

## Transition metal complexes containing quinone ligands: studies on intramolecular metal-ligand electron transfer

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**Abstract** - Charge distribution in complexes containing quinone ligands coordinated with electroactive transition metal ions is determined by the relative energies of metal and quinone electronic levels. Intramolecular metal-quinone electron transfer may result from variations in the form of the complex which change the order of metal and quinone orbital energies. Iron complexes have been prepared with 3,5-di-*t*-butyl-1,2-benzoquinone (DBBQ). The structures of the complexes have been determined using crystallographic methods, the charge on the metal and the charge distribution in the molecule have been studied using spectroscopic techniques, and magnetic coupling between paramagnetic semiquinone ligands and the high spin ferric center has been investigated using variable temperature magnetic susceptibility measurements. Reactions carried out between 3,5-di-*t*-butylcatechol and ammonia in the presence of the divalent metal ions of Fe, Mn, and Co lead to neutral complexes of form  $ML_2$ , where L is a tridentate ligand resulting from Schiff base condensation of two catecholate ligands. This ligand may exist in charges ranging from +1 to -3, and spectroscopic, structural and magnetic methods of analysis have been used to determine charge distribution in the complexes. EPR spectra indicate that complexes containing the more oxidized form of the ligand have surprisingly localized electronic structures.

### INTRODUCTION

Catecholates and semiquinones have filled or partially filled electronic levels that are close to transition metal d-orbitals in energy but which remain discrete in the electronic structure of the complex. As a consequence, modifying complexes in a way which changes the order of metal and quinone orbital energy results in a change in the nature of the electronic ground state of the complex, and this change may be reflected in an effective transfer of charge between the metal and the quinone ligand (ref. 1). The transition down a group results in an increase in metal d-orbital energy. Neutral complexes of the first row metals show charge distributions with partially oxidized metals coordinated by partially reduced semiquinone ligands (ie.  $Cr^{2+}(SQ)_3$ ,  $Mn^{2+}(SQ)_2$ ,  $Fe^{2+}(SQ)_3$ ), while related complexes containing the 5d third row metals contain metal ions in high oxidation states coordinated by reduced catecholate ligands (ie.  $W^{VI}(Cat)_3$ ,  $Re^{VII}(Cat)_3$ ,  $Os^{VII}(Cat)_3$ ). The effect of the donor property of counter ligands on metal orbital energy can also influence charge distribution. With hard nitrogen donor ligands the copper-quinone complexes show structural and magnetic properties which indicate a (N-N)Cu<sup>2+</sup>(Cat) charge distribution, while with soft phosphine donors metal orbital energy drops and the paramagnetic center shifts to the semiquinone ligand in the isoelectronic (P-P)Cu<sup>2+</sup>(SQ) complexes (ref. 2). Overall complex charge influences charge distribution. Reduction of one ligand of neutral  $V^{2+}(SQ)_3$  results in oxidation of the metal ion by two electrons as charge distribution changes to  $V^{IV}(Cat)_3^-$  (ref. 3).

A second feature of the quinone complexes which results from the similarity of metal and semiquinone orbital energies that is found in situations where both metal and ligand are paramagnetic is temperature dependent magnetic behavior (ref. 4). This results from magnetic coupling between metal and paramagnetic ligand which is qualitatively similar to the magnetic exchange interactions more commonly observed for polymetallic complexes. In this report we describe additional results obtained recently in our investigations on iron-quinone complexes and we present new information on the properties of complexes prepared with a Schiff base biquinone ligand.

## EXPERIMENTAL

The quinone ligand used in this investigation was 3,5-di-t-butyl-1,2-benzoquinone (DBBQ). Reactions were carried out using DBBQ and  $\text{Fe}(\text{CO})_5$  in a 2:1 molar stoichiometry in toluene solution to give a dark blue complex of composition  $\text{Fe}(\text{DBBQ})_2$ . The complex was characterized using spectroscopic and crystallographic methods. Mossbauer spectra and variable temperature magnetic susceptibility measurements were made in collaboration with the group of Professor D. H. Hendrickson at the University of Illinois. Only small crystals were obtained for the complex. However, space group analysis and the results of a very rough structure determination using only 488 observed reflections indicated that the complex was isostructural with  $[\text{Mn}(\text{DBBQ})_2]_4$  and provided approximate values for the Fe-Fe separations in the tetramer.

