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Ligand Redox Activity and Mixed Valency in First-Row Transition-Metal Complexes Containing Tetrachlorocatecholate and Radical Tetrachlorosemiquinonate Ligands

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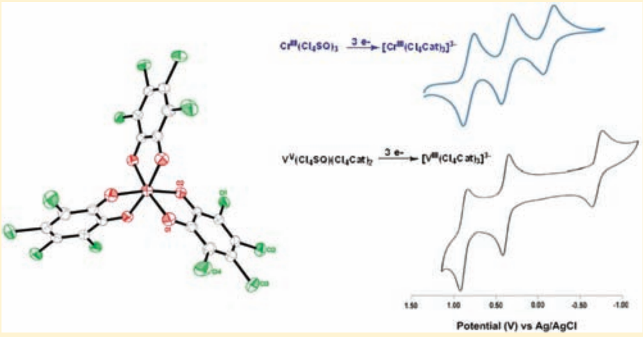

ABSTRACT: Ligand noninnocence occurs for complexes composed of redox-active ligands and metals, with frontier orbitals of similar energy. Usually methods of analysis can be used to define the charge distribution, and cases where the metal oxidation state and ligand charge are unclear are unusual. Ligands derived from *o*-benzoquinones can bond with metals as radical semiquinonates ($SQ^{\bullet-}$) or as catecholates (Cat^{2-}). Spectroscopic, magnetic, and structural properties can be used to assess the metal and ligand charges. With the redox activity at both the metal and ligands, reversible multicomponent redox series can be observed using electrochemical methods. Steps in the series may occur at either the ligand or metal, and ligand substituent effects can be used to tune the range of ligand-based redox steps. Complexes that appear as intermediates in a ligand-based redox series may contain both SQ and Cat ligands "bridged" by the metal as mixed-valence complexes. Properties reflect the strength of metal-mediated interligand electronic coupling in the same way that ligand-bridged bimetallics conform to the Robin and Day classification scheme. In this review, we will focus specifically on complexes of first-row transition-metal ions coordinated with three ligands derived from tetrachloro-1,2-benzoquinone (Cl_4BQ). The redox activity of this ligand overlaps with the potentials of common metal oxidation states, providing examples of metal- and ligand-based redox activity, in some cases, within a single redox series. The strength of the interligand electronic coupling is important in defining the separation between ligand-based couples of a redox series. The complex of ferric iron will be described as an example where coupling is weak, and the steps associated with the $Fe^{III}(Cl_4SQ)_3/[Fe^{III}(Cl_4Cat)_3]^{3-}$ redox series are observed over a narrow range in electrochemical potential.

INTRODUCTION

Studies on coordination complexes containing redox-active ligands took a dramatic turn in the 1960s with the popularity of the 1,2-dithiolene ligands.[1] Some of the most interesting products of this research were complexes that seemed to defy conventional rules of metal charge and spin state,[1a,2] leading to a "noninnocent" designation by Jorgensen.[3] This term is now being used more generally in reference to ligands that form a redox-active unsaturated five-membered chelate ring when bound to a metal ion. Many early questions concerning the ligand and metal oxidation states have been resolved with the aid of modern physical techniques and with improved theoretical methods.

It was striking in the early 1970s that the coordination chemistry of the sulfur-donor ligands had developed before the more common oxygen-containing analogues.[4] Indeed, recent studies on complexes of simple 1,2-ethenediolate ligands have demonstrated that they offer a greater synthetic challenge than their sulfur analogues.[5] Developments in chemical crystallography were important in clarifying the nature of many of the 1,2-dithiolene complexes[1d,f] and have been key in providing a definition of complexes prepared with catecholate (Cat) and *o*-quinone-derived ligands. Prior to 1975, there was but one report of a Cat complex characterized structurally.[4] From 1975 to 1980, as crystallographic methods became generally available, not only were structural studies used to provide a definition of complexes containing Cat and semiquinonate (SQ) ligands, but it became possible to associate the ligand charge with structural features,[4] specifically, the ligand C−O bond length of 1.34 Å for Cat and 1.29 Å for SQ and contraction of the ring C−C bonds for the SQ at the positions that would be double bonds for the parent *o*-benzoquinone. As a striking example, the difference between charge-localized SQ and Cat ligands of $Co^{III}(bpy)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)$ was apparent from their metrical differences.[6] As the coordination chemistry of Cat and SQ ligands has developed, the number of complexes containing mixed-charge ligands has increased and it has become clear that descriptions applied to complexes containing mixed-valence metal ions may be extended to Cat−SQ complexes. Complexes containing two or three "noninnocent" ligands generally exhibit ligand-based redox activity, leading to mixed-charge SQ and Cat species as intermediates in the complex redox series. Occasionally, electronic coupling through the "bridging" metal ion leads to intense intervalence

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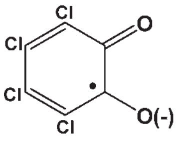
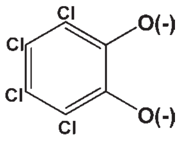
electronic transitions, and the Robin and Day classification scheme normally associated with mixed-valence transition-metal complexes carries over to the complexes containing mixed-charge ligands. The redox series for the quinone complexes of vanadium and chromium were among the earliest examples, although the redox versatility of the 1,2-dithiolene complexes had been demonstrated in the 1960s.[1b,7]

Ligand-based redox activity has taken on new significance with studies on oxidative addition and reductive elimination reactions to metals that are not redox-active using ligand-derived charge. Reactions of this type extend back to early studies on O_2 activation in the mechanism for catechol oxidation, where catecholate charge is used to reduce O_2 in the process of forming a peroxosemiquinonate ligand.[8] In early studies, peroxosemiquinonate complexes of iridium and ruthenium were characterized structurally to confirm the formation of the oxidized ligand.[9] In more recent reports, oxygenated complexes of antimony with Cat and amidophenolate ligands have been reported as species formed with a redox-inactive p-block metal.[10] Heyduk and Soper have studied the oxidative addition of halogens and alkyl halides to d^0 metals, with charge provided by reduced amidophenolate ligands.[11,12] Soper, Chirik, and Heyduk have described C−C coupling reactions as examples of reductive elimination, with charge transferred to oxidized ligands without a change in metal charge.[13−15] Generally, these reactions involve the transfer of two or more electrons requiring multiple accessible ligand-based electronic states.

