal carbonyl and either 3,5- or 3,6-DBBQ, with subsequent addition of the nitrogen ancillary ligand. In the absence of the nitrogen donor, reactions carried out with either $Co_2(CO)_8$ or $Mn_2(CO)_{10}$ and 3,5-DBBQ gave the $[M^{II}(3,5\text{-}DBSQ)_2]_4$, M = Co, Mn tetramers.[9,10] Structural characterization showed that adjacent metal ions were bridged

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by the oxygen atoms at the 1 ring position of the 3,5-DBSQ ligands. With 3,6-DBBQ, bridging interactions are blocked by *tert*-butyl substituents adjacent to both oxygen atoms, and mononuclear products are usually obtained. As an example, the reaction between $Co_2(CO)_8$ and 3,6-DBBQ gave Co^{III}(3,6-DBSQ)$_3$.[11] In the present report we describe the results of a similar reaction carried out with $Mn_2(CO)_{10}$ and 3,6-DBBQ.

Experimental Section

Materials. 3,6-Di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ) was prepared following a literature procedure.[12] Dimanganese decacarbonyl was purchased from Strem Chemical Co.

***trans*-Mn(thf)$_2$(3,6-DBSQ)(3,6-DBCat).** $Mn_2(CO)_{10}$ (0.17 g, 0.43 mmol) and 3,6-DBBQ (0.33 g, 1.5 mmol) dissolved in 50 mL of a 1:2 THF/hexane solution were combined at room temperature under N_2. The mixture was irradiated with a sun lamp 3 h. Slow evaporation of the solvent produced green crystals of *trans*-Mn(thf)$_2$(3,6-DBSQ)(3,6-DBCat) in 42% yield. It was noted that, when the crystals were ground to powder, the actual color of the complex was orange-brown. Anal. Calcd for $C_{36}H_{56}O_6Mn$: C, 67.5; H, 8.8. Found: C, 68.3; H, 9.2. IR (KBr): 2955 (vs), 2909 (sh), 2870 (sh), 1551 (s), 1481 (w), 1462 (sh), 1416 (m), 1381 (m), 1281 (s), 1161 (s), 1034 (vs), 976 (vs), 973 (m) cm^{-1}.

Mn(3,6-DBQ)$_3$. $Mn_2(CO)_{10}$ (0.25 g, 0.65 mmol) and 3,6-DBBQ (0.76 g, 3.5 mmol) were dissolved in 40 mL of THF at room temperature under N_2. 2,2′-Bithiophene (0.18 g, 1.12 mmol) was added to the mixture, and the solution was irradiated with a sun lamp for 7 h. Mn(3,6-DBQ)$_3$ was obtained from the reaction mixture as a crude purple powder. Recrystallization from hexane gave dark purple crystals in 56% yield. (See below for a description of the spectral properties.) Anal. Calcd for $C_{42}H_{60}O_6Mn$: C, 70.4; H, 8.4. Found: C, 70.2; H, 8.7.

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic measurements were made using a Quantum Design SQUID magnetometer at a field of 5 kG. Diamagnetic corrections were made using Pascal's constants. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR with samples prepared as KBr pellets. EPR spectra were measured using a Bruker ESP 300e spectrometer at X-band frequency using DPPH as the *g*-value standard.

Crystallographic Characterization of *trans*-Mn(thf)$_2$(3,6-DBSQ)-(3,6-DBCat). A dark green crystal of the complex was mounted and aligned on a Siemens P3F automated diffractometer. The centered settings of 25 reflections in the 2Θ range 19−32° were used to obtain the unit cell dimensions listed in Table 1. Crystals were found to form in the tetragonal crystal system, space group $P4_2/mnm$, with $Z = 2$. A difference Fourier calculated with the Mn atom located at the origin of the unit cell, a site of *mmm* symmetry, revealed the positions of other independent non-hydrogen atoms of the complex.

Crystallographic Characterization of Mn(3,6-DBQ)$_3$. A dark purple crystal was mounted and aligned on a Siemens P3F automated diffractometer. The centered settings of 25 reflections in the 2Θ range 19−34° were used to obtain the unit cell dimensions listed in Table 1. Crystals were found to form in the triclinic crystal system, space group $P\bar{1}$, with $Z = 2$. A sharpened Patterson map was used to determine the locations of the Mn and most of the atoms of the complex molecule. Missing atoms were located on a difference Fourier map. Additional details for both structure determinations are given with the Supporting Information.