Neutral complexes containing the 3,5-di-t-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-t-butylphenyl)imine anion (Cat-N-BQ) were prepared by treating a solution containing 3,5-di-t-butylcatechol and aqueous ammonia with the salt of a divalent metal (ref. 5). Metals used in this investigation included Fe, Mn and Co. Bis complexes of the tridentate ligand were obtained by this procedure and were characterized using spectroscopic, magnetic, electrochemical, and crystallographic methods.

## IRON COMPLEXES OF 3,5-DI-t-BUTYLSEMIQUINONE AND 3,5-DI-t-BUTYLCATECHOL

The study of magnetic exchange interactions between metal ions and paramagnetic organic radicals is a topic of growing interest as the physical properties of metal complexes in biological systems become known. In particular, studies on electron transfer within Photosystem II of the photosynthetic unit of plants and within the reaction centers of photosynthetic bacteria indicate intermediate species with both the primary ( $Q_A$ ) and secondary ( $Q_B$ ) quinone acceptors coupled antiferromagnetically as semiquinones to a high-spin iron(II) center (ref. 6). Loss of EPR signal observed in experiments carried out at low temperature has been attributed to formation of a transient  $Q_A^{\cdot-}\text{-Fe-Q}_B^{\cdot-}$  species (ref. 7).

The tris(semiquinone)iron(III) complexes were among the earliest examples of simple chemical systems where iron-radical magnetic exchange interactions could be studied (ref. 8). These complexes show temperature-dependent effective magnetic moments ( $\mu_{\text{eff}}$ ) with  $S=1$  ground states arising from antiferromagnetic coupling between the  $S=5/2$  metal ion and the three  $S=1/2$  ligands. The  $\text{Fe}(\text{SQ})_3$  complexes were prepared by treating  $\text{Fe}(\text{CO})_5$  with a slight excess of the benzoquinone form of the ligand. When carried out using 3,5-di-t-butyl-1,2-benzoquinone, the reaction produced the green  $\text{Fe}(\text{DBSQ})_3$  complex. The exchange interaction in this complex is relatively strong, resulting in a temperature-invariant (4.2-285K)  $\mu_{\text{eff}}$  of  $2.82 \mu_B$ . If this synthetic procedure is carried out using an Fe:quinone ratio which is less than 1:3, a dark purple complex is formed. Elemental analyses and the results of a preliminary crystallographic investigation indicate that the complex forms with two quinone ligands per metal ion in a tetrameric molecule which is isostructural with the Mn(II), Co(II), and Ni(II) complexes  $M_4(\text{DBSQ})_8$  reported earlier and shown in Fig. 1. Characterization of the complex using Mossbauer spectroscopy at 100°K gives the spectrum shown in Fig. 2, which is best fit with two quadrupole-split doublets with isomer shift values of 0.476(2) and 0.466(1) mm/s (vs. iron foil) and quadrupole splitting parameters of 1.714(2) and 1.304(2) mm/s, respectively.

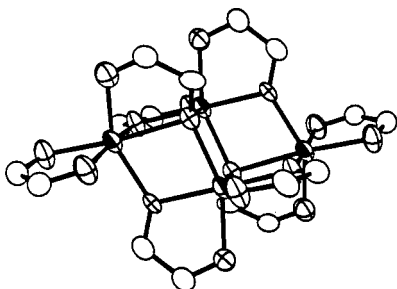


Fig. 1. Inner coordination structure of the  $M_4(\text{DBSQ})_8$  and  $\text{Fe}_4(\text{DBSQ})_4(\text{DBCat})_4$  tetramers.

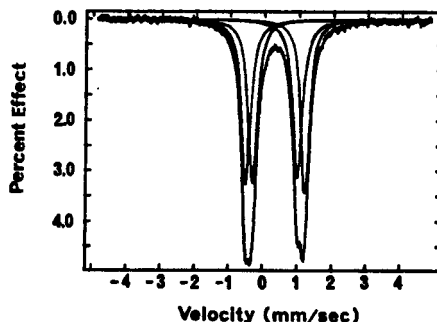


Fig. 2. Mossbauer spectrum of  $\text{Fe}_4(\text{DBSQ})_4(\text{DBCat})_4$ .