Definition of the electrochemical properties of "simple" Cat and SQ complexes provided an introduction to the redox activity of members of the $[MQ_3]^{n(\pm)}$ series. This research was carried out with metals of the first transition series where ligand and metal frontier electronic levels are close in energy. Related complexes of metals containing 4d and 5d valence configurations generally tend to have fully reduced Cat ligands.[16] The results of studies with 3d metal ions showed that either the metal or ligands could undergo electron transfer, leading to a series of complexes with rich electronic and magnetic properties. The most widely studied complexes have contained the tetrachloro-1,2-semiquinonate (Cl_4SQ) and tetrachlorocatecholate (Cl_4Cat) ligands, and these will be the subjects of this comparative review.



Cl_4SQ^-



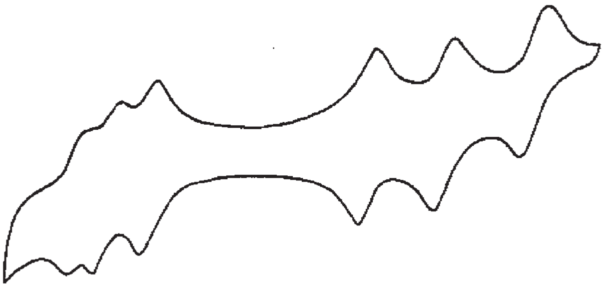
Cl_4Cat^{2-}

■ $[Cr(Q)_3]^{n(\pm)}$ REDOX SERIES

The structural, magnetic, and spectroscopic properties of the neutral $Cr^{III}(SQ)_3$ series, with SQ ligands derived from tetrachloro-1,2-benzoquinone (Cl_4BQ), 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-DBBQ), and 9,10-phenanthrenequinone (phenBQ), demonstrated that the central metal was $S = {}^3/_2$ Cr^{III} coupled antiferromagnetically with the three chelated radical SQ ligands. Electrochemical characterization showed that $Cr^{III}(SQ)_3$ could be oxidized or reduced through ligand-based redox steps to give the seven-membered redox series shown below for complexes prepared with 9,10-phenanthrenequinone (**1**).[17] The kinetic stability of Cr^{III} is important in keeping

$$\begin{aligned}&[Cr^{III}(BQ)_3]^{3+} \leftrightarrows [Cr^{III}(BQ)_2(SQ)]^{2+} \leftrightarrows [Cr^{III}(BQ)(SQ)_2]^{+}\\ &\leftrightarrows [Cr^{III}(SQ)_3] \leftrightarrows [Cr^{III}(SQ)_2(Cat)]^{-}\\ &\leftrightarrows [Cr^{III}(SQ)(Cat)_2]^{2-} \leftrightarrows [Cr^{III}(Cat)_3]^{3-}\end{aligned} \quad (1)$$

weak-donor *o*-benzoquinone forms of the ligand bound to the metal under electrochemical conditions of polar solvent and high electrolyte concentration for oxidized members of the series. Electron paramagnetic resonance (EPR) spectra recorded on $[Cr(BQ)(SQ)_2]^+$ and $[Cr(SQ)_2(Cat)]^-$ showed that they both had a single metal-based spin formed by spin decoupling from one radical ligand upon one-electron oxidation or reduction.[18] The positive shift of nearly 1 V for the redox series with the Cl_4BQ ligand (Figure 1), relative to 3,5-DBBQ, demonstrated a ligand substituent dependence that could be used to vary the potential range of the redox series. Chang and Kitagawa have investigated the $Cr^{III}(Cl_4SQ)_3$/$[Cr^{III}(Cl_4Cat)_3]^{3-}$ redox series in detail.[19] Structural characterization on the intermediate redox isomers $[Cr^{III}(Cl_4SQ)_2(Cl_4Cat)]^-$ and $[Cr^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$ showed an increase in the ligand C−O bond length with reduction and a constant Cr−O bond length through the series. Magnetic measurements demonstrated progressive spin decoupling with the $S = {}^3/_2$ metal as ligands were reduced from Cl_4SQ to Cl_4Cat. While the features of $[Cr^{III}(Cl_4SQ)_2(Cl_4Cat)]^-$ and $[Cr^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$ failed to show clear structural differences for the mixed-charge ligands, both redox isomers had intense intervalence charge-transfer (IVCT) transitions at low energy as an indication of type II mixed valency (Figure 2).[20] Features of



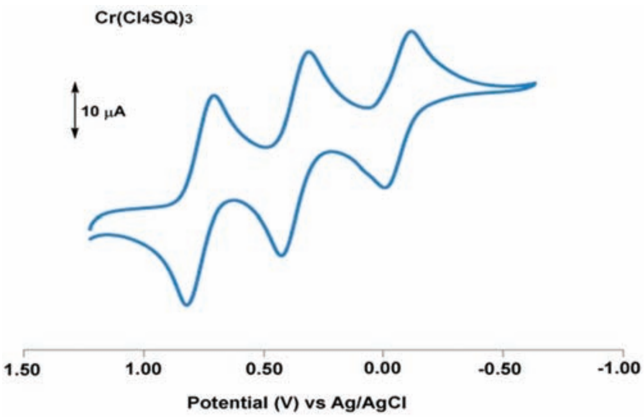


Figure 1. Cyclic voltammogram of $Cr^{III}(Cl_4SQ)_3$ recorded in a dichloromethane solution containing 0.1 M $(Bu_4N)(PF_6)$ as the electrolyte at a scan rate of 50 mV/s.