Table 1. Crystallographic Data for *trans*-Mn(thf)$_2$(3,6-DBSQ)(3,6-DBCat) and Mn(3,6-DBSQ)$_2$(3,6-DBCat)

	trans-Mn(thf)$_2$-(3,6-DBSQ)(3,6-DBCat)	Mn(3,6-DBSQ)$_2$-(3,6-DBCat)
formula	$C_{36}H_{56}O_6Mn$	$C_{42}H_{60}O_6Mn$
fw	639.7	715.8
space group	$P4_2/mnm$	$P\bar{1}$
a (Å)	10.190(2)	10.300(1)
b (Å)	10.190(2)	10.951(1)
c (Å)	18.270(5)	19.298(3)
α (deg)	90	88.97(1)
β (deg)	90	79.60(1)
γ (deg)	90	82.27(1)
vol (Å^3)	1897.1(7)	2121.5(4)
Z	2	2
λ (Mo Kα, Å)	0.710 73	0.710 73
D_{calcd} (g cm^{-3})	1.120	1.121
μ (mm^{-1})	0.370	0.337
R, R_w	0.052, 0.061[a]	0.066, 0.069[a]

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

Results and Discussion

Synthetic Routes to the Mn−Quinone Complexes. Early studies on the coordination chemistry of semiquinone radicals were carried out with compounds formed by the addition of benzoquinones to $Mn_2(CO)_{10}$.[13] Reactions proceed by the initial formation of a 6-coordinate product, Mn^I(SQ)(CO)$_5$, with SQ coordination through a single oxygen. Displacement of an additional CO ligand gives Mn^I(SQ)(CO)$_4$ with a chelated SQ as verified structurally for Re(3,5-DBSQ)(PPh$_3$)(CO)$_3$.[14] The addition of 3,5-DBBQ to $Mn_2(CO)_{10}$ appears to proceed in this way, and reactions carried out with an excess of benzoquinone have been found to ultimately give a product with empirical formulation Mn^{II}(3,5-DBSQ)$_2$ by complete displacement of the CO ligands.[10] Structural characterization on this product indicated that it forms as a tetramer, [Mn^{II}(3,5-DBSQ)$_2$]$_4$, with bridging SQ oxygens linking adjacent metal ions. The oxygen atom bonded at the 1-position of the semiquinone ring of 3,5-DBSQ and 3,5-DBCat is commonly found to bridge metal ions,[15] and the nonselective formation of dimers and higher order oligomers complicates the isolation and characterization of complexes prepared with this ligand. Similar reactions carried out with 3,6-DBBQ proceed to give more simple, chelated products due to the blocking effect of the *tert*-butyl groups adjacent to both ring oxygen atoms. Reactions carried out with $Co_2(CO)_8$ and 3,5-DBSQ give [Co^{II}(3,5-DBSQ)$_2$]$_4$,[9] as with Mn, but with 3,6-DBBQ, Co^{III}(3,6-DBSQ)$_3$ is obtained, illustrating this difference in chemistry.[11] Related observations have been made for reactions of Fe and Ni.[16,17] The reaction between $Mn_2(CO)_{10}$ and 3,6-DBBQ has been investigated as a potential route to "Mn(3,6-DBQ)$_3$". This product may form with three possible charge distributions. Following the product obtained with Ni, Mn^{II}(3,6-DBBQ)(3,6-DBSQ)$_2$ may be a potential redox isomer.[17] With Co the product contained Co(III), and Mn^{III}(3,6-DBSQ)$_3$ may be obtained.[11] Finally, the strong π donation of catecholate ligands stabilizes Mn(IV), and Mn^{IV}(3,6-DBSQ)$_2$-(3,6-DBCat) is a potential charge distribution for the product of this reaction. Characteristic structural differences may be used to distinguish between the d^3, d^4, and d^5 metal ion configurations, and redox isomers containing quinone ligands of mixed charge may exhibit low-energy LL′CT transitions.[2]