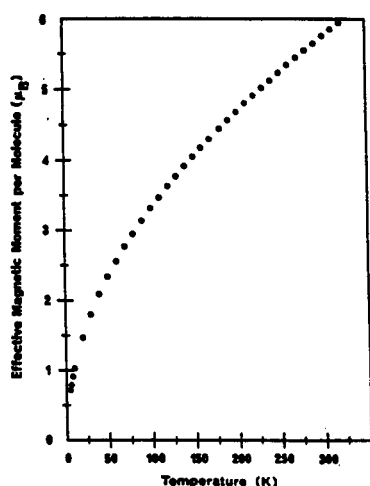


Fig. 3. Temperature dependence of the magnetic moment of  $\text{Fe}_4(\text{DBSQ})_4(\text{DBCat})_4$ .

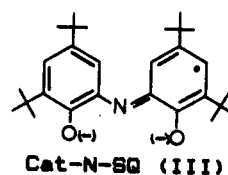
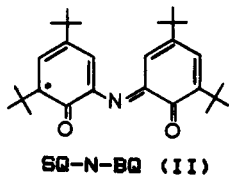
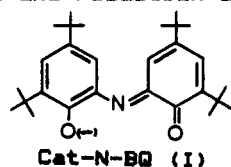
These parameters are indicative of high-spin ferric iron, and compare well with values obtained on other ferric semiquinone complexes (ref. 8 and 9). In contrast with the series of isostructural tetrameric semiquinone complexes,  $\text{M}_4(\text{DBSQ})_4$ ,  $\text{M} = \text{Mn, Co, Ni}$ , the iron analog has charge distribution  $\text{Fe}_4(\text{DBSQ})_4(\text{DBCat})_4$  (ref. 10 and 11). In this form, each unit of the tetramer contains six unpaired electrons due to the  $S=5/2$  metal ion and the semiquinone radical, and the tetrameric molecule contains 24 unpaired electrons. At 321°K the magnetic moment of the complex was determined to be  $5.94 \mu_B$  per tetrameric  $\text{Fe}_4(\text{DBSQ})_4(\text{DBCat})_4$  unit. This value clearly shows evidence of antiferromagnetic spin coupling, and as the sample temperature is decreased to 5.0°K  $\mu_{\text{tet}}$  drops to  $0.72 \mu_B$  per tetramer as shown in Fig. 3.

Further, the slope of the  $\mu_B$  vs T curve is clearly directed toward a fully coupled, diamagnetic spin state at a somewhat lower temperature. This unprecedented magnetic behavior requires both iron-semiquinone and iron-iron antiferromagnetic exchange interactions.

Structurally, the tetramer consists of two coplanar  $\text{Fe}_3$  triangles sharing a common edge. Figures showing the structural features of the Mn, Co and Ni tetramers have appeared in previous publications (ref. 4, 10 and 11). While our structural characterization on  $\text{Fe}_4(\text{DBSQ})_4(\text{DBCat})_4$  has not been of the quality to allow distinction between semiquinone and catecholate ligands and it is possible that ligands of different charge are disordered in the structure, it is clear that the Fe-Fe separations are similar to the Co-Co separations of  $\text{Co}_4(\text{DBSQ})_4$ . The Fe-Fe separation between metal atoms related by crystallographic inversion symmetry along the edge common to both triangles is 3.15(2)Å, slightly shorter than the other two edge values of 3.27(2) and 3.42(3)Å. In the Co and Ni tetramers where the metal-semiquinone antiferromagnetic interaction is the strongest the magnetic moment per tetramer decreases from 9.16 and  $8.69 \mu_B$ , respectively at 286°K, to 4.63 and  $5.73 \mu_B$  at 4.2°K, and exchange between bridged  $\text{M}(\text{DBSQ})_2$  units was observed to be insignificant (ref. 4). In the Mn tetramer,  $\text{Mn}_4(\text{DBSQ})_4$ , the magnetic moment per tetramer increases from  $10.2 \mu_B$  at 286°K to  $11.3 \mu_B$  at 10°K and the interaction between adjacent  $S=5/2$  metal ions appears to be weakly ferromagnetic (ref. 10). The contrast between this result and the iron tetramer is quite striking. Structural features of the tetramers include quinone oxygen atom bridges between adjacent metal ions. The magnetic properties of the iron tetramer, in comparison with the Mn analog, seem to indicate that reduction of bridging semiquinone ligands markedly changes the nature of the exchange interaction between metals.