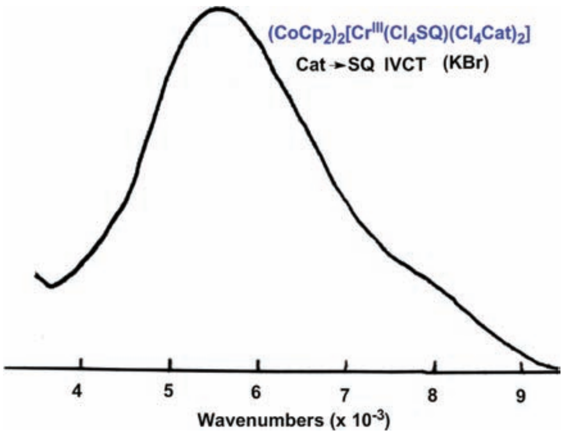


Figure 2. Near-IR Cat → SQ IVCT band at 1700 nm for $(CoCp_2)_2[Cr^{III}(Cl_4SQ)(Cl_4Cat)_2]$ recorded as a solid KBr pellet.

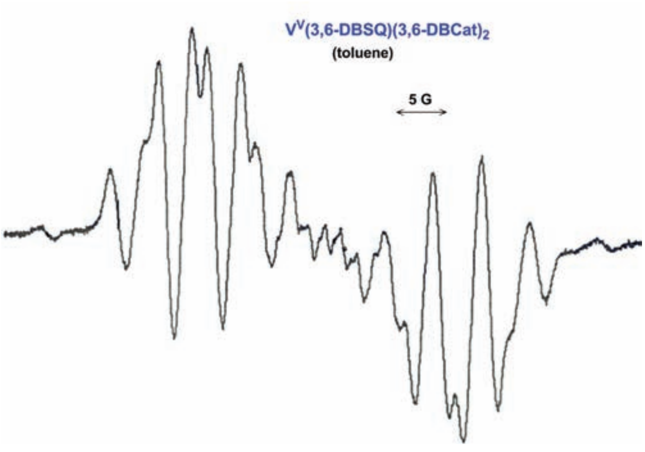


Figure 3. Isotropic EPR spectrum of $V^V(3,6\text{-}DBSQ)(3,6\text{-}DBCat)_2$ in a toluene solution (23 °C). The spectrum is centered about a $\langle g \rangle$ value of 2.0058 with hyperfine coupling to the ^{51}V nucleus ($I = {}^7/_2$) of 3.47 G and to equivalent ring protons at the 4 and 5 ring positions of one radical 3,6-DBSQ ligand of 4.53 G.

the Cat → SQ IVCT bands were used with the Hush relationship to calculate the strength of the interligand electronic coupling through the Cr^{III} bridge.[19,20]

$[V(Q)_3]^{n-}$ REDOX SERIES

The neutral complex of vanadium $V(Cl_4Q)_3$ gave an IR spectrum similar to that of $Cr^{III}(Cl_4SQ)_3$, and it was assigned the $V^{III}(Cl_4SQ)_3$ charge distribution.[21] Recent characterization on $V^V(3,6\text{-}DBSQ)(3,6\text{-}DBCat)_2$ showed clear structural differences between the SQ and Cat ligands, consistent with the mixed-charge ligand formulation, but the complex failed to show a low-energy IVCT transition.[22] Both complexes give EPR spectra with extremely weak ^{51}V hyperfine coupling as a SQ-localized radical spin consistent with either charge formulation. The spectrum of $V(Cl_4SQ)_3$ was centered about a g value of 2.0028 with ^{51}V hyperfine coupling of 2.1 G (toluene), and for $V(3,6\text{-}DBSQ)(3,6\text{-}DBCat)_2$, the g value and metal hyperfine coupling are 2.0058 and 3.47 G (Figure 3). It is possible that the $V^{III}(SQ)_3$ and $V^V(SQ)(Cat)_2$ redox isomers are close in energy, but with either charge distribution, it is known that the product of one-electron reduction is the $[V^V(Cat)_3]^-$ redox isomer.[23] The cyclic voltammogram of the $[V(Cl_4Q)_3]^n$ ($n = 0-3$) redox series is shown in Figure 4, and the V^V charge distribution has been confirmed structurally for $[V^V(3,5\text{-}DBCat)_3]^-$. The $V^V(Cl_4SQ)(Cl_4Cat)_2/[V^V(Cl_4Cat)_3]^-$ couple appears at 0.83 V (vs Ag/AgCl), and a second reduction to $[V^{IV}(Cl_4Cat)_3]^{2-}$ appears at 0.29 V. This is clearly a metal-based reduction, with the appearance of an EPR spectrum with coupling of 80.5 G to the ^{51}V nucleus at a g value of 1.960 and the appearance of axial anisotropy at low temperature. The potential of this reduction is close to that of the V^{IV}/V^V reductions of other $[V^V(Cat)_3]^-$ complexes, and a third reduction at −1.11 V to $[V^{III}(Cl_4Cat)_3]^{3-}$ is also commonly observed for other $V^{IV}(Cat)_3]^{2-}$ complexes near this potential.[24] In contrast with the strictly ligand-based redox series of $Cr(SQ)_3$ (eq 1), the four-membered reduction series of the vanadium analogues contains steps that involve reduction of the metal (eq 2) as a clear difference.