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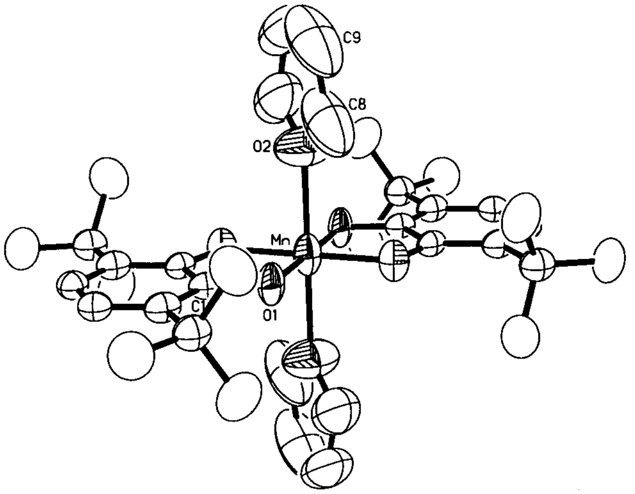

Figure 1. View of the $Mn^{III}(thf)_2$(3,6-DBSQ)(3,6-DBCat) molecule.

Table 2. Selected Bond Lengths and Angles for *trans*-$Mn(thf)_2$(3,6-DBSQ)(3,6-DBCat)

Bond Lengths (Å)			
Mn−O1	1.893(1)	Mn−O2	2.353(1)
O1−C1	1.333(6)	C1−C2	1.405(8)
C1−C1′	1.411(9)	C2−C3	1.361(8)
C3−C3′	1.418(19)		
Bond Angles (deg)			
O1−Mn−O1′	85.3(4)	Mn−O1−C1	111.7(5)
O1−C1−C2	123.1(8)	O1−C1−C1′	115.6(4)

An initial reaction was carried out between $Mn_2(CO)_{10}$ and 3,6-DBBQ using THF as a solvent that would dissolve both components. Irradiation of the mixture gave as the product $Mn(thf)_2(3,6\text{-DBQ})_2$. A similar reaction was carried out that included 2,2-bithiophene in an attempt to investigate Mn−quinone complexes that contain sulfur-donor ancillary ligands. The product obtained in this case was found to be $Mn(3,6\text{-DBQ})_3$. We report herein the structural, magnetic, and spectroscopic properties on both complexes.

***trans*-$Mn(thf)_2(3,6\text{-DBQ})_2$.** Bond lengths within the coordination sphere of octahedral Mn may provide information on metal d configuration and charge. Mn(IV) is d^3 and generally has short lengths to all ligand positions of the octahedron. High-spin d^5 Mn(II) typically has a symmetrical coordination sphere, but with Mn−L lengths that are 0.2 Å longer than lengths to equivalent donor atoms of Mn(IV). High-spin d^4 Mn(III) generally shows the effect of a Jahn−Teller distortion. Axially coordinated trans isomers exhibit lengthening of axial bonds with values that approach Mn(II) lengths, and values at equatorial sites that are close to the lengths of Mn(IV). Crystallographic characterization of the product of the $Mn_2(CO)_{10}$/3,6-DBBQ reaction carried out in a hexane/THF mixture revealed that the molecule contained trans thf ligands coordinated to $Mn(3,6\text{-DBQ})_2$. A view of the molecule is shown in Figure 1. Mirror symmetry imposed on the molecule by its location in the unit cell averages the structural features of the two quinone ligands, but the long Mn−O lengths to the axial thf oxygen atoms (2.353(1) Å) and the short lengths to the quinone oxygens (1.893(1) Å) are a clear indication of axially elongated Mn(III).[2,3] Bond lengths and angles of the molecule are listed in Table 2. As a complex of Mn(III) the combined charge for the quinone ligands requires that one be SQ and the other Cat. Characterization of complexes that contain mixed-charge SQ and Cat ligands has, in some cases, provided resolution of structural features that are indicative of localized charge.[1] In many cases, though, crystallographic symmetry averages the dissimilar ligands giving lengths for the C−O and ring C−C bonds that are intermediate between SQ and Cat values. This has been observed for *trans*-$Mn^{III}(4,4\text{-bpy})_2$(3,6-DBSQ)(3,6-DBCat)[2] and for the [*trans*-$Mn^{III}(\mu\text{-pyz})$(3,6-DBSQ)(3,6-DBCat)]$_n$ polymer,[18] and it is the case for *trans*-$Mn^{III}(thf)_2$(3,6-DBSQ)(3,6-DBCat).