#### COMPLEXES CONTAINING A SHIFF BASE BIQUINONE LIGAND

Treatment of an ethanol solution containing 3,5-di-*t*-butylcatechol with concentrated ammonium hydroxide in air leads to formation of the 3,5-di-*t*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*t*-butylphenyl)imine anion (I, Cat-N-BQ). When carried out in the presence of a divalent metal ion neutral complexes of form  $\text{M}(\text{Cat-N-BQ})_2$  can be formed (ref. 5). One-electron oxidation and reduction of (I)



leads to formation of the neutral SQ-N-BQ radical (II) and the Cat-N-SQ radical dianion (III), respectively. Both radical forms of (I), as well as other forms of higher and lower charge, may potentially contribute to the coordination properties of this interesting ligand system. When this reaction is carried out in the presence of  $Fe^{2+}$ , the  $Fe(Cat-N-BQ)_2$  complex is formed. The room temperature magnetic moment of the complex is  $5.25 \mu_B$ , and the results of a molecular structure determination (Fig. 4) show Fe-O and Fe-N lengths of 1.987(1) and 2.117(1)Å, respectively. These features are consistent with the  $Fe^{2+}(Cat-N-BQ)_2$

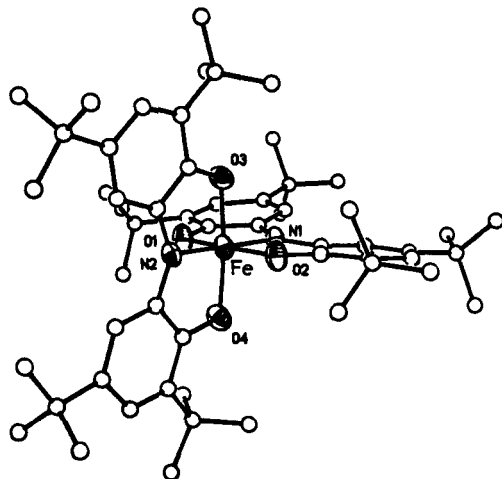


Fig. 4. Molecular structure of  $Fe(Cat-N-BQ)(Cat-N-SQ)$ .

form of the complex. However, the Mossbauer spectrum shows an isomer shift of 0.4164(5) mm/sec and quadrupolar splitting of 0.479(1) mm/sec, values which clearly indicate Fe(III). The complex must, therefore, contain mixed charge ligands,  $Fe^{3+}(Cat-N-SQ)(Cat-N-BQ)$ , and the value for the magnetic moment must result from antiferromagnetic coupling between the  $S = 5/2$  metal and the  $S = 1/2$  radical ligand. No structural difference was found between ligands, suggesting charge delocalization over the entire organic region of the molecule.

Interest in metal complexes which may bear similarity to the polynuclear manganese complex which serves as the catalytic agent for water oxidation in Photosystem II of the photosynthetic unit has focused upon high oxidation state complexes of manganese (ref. 12). Catecholate ligands have been shown to form stable complexes of manganese(IV) in the absence of strongly bound oxo ligands (ref. 13 and 14). We have additionally reported intramolecular manganese-quinone electron transfer for  $trans-Mn^{IV}(py)_2(DBCat)_2$  with the 3,5-di-tert-butylcatecholate ligands changing in charge from catecholate to semiquinone as the metal ion changes from Mn(IV) to Mn(II) (eq. 1) (ref. 10). The stability of Mn(II), Mn(III) and Mn(IV) complexes (ref. 10, 14 and 15) containing catecholate



and semiquinone ligands with the possibility for varying metal ion oxidation state by intramolecular electron transfer makes manganese quinone complexes reasonable functional models for biological manganese metalloenzymes.