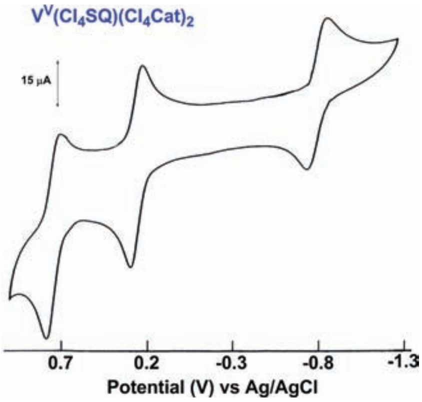


Figure 4. Cyclic voltammogram of $(PPh_4)_2[V^{IV}(Cl_4Cat)_3]$ recorded in a dichloromethane solution containing 0.1 M $(Bu_4N)(PF_6)$ as the electrolyte at a scan rate of 100 mV/s.

$$V^V(SQ)(Cat)_2 \leftrightarrows [V^V(Cat)_3]^- \leftrightarrows [V^{IV}(Cat)_3]^{2-} \leftrightarrows [V^{III}(Cat)_3]^{3-} \tag{2}$$

$[Mn(Q)_3]^{n-}$ REDOX SERIES

Redox series of the type shown in Figures 1 and 4 for vanadium and chromium have been impossible to obtain for related tris(catecholate) complexes of manganese. This appears to be due to the formation of $[Mn^{III}(Cat)_2]^-$ species by ligand dissociation, giving a solution of mixed redox-active species.[25,26] Isolated members of the redox series have been characterized, and it is possible to draw tentative conclusions regarding the charge distribution.

The neutral complex "$Mn(3,6\text{-}DBQ)_3$" was prepared by the addition of 3,6-DBBQ to $Mn_2(CO)_{10}$.[27] A similar reaction carried out earlier with 3,5-DBSQ gave the $[Mn^{II}(3,5\text{-}DBSQ)_2]_4$ tetramer,[28] and with this result, there may be redox isomers for $Mn(3,6\text{-}DBQ)_3$, with the metal ion ranging in charge from 2+ to 4+. Metrical parameters for "$Mn(3,6\text{-}DBQ)_3$" at room temperature were consistent with a complex of Mn^{IV} as $Mn^{IV}(3,6\text{-}DBSQ)_2(3,6\text{-}DBCat)$. In agreement with the mixed-ligand formulation, the complex had an intense IVCT transition at

2300 nm in the solid state. Upon an increase in the temperature of the solid sample, the intensity of the 2300 nm transition was observed to broaden and decrease, while the band at 850 nm increased. This was interpreted as a shift to the Mn^{III}(3,6-DBSQ)$_3$ redox isomer at higher temperature (eq 3).

$$Mn^{IV}(3,6\text{-DBSQ})_2(3,6\text{-DBCat}) \leftrightharpoons Mn^{III}(3,6\text{-DBSQ})_3 \quad (3)$$

The electrochemistry on this compound has not provided a clear result, but cyclic voltammetry has been studied for $[Mn^{IV}(Cl_4Cat)_3]^{2-}$ compared with the chromium and vanadium analogues. In two independent reports, $[Mn^{III}(Cl_4Cat)_2]^-$ species have been obtained in solvent-dependent syntheses that under different conditions would give $[Mn^{IV}(Cl_4Cat)_3]^{2-}$.[25,26] The relationship between the two complexes remains unclear, but the solution prepared for our electrochemical experiment gave a redox couple associated with $[Mn^{III}(Cl_4Cat)_2]^-$ superimposed on a series of redox couples that may be associated with $[Mn^{IV}(Cl_4Cat)_3]^{2-}$, among other redox-active components in the solution. The redox activity of $[Mn^{IV}(3,5\text{-DBCat})_3]^{2-}$ was reported much earlier by Sawyer et al.,[29] and, in this case as well, dissociation to a $[Mn^{III}(3,5\text{-DBCat})_2]^-$ species was observed with reduction to an uncharacterized $[Mn^{III}(3,5\text{-DBCat})_3]^{3-}$ ion. Reduction of the neutral species (eq 3) could take place either at a ligand or at the metal to give a variety of redox isomers. Unraveling the electrochemical properties of the $[Mn(Q)_3]^{n-}$ redox series will be far more challenging than with other metals of the series.

■ $[Co(Q)_3]^{n-}$ REDOX SERIES

Members of the $[Co(Q)_3]^{n-}$ redox series might be expected to resemble the $[Cr^{III}(Q)_3]^{n-}$ series with the similarity between d^3 Cr^{III} and low-spin d^6 Co^{III}. Characterization on Co^{III}(3,6-DBSQ)$_3$ has confirmed this similarity,[30] however, in chemistry resembling manganese, the reaction between $Co_2(CO)_8$ and 3,5-DBBQ gave the $[Co^{II}(3,5\text{-DBSQ})_2]_4$ tetramer.[31] Antiferromagnetic exchange between the three radical ligands of Co^{III}(3,6-DBSQ)$_3$ was found to be moderately strong, $J_{SQ,SQ} = -39.1\ cm^{-1}$, giving an $S = {}^3/_2$ magnetic ground state. Structural features of the complex were as expected for diamagnetic low-spin Co^{III} with short Co−O bond lengths [1.876 (2) Å] and ligand features that are consistent with their SQ electronic structure. The magnetic properties of Co^{III}(3,6-DBSQ)$_3$ contrast with those of Ga^{III}(3,6-DBSQ)$_3$, which shows ferromagnetic coupling for the radical ligands. It may also be compared with the iminosemiquinone complex $Co^{III}(isq)_3$, which also shows an increasing magnetic moment with decreasing temperature as a consequence of ferromagnetic spin coupling.[32]