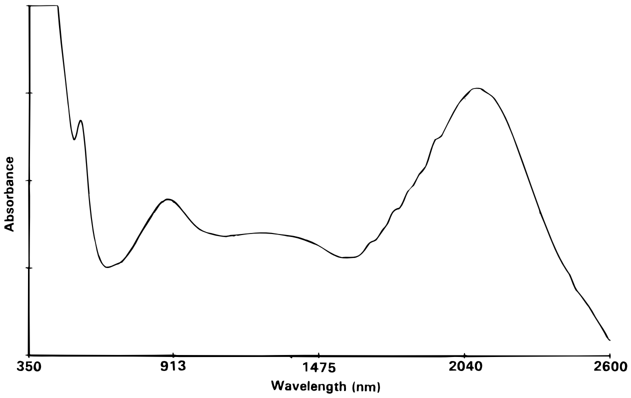

Figure 2. Electronic spectrum of *trans*-$Mn^{III}(thf)_2$(3,6-DBSQ)(3,6-DBCat) recorded in the solid state (KBr) at room temperature.

Electronic spectra recorded on *trans*-$Mn^{III}(thf)_2$(3,6-DBSQ)(3,6-DBCat) in the solid state are similar to spectra obtained on *trans*-$Mn^{III}(4,4\text{-bpy})_2$(3,6-DBSQ)(3,6-DBCat), reinforcing the similarity in charge distribution for the two compounds.[2] The spectrum, shown in Figure 2, consists of two intense transitions at 880 and 2100 nm and a broad band of lower intensity at 1350 nm. Related bands appear at 880, 1400, and 2170 nm for *trans*-$Mn^{III}(4,4\text{-bpy})_2$(3,6-DBSQ)(3,6-DBCat). The 880 nm transition appears for both the Mn(III) and Mn(IV) redox isomers and has been assigned as a Cat → Mn CT transition. Complexes that contain weakly coupled SQ and Cat ligands exhibit LL′CT transitions at low energy, and bands appear characteristically in the 2100 nm region for the Mn^{III}(N-N)(DBSQ)(DBCat) series.[2,3] It was of interest to see if changes in the spectrum with temperature might indicate a shift in charge distribution to either a Mn(IV) or Mn(II) redox isomer. No spectral change was observed for the solid sample over the temperature range 250−350 K. Magnetic measurements recorded over the temperature range 325−30 K indicated a decrease in magnetic moment, from 3.85 μ_B to 3.58 μ_B, that is nearly linear. There are a number of factors that may contribute to the change in magnetism, among them Mn−SQ and SQ−SQ magnetic coupling, and a potential shift in charge distribution at low temperature. Similar behavior has been observed for Mn complexes with all three charge distributions.[2,3] However, the structural and spectral properties are uniquely consistent with a charge distribution containing Mn(III), *trans*-$Mn^{III}(thf)_2$(3,6-DBSQ)(3,6-DBCat), and the complex shows no evidence for a shift in charge distribution in the solid state at temperatures near room temperature.

$Mn(3,6\text{-DBQ})_3$. The formation of $Mn(3,6\text{-DBQ})_3$ from a reaction that was similar to the procedure used to form *trans*-$Mn^{III}(thf)_2$(3,6-DBSQ)(3,6-DBCat) was surprising. The addition of bithiophene must change the mechanism of complex formation, for the thf complex shows no tendency to add an additional quinone ligand upon reaction with 3,6-DBBQ. Structural characterization was carried out to potentially identify the charge on the metal ion. A view of the complex molecule is shown in Figure 3; Table 3 contains selected bond lengths and angles. The molecule has approximate D_3 symmetry with a twist angle