When the 3,5-di-*t*-butylcatechol Schiff base condensation reaction is carried out in the presence of Mn(II) ion, a dark green complex is formed. Crystals of the complex obtained by slow evaporation of a toluene solution have been examined crystallographically. The results of this structure determination show that the molecule has the same general structure found for the iron complex. The Mn-O and Mn-N lengths of 1.896(5) and 1.910(5)Å are much shorter than values expected for Mn(II), but compare well with Mn-O and Mn-N values of 1.854(2) and 2.018(3) found for the Mn(IV) center of  $trans-Mn(py)_2(DBCat)_2$ . As a complex of Mn(IV) both ligands would be in the reduced dianionic radical form (II),  $Mn^{IV}(Cat-N-SQ)_2$ , with reduction resulting from transfer of two electrons from the metal, one to each ligand (eq. 2).



As before, structural features of the ligands given in Table 1 indicate charge delocalization over the entire unsaturated region; C-O and C-N bonds are of lengths which are intermediate between double and single bond values.

As a complex of  $d^2$  Mn(IV), which also contains two paramagnetic organic ligands, intramolecular spin-spin coupling between ligands and metal may occur as found in the iron complex and in semiquinone complexes of paramagnetic metal ions. In solid state at room temperature Mn(Cat-N-SQ)<sub>2</sub> has a magnetic moment of  $1.79 \mu_B$ , consistent with a  $S=1/2$  magnetic ground state. This must arise from strong antiferromagnetic coupling between the two  $S=1/2$  ligands and the  $S=3/2$  metal ion. The isotropic EPR spectrum of the complex, shown in Fig. 5, is centered about a  $\langle g \rangle$  value of 2.013, and shows coupling of 104 G to the  $I=5/2$   $^{55}\text{Mn}$  nucleus and coupling of 3.8 G to the two equivalent  $^{14}\text{N}$  nuclei. In a toluene-chloroform glass at  $-196^\circ\text{C}$  an anisotropic spectrum is obtained which has parameters of  $g_{\parallel}$  of 1.977,  $g_{\perp}$  of 2.040,  $A_{\parallel}$  of 153 G and  $A_{\perp}$  of 84.2 G. The electronic spectrum is dominated by four strong charge transfer bands in the UV and visible regions at 346(22,000), 476(11,200), 586(10,000), and 900(9,300)nm. The close energy separation between metal and ligand electronic levels gives rise to three intense transitions at 1087(4,800), 1200, and 1268(4,300)nm in the near infrared. Cyclic voltammograms on the complex show a reversible one-electron oxidation at +0.208V (vs. Fc/Fc<sup>+</sup>) and two reversible one-electron reductions at -0.945 and -1.484 V. Oxidation of the complex appears to occur at the ligand to give the mixed-charge ligand cation Mn<sup>IV</sup>(Cat-N-BQ)(Cat-N-SQ)<sup>+</sup>, reduction occurs at the metal to give the Mn(III) and Mn(II) forms of the complex. None of these species has yet been isolated and characterized, however.

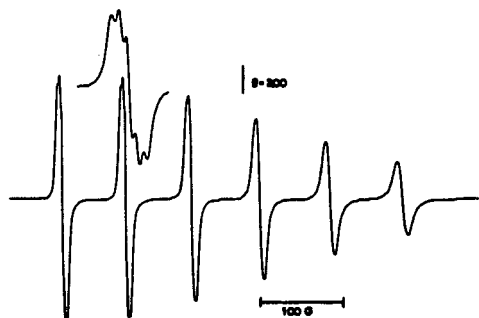


Fig. 5. Isotropic EPR spectrum of Mn(Cat-N-SQ)<sub>2</sub>.

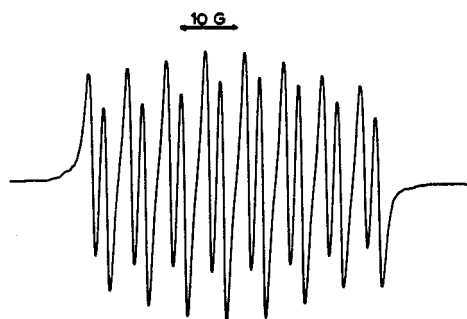
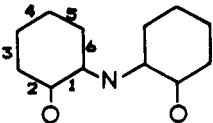


Fig. 6. Isotropic EPR spectrum of Co(Cat-N-BQ)(Cat-N-SQ).