In preliminary experiments on the anticipated synthesis of $[Co^{III}(Cl_4Cat)_3]^{3-}$, the unexpected product of the reaction between $Co(OAc)_2$ and tetrachlorocatechol was found from crystallographic characterization to be $[Co^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$.[33] Short Co−O lengths show clearly that the metal is low-spin Co^{III}. The complex gives a single EPR resonance at $\langle g \rangle = 2.0034$ with no hyperfine coupling to the ^{58}Co center, a spectrum similar to the low-temperature spectrum of Co^{III}(bpy)(3,5-DBSQ)(3,5-DBCat), where interligand electron transfer is thought to contribute to the loss of resolved metal hyperfine coupling. Consistent with the mixed-charge ligand formulation, $[Co^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$ has a broad LL′ IVCT band centered at 1450 nm. Structural features of the ligands fail to show a clear difference between the SQ and Cat ligands of the type observed for V^V(3,6-DBSQ)(3,6-DBCat)$_2$ but with ligand features similar to the $[Cr^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$ dianion reported by Chang and Kitagawa.[19,20] It was of interest to see if $[Co^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$ was associated with a redox series similar to the $[Cr^{III}(Cl_4Q)_3]^{n-}$ series. The cyclic voltammogram recorded on $[Co^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$, shown in Figure 5, shows the current for a series of three oxidations but only one clear reduction. The range in potential is similar to that of the $[Cr^{III}(Cl_4Q)_3]^{n-}$ series, as might be expected for ligand-based reductions. At slow scan rates, the current for three separate couples can be observed, as would be expected for a four-membered redox series. This scan rate dependence is something that we have observed only for the related redox series with iron. It may be related to the difficulty in reducing complex ligands rapidly switching between SQ and Cat. It is not observed for the chromium series, potentially indicating a dependence on the electron-transfer rate, but this is speculative.

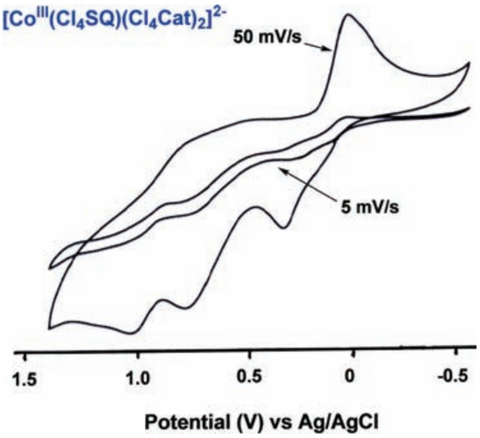


Figure 5. Cyclic voltammogram of $(NPr_4)_2[Co^{III}(Cl_4SQ)(Cl_4Cat)_2]$ recorded in an acetonitrile solution containing 0.1 M $(Bu_4N)(PF_6)$ as the electrolyte at scan rates of 50 and 5 mV/s.

■ $[Fe(Q)_3]^{n-}$ REDOX SERIES

Homoligated tris(semiquinonate) complexes of iron are now well-known and were important in establishing the high-spin Fe^{III} charge and spin state for the metal in the $Fe^{III}(SQ)_3$ series.[34] Both Fe−SQ and SQ−SQ exchange interactions are antiferromagnetic for Fe^{III}(3,6-DBSQ)$_3$, and structural characterizations on Fe^{III}(3,5-DBSQ)$_3$, Fe^{III}(3,6-DBSQ)$_3$, and $Fe^{III}(Cl_4SQ)_3$ have provided metrical parameters for the ligands that are consistent with their radical SQ electronic structures.[35,36] The short C−O bond lengths (1.28 Å) and contracted C−C bond lengths (1.36 Å) at the ring positions that would contain double bonds for the parent *o*-benzoquinone are found typically for SQ ligands and contrast with the features of $[Fe^{III}(Cat)_3]^{3-}$ reported by Raymond, which has elongated C−O bond lengths of 1.34 Å and aromatic ring C−C bond lengths consistent with the product of three-electron ligand-based reduction.[37] As expected, Fe^{III}(3,6-DBSQ)$_3$ shows three reduction, and corresponding oxidation, peaks in its cyclic voltammogram with three additional irreversible SQ oxidations at more positive potentials.[35] Through the redox series, the metal center remains high-spin Fe^{III}.

Recent studies have concentrated on the chemistry and electrochemistry of $Fe^{III}(Cl_4SQ)_3$. Electrochemical characterization will be described in detail in a publication to follow, but the