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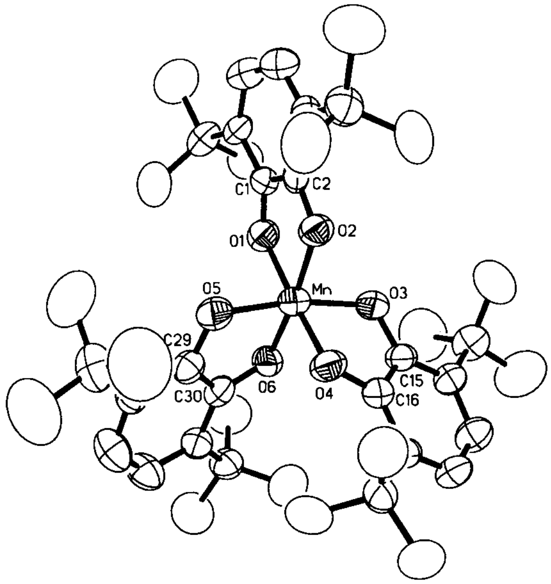

Figure 3. View of the Mn^{IV}(3,6-DBSQ)$_2$(3,6-DBCat) molecule.

Table 3. Selected Bond Lengths and Angles for Mn(3,6-DBSQ)(3,6-DBCat)

	Bond Lengths (Å)		
Mn−O1	1.927(5)	Mn−O2	1.910(5)
Mn−O3	1.897(4)	Mn−O4	1.871(5)
Mn−O5	1.885(5)	Mn−O6	1.863(5)
C1−O1	1.279(9)	C2−O2	1.279(8)
C1−C2	1.450(11)	C2−C3	1.429(11)
C3−C4	1.353(10)	C4−C5	1.420(12)
C5−C6	1.354(11)	C1−C6	1.413(9)
C15−O3	1.311(8)	C16−O4	1.312(8)
C15−C16	1.438(10)	C16−C17	1.404(9)
C17−C18	1.369(10)	C18−C19	1.403(10)
C19−C20	1.361(10)	C15−C20	1.416(10)
C29−O5	1.310(9)	C30−O6	1.305(8)
C29−C30	1.424(11)	C30−C31	1.414(10)
C31−C32	1.375(10)	C32−C33	1.415(12)
C33−C34	1.373(11)	C29−C34	1.413(10)
	Bond Angles (deg)		
O1−Mn−O2	81.3(2)	O1−Mn−O3	96.2(2)
O1−Mn−O4	176.8(2)	O1−Mn−O5	91.7(2)
O1−Mn−O6	93.1(2)	O2−Mn−O3	94.9(2)
O2−Mn−O4	95.5(2)	O2−Mn−O5	92.8(2)
O2−Mn−O6	173.8(2)	O3−Mn−O4	83.6(2)
O3−Mn−O5	169.7(2)	O3−Mn−O6	88.3(2)
O4−Mn−O5	89.0(2)	O4−Mn−O6	90.1(2)
O5−Mn−O6	84.7(2)		

between triangular faces of the octahedron of 52.5°. Tris complexes of Mn(III) chelated by bidentate oxygen-donor ligands have been of interest in the study of Jahn−Teller distortions in octahedral complexes that would, otherwise, have regular structures. The most common distortion is axial elongation, and this appears for the structures of the tropolonate complex, Mn(trop)$_3$, and for the structures of the acetylacetonate complexes Mn(acac)$_3$ and Mn(hfac)$_3$.[19−21] However, the Mn−O lengths of Mn(3,6-DBQ)$_3$ are shorter than even the shortest equatorial lengths of these molecules. On this basis the metal more closely resembles d^3 Mn(IV) than high-spin d^4 Mn(III). In this respect, the metal differs in charge from the analogous complexes containing Fe and Co which have the M^{III}(3,6-DBSQ)$_3$ charge distribution.[11,16] Related complexes of Tc and Re have been investigated and found to have the M^{VI}(3,5-DBCat)$_3$ charge distribution from structural features and from strong metal hyperfine coupling in the EPR spectra of the $S = {}^1/_2$ molecules.[22,23] The magnetic moment of Mn(3,6-DBQ)$_3$ at room temperature (vide infra) is well above the $S = {}^1/_2$ value placing charge on the Mn at +4 or +5 with mixed-charge SQ and Cat ligands. Structural features of the ligands, with the pattern of Mn−O lengths, appear more consistent with the Mn(IV) formulation. The Mn−O lengths to oxygens O1 and O2 are the longest of the structure, and the C−O and C−C lengths within this ligand are typical of values found for semiquinone ligands, particularly the contracted C−C lengths at the C3−C4 and C5−C6 bonds of the ring. The remaining two quinone ligands are more similar. The Mn−O lengths are slightly shorter at the positions trans to O1 and O2, and close to the Mn−O lengths of [Mn^{IV}(3,5-DBCat)$_3$]$^{2-}$ (Table 4),[24] related to the present complex by the addition of two electrons. Quinone C−O and C−C lengths of these ligands are intermediate between SQ and Cat values, and they are similar to features of the disordered or delocalized SQ and Cat ligands of *trans*-Mn^{III}(thf)$_2$(3,6-DBSQ)(3,6-DBCat), *trans*-Mn^{III}(4,4-bpy)$_2$(3,6-DBSQ)(3,6-DBCat), and other complexes which have mixed-charge SQ and Cat ligands related by crystallographically imposed molecular symmetry. From the analysis of the structural features the molecule is best formulated as a complex of Mn(IV), Mn^{IV}(3,6-DBSQ)$_2$(3,6-DBCat), with the catecholate ligand disordered with one of the semiquinone ligands.