Our formulation for the complex as containing Mn(IV) is based primarily on the structural and magnetic properties of the complex, but other valence tautomers exist. A second form consisting of two diamagnetic ligands of form (I) chelated to a low spin Mn(II) center must be considered as a possibility. However, this spin state is only found with very strong field ligands, cyanide and isocyanides, and Mn(II) complexes of ligands with similar structures, terpyridine and 2,6-diacetylpyridine dioxime, are exclusively high spin. An additional charge distribution which is consistent with the magnetic property of the complex would contain  $d^1$  Mn(VI) chelated by two reduced ligands in the form of the bis(2-hydroxyphenyl)amide trianion, Mn(Cat-N-Cat)<sub>2</sub>. However, the structural features of the ligands show C-O and C-N bond lengths which are shorter than single bond values, lengths which are more in accord with radical ligands characterized structurally in complexes containing other metal ions.

Schiff base condensation of 3,5-di-*t*-butylcatechol molecules in the presence of Co<sup>2+</sup> leads to the neutral bis(biquinone) complex which is structurally similar to the Fe and Mn complexes. Bond lengths of 1.896(5) and 1.868(5)Å for the Co-O and Co-N bonds are clearly indicative of Co(III) rather than Co(II), and a charge formulation with mixed-charge ligands, Co<sup>III</sup>(Cat-N-BQ)(Cat-N-SQ), is required. In accord with this charge distribution the complex has a magnetic moment of  $1.92 \mu_B$  indicating a single unpaired electron, which in the Co(III) formulation would be contained in an orbital localized on the ligands. The EPR spectrum of the complex shown in Fig. 6 is centered about a  $g$  value of 1.9974 and consists of 16 lines. This spectrum arises from an eight line pattern due to coupling to the  $^{59}\text{Co}$  ( $I=7/2$ ) nucleus of 9.3 G, with additional coupling to a single ring proton, of 3.4 G. Coupling to a single ring proton requires a considerably more localized electronic structure for the ligand than might be expected from the structural features of the complex. Structural characterization on the Ni(II) complex which has the Ni(Cat-N-BQ)<sub>2</sub> charge distribution has

Table 1. Summary of structural features of Schiff base biquinone complexes.

	Mn(Cat-N-SQ) <sub>2</sub>	Co(Cat-N-BQ) (Cat-N-SQ)	Fe(Cat-N-BQ) (Cat-N-SQ)	Ni(Cat-N-BQ) <sub>2</sub>	
	C-O	1.325(7)	1.305(7)	1.287(3)	1.264(5)
	C-N	1.380(7)	1.361(6)	1.357(3)	1.344(5)
	C-C(1)	1.417(8)	1.445(7)	1.452(3)	1.464(4)
	C-C(2)	1.408(8)	1.450(7)	1.430(3)	1.450(4)
	C-C(3)	1.380(9)	1.376(7)	1.368(4)	1.353(4)
	C-C(4)	1.412(8)	1.416(7)	1.420(4)	1.429(4)
	C-C(5)	1.367(8)	1.360(7)	1.355(3)	1.344(4)
	C-C(6)	1.410(9)	1.419(7)	1.420(3)	1.430(4)

recently been completed and a summary of ligand bond lengths for all four structure determinations appears in Table 1.

These values show that as ligand oxidation increases from Mn(Cat-N-SQ)<sub>2</sub> to Ni(Cat-N-BQ)<sub>2</sub> bond lengths for the C-C bonds of the rings approach localized quinone values. Bonds at the 3 and 5 ring positions in the drawing above approach localized double bond values in Ni(Cat-N-BQ)<sub>2</sub> indicating a far more localized ligand electronic structure than might be expected. This localized ligand structure may be responsible for the surprising coupling pattern observed for the EPR spectrum of Co(Cat-N-BQ)(Cat-N-SQ).

#### Acknowledgement

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