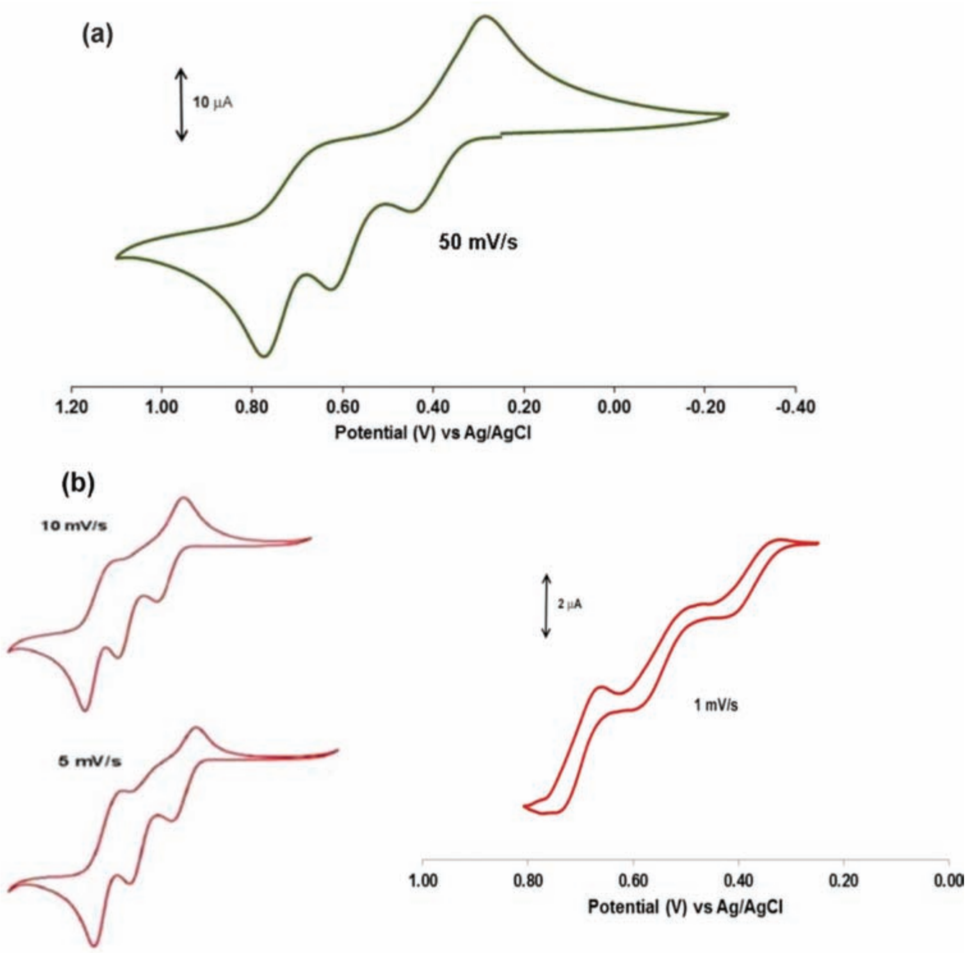


Figure 6. Cyclic voltammograms of $Fe^{III}(Cl_4SQ)_3$ recorded in a methanol solution, containing 0.1 M $(Bu_4N)(PF_6)$ as the electrolyte, showing the scan rate dependence.

result of CV scans at different scan rates is shown in Figure 6. As was observed for the cyclic voltammogram on $[Co^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$, the current for the $Fe^{III}(Cl_4SQ)_3/[Fe^{III}(Cl_4SQ)_2(Cl_4Cat)]^-$ and $[Fe^{III}(Cl_4SQ)_2(Cl_4Cat)]^-/[Fe^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$ reduction steps is unresolved at a scan rate of 50 mV/s; only the current for the final reduction step to $[Fe^{III}(Cl_4Cat)_3]^{3-}$ appears prominently. The oxidation current for the three steps back to $Fe^{III}(Cl_4SQ)_3$ appears normally. Also, as was observed for the cobalt analogue and is shown in Figure 6, at a slow scan rate of 1 mV/s, the three redox steps appear as separate couples with reduced current, as is expected for a diffusion-limited process. A striking feature of the $Fe^{III}(Cl_4SQ)_3/[Fe^{III}(Cl_4Cat)_3]^{3-}$ redox series is the range in the electrochemical potential. Cyclic voltammograms for the series are superimposed on the $Cr^{III}(Cl_4SQ)_3/[Cr^{III}(Cl_4Cat)_3]^{3-}$ series in Figure 7. While the range in potential for the chromium series is roughly 1.0 V, the iron series is considerably more compressed, with the three-electron redox processes taking place within the range of 330 mV. Further, spectral characterization on intermediate species in the redox series, $[Fe^{III}(Cl_4SQ)_2(Cl_4Cat)]^-$ and $[Fe^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$, has failed to show the low-energy Cat → SQ IVCT transitions observed for corresponding members of the Cr^{III} redox series. This had been observed previously for $Fe^{III}(bpy)(3{,}6\text{-}DBSQ)(3{,}6\text{-}DBCat)$, which fails to show an IVCT band in contrast to its Co^{III} analogue, which has an intense IVCT band at 2500 nm.[38,39] In conclusion, it appears that Fe^{III} is much less effective in propagating intramolecular interligand electronic coupling than most other 3d metals. In the case of $Fe(Cl_4SQ)_3$, this results in a four-membered series associated with three reversible redox steps within an unusually narrow range in the electrochemical potential. The chemical consequence of this in multielectron oxidation reactions may be important.

Structural characterization on both $Fe^{III}(Cl_4SQ)_3$ and $[Fe^{III}(Cl_4Cat)_3]^{3-}$, obtained as the $CoCp_2^+$ salt by reduction of the neutral complex with 3 equiv of cobaltocene, has provided a result relevant to the structural features of species containing mixed-charge Cl_4SQ and Cl_4Cat ligands described above with Cr^{III} and Co^{III} (Table 1). In these complex ions, the structural difference between SQ and Cat ligands was far less clear than that found, for example, with $V^V(3{,}6\text{-}DBSQ)(3{,}6\text{-}DBCat)_2$ and $Co(bpy)(3{,}5\text{-}DBSQ)(3{,}5\text{-}DBCat)$.[6,22] Structural characterization on complexes containing Cat ligands generally show C−O bond lengths for the ligands close to the 1.34 Å value, and this has been used as a diagnostic structural feature.[4,40,41] The ligand C−O bond lengths of $[Fe^{III}(Cl_4Cat)_3]^{3-}$ are 1.313(2) Å, in contrast with the 1.349(3) Å length for $[Fe^{III}(Cat)_3]^{3-}$. The reason for this anomaly appears in the contrasting C−Cl bond lengths for

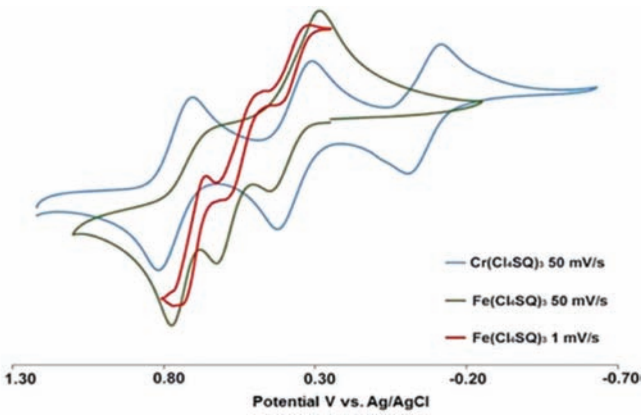


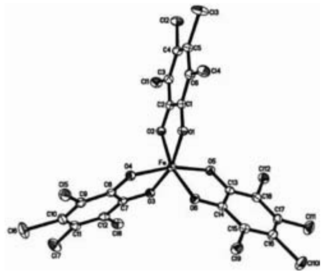
Figure 7. Superposition of cyclic voltammograms of $Cr^{III}(Cl_4SQ)_3$ at 50 mV/s, $Fe^{III}(Cl_4SQ)_3$ at 50 mV/s, and $Fe^{III}(Cl_4SQ)_3$ at 1 mV/s showing the compressed range in potential for the $Fe^{III}(Cl_4SQ)_3/[Fe(Cl_4Cat)_3]^{3-}$ redox series.