Table 4. Mn−O Bond Lengths for Complexes of Mn(III) and Mn(IV) That Contain the MnO$_6$ Core

complex	Mn−O	ref
Mn^{IV}(3,6-DBSQ)$_2$(3,6-DBCat)	1.863(5)−1.927(5)	
[Mn^{IV}(3,5-DBCat)$_3$]$^{2-}$	1.874(6)−1.891(6)	24
Mn^{III}(trop)$_3$	1.93(1)−2.14(1)	19
Mn^{III}(acac)$_3$	1.933(3)−2.112(4)	21
Mn^{III}(hfac)$_3$	1.906(2)−2.147(3)	20

Infrared spectra recorded on Mn^{IV}(3,6-DBSQ)$_2$(3,6-DBCat) further confirm the mixed-charge quinone ligand formulation. The spectral region between 1500 and 1200 cm^{-1} contains strong bands associated with C−O and ring C−C stretching modes that are sensitive to quinone charge.[25] Figure 4 shows this region of the spectrum compared with the corresponding region of Fe(3,6-DBSQ)$_3$.[16] The additional complexity of the Mn spectrum, particularly in the 1400 cm^{-1} region, is consistent with the presence of both SQ and Cat ligands.

The magnetism of Mn^{IV}(3,6-DBSQ)$_2$(3,6-DBCat) has been measured with varying temperature. At 305 K the magnetic moment of the complex is 3.71 μ_B, dropping to a value of 1.67 μ_B at 5 K. The decrease in magnetic moment, shown in Figure 5, appears related to the effects of both Mn−SQ and SQ−SQ antiferromagnetic exchange interactions, rather than to a shift in charge distribution. Attempts at modeling the drop in moment have failed to provide meaningful values for J_{Mn-SQ} and J_{SQ-SQ} since both values are negative in sign and appear to be of approximately the same magnitude as found for Fe(3,6-

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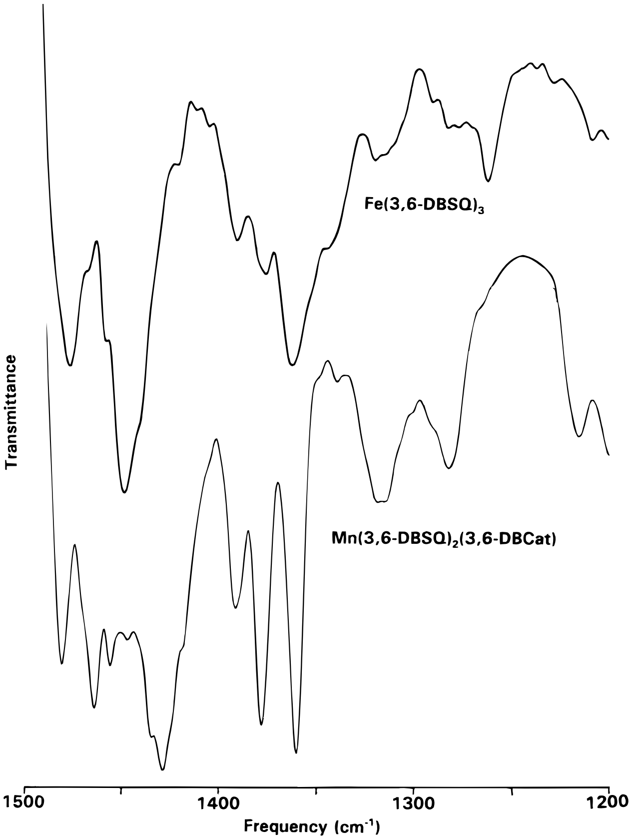