$Fe(Cl_4SQ)_3$ and $[Fe^{III}(Cl_4Cat)_3]^{3-}$. Lengths of the C−Cl bonds of $Fe(Cl_4SQ)_3$ are 1.706(2) Å, while for $[Fe^{III}(Cl_4Cat)_3]^{3-}$, the lengths are 1.735(2) Å, indicating significant charge delocalization into the C−Cl bonds. This anomaly does not appear for all structures containing Cl_4Cat ligands. In cases where there is significant Cat → metal π donation, C−O bond lengths conform to the 1.34 Å length with examples that include $[M^{VI}(Cl_4Cat)_3]$ (M = Mo, W) and $Re^{VI}(Cl_4Cat)_3$.[42,43]

SUMMARY

Ligand noninnocence implies a need to define the charge distribution within the metal complex for cases where metal and ligand frontier orbitals are of similar energy. The $[M(Cl_4Q)_3]^{n-}$ redox series of chromium and vanadium, as adjacent metals on the periodic table, are illustrations of noninnocence. Shifts in charge for the vanadium series take place at the metal (eq 2), while for chromium, the metal remains Cr^{III} and the ligands are the centers of the redox activity (eq 1). The electronic structures of intermediate species in the $[Cr^{III}(Cl_4Q)_3]^{n-}$ series, ions containing mixed-charge SQ and Cat ligands, exhibit IVCT transitions and can be analyzed using the Hush relationship to estimate the strength of metal-mediated electronic coupling. This is a clear illustration of charge localization within a complex prepared with oxygen-donor quinone-derived ligands. The $[Mn(Cl_4Q)_3]^{n-}$ redox series is complicated by ligand dissociation to give a $[Mn^{III}(Cl_4Cat)_2]^-$ species. Soper has associated this with O_2 oxidation, but it has also been observed in electrochemical studies carried out under anaerobic conditions. The ligand lability may be associated with the pronounced Jahn−Teller distortion of $3d^4$ Mn^{III}, although a Mn^{II} species formed by intramolecular shifts in charge must also be considered. Manganese(II) species have been characterized for the $Mn^{II}(N{-}N)(SQ)_2$ molecules in equilibrium with $Mn^{III}(N{-}N)(SQ)(Cat)$ and $Mn^{IV}(N{-}N)(Cat)_2$ redox isomers, and oxidation of $[Mn^{III}(3,5\text{-}DBCat)_2]^-$ gives $Mn^{II}(3,5\text{-}DBSQ)_2$ isolated as a tetramer.[44] Studies on the $[Co(Cl_4Q)_3]^{n-}$ series are in a preliminary stage, but isolation of the $[Co^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$ redox isomer as an intermediate in the series suggests similarity with Cr^{III}. The appearance of the cyclic voltammogram for the series is unusually different in failing to show the current for individual reduction steps except at slow scan rates. The origin of this anomaly is unclear, but the cyclic voltammogram of the $[Fe^{III}(Cl_4Q)_3]^{n-}$ series has a similar appearance. At a scan rate of 1 mV/s, separate steps for the reduction of $Fe^{III}(Cl_4SQ)_3$ to $[Fe^{III}(Cl_4Cat)_3]^{3-}$ can be resolved, but three-electron reduction takes place over a narrow range in potential of 330 mV. This is the effect of weak interligand electronic coupling with Fe^{III} and may prove important in multielectron oxidation applications using $Fe^{III}(Cl_4SQ)_3$ as an electrocatalytic oxidant.

Table 1. Bond Lengths (Å) for $Fe^{III}(Cl_4SQ)_3$, $[Fe^{III}(Cl_4Cat)_3]^{3-}$, and $[Fe(Cat)_3]^{3-}$



	$Fe(Cl_4SQ)_3$	$[Fe(Cl_4Cat)_3]^{3-}$	$[Fe(Cat)_3]^{3-}$ [a]
Fe−O	2.019(2)	2.029(1)	2.015(6)
C1−O	1.275(3)	1.313(2)	1.349(3)
C1−C2	1.461(3)	1.433(2)	1.409(6)
C2−C3	1.420(3)	1.393(2)	1.383(2)
C3−C4	1.372(3)	1.404(3)	1.385(4)
C4−C5	1.439(3)	1.380(3)	1.350(9)
C−Cl	1.706(2)	1.735(2)	

[a] From ref 37.

CONCLUSIONS

Within the $[M(Cl_4Q)_3]^{n-}$ redox series for vanadium, chromium, manganese, iron, and cobalt, there are examples of ambiguity in the metal−ligand charge distribution for individual redox products and, in specific cases, dynamic shifts between redox isomers under equilibrium conditions. Jorgensen's view of noninnocence was based mainly on the innocence for ligands of well-defined charge.[2] His sense of noninnocence developed after a conference lecture by Harry Gray on the 1,2-dithiolene complexes and is described in two 1966 publications that followed this lecture.[1a,2,3] Much of the ambiguity in ligand charge for the 1,2-dithiolenes has been associated with metal−ligand orbital mixing, adding complexity to even theoretical models for the dithiolene complexes. With the quinone-derived oxygen-donor ligands, it is rare that ligand charge remains unresolved as SQ or Cat (or, in rare cases, BQ) after thorough analysis, and metal−ligand charge delocalization has a far less significant effect than that for the sulfur analogues.