Figure 4. Infrared spectra recorded on $Fe(3,6\text{-}DBSQ)_3$ and $Mn(3,6\text{-}DBQ)_3$ as KBr pellets at room temperature. At this temperature $Mn(3,6\text{-}DBQ)_3$ exists as a mixture of $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$ and $Mn^{III}(3,6\text{-}DBSQ)_3$ redox isomers.

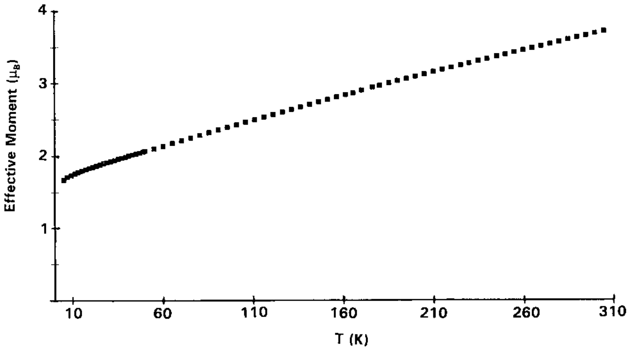

Figure 5. Temperature-dependent changes in magnetic moment for $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$.

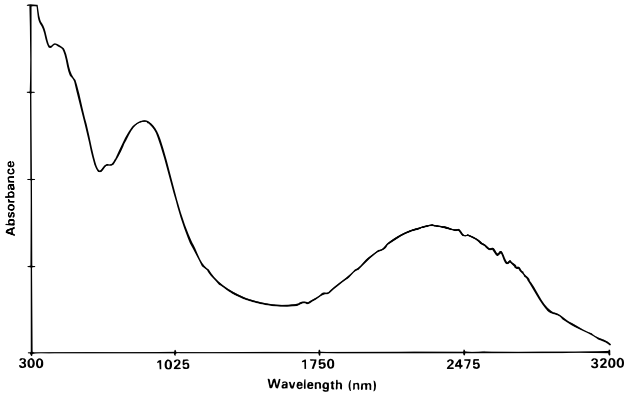

Figure 6. Electronic spectrum of $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$ recorded in the solid state (KBr) at room temperature.

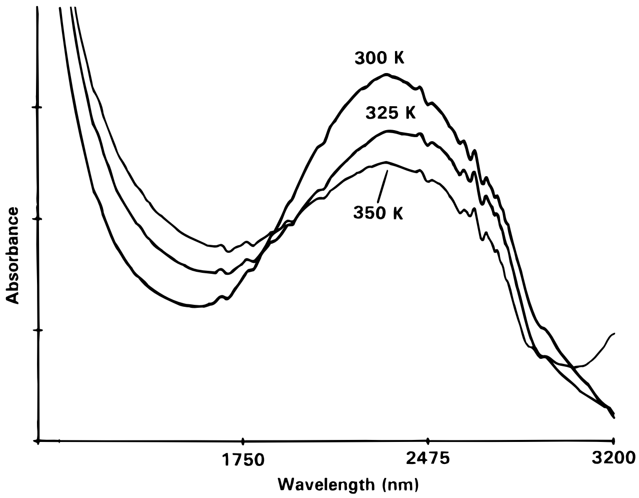

Figure 7. Temperature-dependent changes in the intensity of the Cat → SQ interligand IT transition at 2300 nm of $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$.

$DBSQ)_3$.[16] EPR spectra, recorded on the complex in toluene solution, are similar to spectra obtained on $Mn^{IV}(Cat\text{-}N\text{-}SQ)_2$.[26] This complex is also a case where strong antiferromagnetic exchange between d^3 Mn(IV) and two quinone radical ligands result in an $S = {}^1\!/_2$ spin ground state. Anisotropic spectra obtained on $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$ in a toluene/chloroform glass at 77 K consist of two components at $g_{\parallel} = 1.998$ and $g_{\perp} = 2.048$ with hyperfine coupling to the $I = {}^5\!/_2$ ^{55}Mn nucleus of $A_{\parallel} = 0.0137\ cm^{-1}$ and $A_{\perp} = 0.0080\ cm^{-1}$. The metal-based $S = {}^1\!/_2$ ground state is not uniquely consistent with the Mn(IV) charge distribution for the complex. This could result from strong metal−radical coupling in redox isomers with metal charge ranging from +5 to +3, the Mn(VI) redox isomer, $Mn^{VI}(3,6\text{-}DBCat)_3$, would be d^1, and magnetic measurements fail to provide a unique indication of charge distribution for the molecule.

Electronic spectra recorded on $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$ in the solid state provide further evidence for a charge distribution with mixed-charge quinone ligands. Prominent features of the spectrum in the visible−near-IR region include an intense band at 850 nm and a broad transition at 2300 nm (Figure 6). Spectra of the $Mn^{III}(N\text{-}N)(SQ)(Cat)$ redox isomers differ from the Mn(IV) species, $Mn^{IV}(N\text{-}N)(Cat)_2$, with the appearance of an intense band typically in the 2100 nm region that has been assigned as a LL′CT transition between mixed-charge SQ and Cat ligands. The 2300 nm transition of the tris quinone complex can be assigned similarly, in agreement with the $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$ charge distribution.

Valence Tautomerism for $Mn(3,6\text{-}DBQ)_3$. The potential utility of complexes that exhibit valence tautomerism in data storage applications has been noted.[4,27] Consequently, our experiments have been focused on samples that may exhibit shifts in equilibria between redox isomers at temperatures in the 200−300 K range in the solid state. Changes in charge distribution occur over a temperature range that is defined by the ratio of enthalpy and entropy changes for the equilibrium.[28]

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Large positive values for ΔS that define the temperature dependence of a particular equilibrium are primarily the result of low-frequency shifts in vibrational modes that result from population of the antibonding dσ (e_g in octahedral symmetry) orbitals of the metal that are directed at ligand bonding sites.[29] For the equilibria described in eqs 2 and 3, the Mn(III) (2) and Mn(II) (3) redox isomers are the species favored at high temperature in the two steps.

Solid-state electronic spectra were measured for $\mathrm{Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)}$ at temperatures between 300 and 350 K. The band at 850 nm was observed to increase in intensity with increasing temperature, while the intensity of the band at 2300 nm decreased. Intensity changes for the low-energy transition are shown in Figure 7, and the changes in intensity with temperature are completely reversible. With the assignment of the low-energy transition as a Cat → SQ IT band, the product of the solid-state shift in equilibrium is likely to be a species with quinone ligands of the same charge, specifically $\mathrm{Mn^{III}(3,6\text{-}DBSQ)_3}$, and the shift in charge distribution is shown in eq 4.

This is the first observation of valence tautomerism (VT) between redox isomers of a transition metal complex outside the $\mathrm{M(N\text{-}N)(DBQ)_2}$, M= Co, Mn series. There is no reason VT should be restricted to complexes of this group, and the present result indicates that it may appear more generally, subject to the conditions (i) that metal and quinone frontier orbitals are localized and of similar energy and (ii) that changes in enthalpy and entropy for the equilibrium combine to give a favorable value for transition temperature.

$$\underset{(d\pi)^3(d\sigma)^0(Q\pi_1)^2(Q\pi_2)^1(Q\pi_3)^1}{\mathrm{Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)}} \rightleftharpoons \underset{(d\pi)^3(d\sigma)^1(Q\pi_1)^1(Q\pi_2)^1(Q\pi_3)^1}{\mathrm{Mn^{III}(3,6\text{-}DBSQ)_3}} \quad (4)$$

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Supporting Information Available: Complete listings of crystallographic details, atomic coordinates, bond lengths and bond angles, thermal displacement parameters, and calculated H positional parameters for *trans*-$\mathrm{Mn(thf)_2(3,6\text{-}DBSQ)(3,6\text{-}DBCat)}$ and $\mathrm{Mn(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)}$ (22 pages). Ordering information is given on any current masthead page.

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