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REFERENCES

(1) (a) Gray, H. B. *Coord. Chem. Rev.* **1966**, *1*, 156. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (c) Schrauzer, G. N. *Acc. Chem. Res.*

1969, *2*, 72. (d) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295.(e) Dithiolene Chemistry: Synthesis, Properties, and Applications. In *Progress in Inorganic Chemistry*; Stiefel, E. I., Ed.; John Wiley and Sons: Hoboken, NJ, 2004; Vol. 52. (f) Eisenberg, R. *Coord. Chem. Rev.* **2011**, *255*, 825.

(2) Jorgensen, C. K. *Coord. Chem. Rev.* **1966**, *1*, 164.

(3) Jorgensen, C. K. *Struct. Bonding (Berlin)* **1966**, *1*, 234.

(4) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(5) Spikes, G. H.; Sproules, S.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2008**, *47*, 10935.

(6) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.

(7) (a) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1965**, *4*, 55. (b) Wharton, E. J.; McCleverty, J. A. *J. Chem. Soc. A* **1969**, 2258. (c) Banerjee, P.; Sproules, S.; Weyhermüller, T.; DeBeer, S.; Wieghardt, K. *Inorg. Chem.* **2009**, *48*, 5829. (d) Sproules, S.; Weyhermüller, T.; DeBeer, S.; Wieghardt, K. *Inorg. Chem.* **2010**, *49*, 5241.

(8) (a) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Jr. *Chem. Rev.* **2004**, *104*, 939. (b) Hitomi, Y.; Yoshida, M.; Higuchi, M.; Minami, H.; Tanaka, T.; Funabiki, T. *J. Inorg. Biochem.* **2005**, *99*, 755.

(9) (a) Barbaro, P.; Bianchini, C.; Linn, K.; Mealli, C.; Meli, A.; Vizza, F. *Inorg. Chim. Acta* **1992**, *198–200*, 31. (b) Dutta, S.; Peng, S.-M.; Bhattacharya, S. *Inorg. Chem.* **2000**, *39*, 2231.

(10) (a) Cherkasov, V. K.; Abakumov, G. A.; Grunova, E. V.; Poddel'sky, A. I.; Fukin, G. K.; Baranov, E. V.; Kurskii, Y. V.; Abakumova, L. G. *Chem.—Eur. J.* **2006**, *12*, 3916. (b) Fedushkin, I. L.; Nikipelov, A. S.; Lyssenko, K. A. *J. Am. Chem. Soc.* **2010**, *132*, 7874.

(11) (a) Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2005**, *44*, 5559. (b) Blackmore, K. J.; Sly, M. B.; Haneline, M. R.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2008**, *47*, 10522. (c) Nguyen, A. I.; Blackmore, K. J.; Carter, S. M.; Zarkesh, R. A.; Heyduk, A. F. *J. Am. Chem. Soc.* **2009**, *131*, 3307.

(12) Rolle, C. J., III; Hardcastle, K. I.; Soper, J. D. *Inorg. Chem.* **2008**, *47*, 1892.

(13) Haneline, M. R.; Heyduk, A. F. *J. Am. Chem. Soc.* **2006**, *128*, 8410–8411.

(14) Smith, A. L.; Hardcastle, K. I.; Soper, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 14358.

(15) (a) Chirik, P.; Wieghardt, K. *Science* **2010**, *327*, 794. (b) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901. (c) Bowman, A. C.; Milsmann, C.; Atienza, C. C. H.; Lobkovsky, E.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 1676.

(16) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *219–221*, 415.

(17) Downs, H. H.; Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1736.

(18) Buchanan, R. M.; Claflin, J.; Pierpont, C. G. *Inorg. Chem.* **1983**, *22*, 2552.

(19) (a) Chang, H.-C.; Ishii, T.; Kondo, M.; Kitagawa, S. *J. Chem. Soc., Dalton Trans.* **1999**, 2467. (b) Chang, H.-C.; Miyasaka, H.; Kitagawa, S. *Inorg. Chem.* **2001**, *40*, 146. (c) Chang, H.-C.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 130.

(20) Kitagawa, S.; Chang, H.-C. In *Inorganic Chromotropism. Basic Concepts and Applications of Colored Materials*; Fukuda, Y., Ed.; Kodansha Springer: Tokyo, Japan, 2007; p 337.

(21) (a) Cass, M. E.; Gordon, N. R.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3962. (b) Simpson, C. L.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 4308.

(22) Morris, A. M.; Pierpont, C. G.; Finke, R. G. *Inorg. Chem.* **2009**, *48*, 3496.

(23) Sproules, S.; Weyhermüller, T.; DeBeer, S.; Wieghardt, K. *Inorg. Chem.* **2010**, *49*, 5241.

(24) Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092.

(25) (a) Sheriff, T. S.; Carr, P.; Coles, S. J.; Hursthouse, M. B.; Lesin, J.; Light, M. E. *Inorg. Chim. Acta* **2004**, *357*, 2494. (b) Ruiz, R.; Caneschi, A.; Gatteschi, D.; Sangregorio, C.; Sorace, L.; Vazquez, M. *Inorg. Chem. Commun.* **2000**, *3*, 76.

(26) Rolle, C. J., III; Hardcastle, K. I.; Soper, J. D. *Inorg. Chem.* **2008**, *47*, 1892.

(27) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1998**, *37*, 3051.

(28) (a) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1981**, *103*, 3961. (b) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041.

(29) Chin, D.-H.; Sawyer, D. T.; Schaefer, W. P.; Simmons, C. J. *Inorg. Chem.* **1983**, *22*, 752.

(30) Lange, C. W.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 1276.

(31) Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439.

(32) Verani, C. N.; Gallert, S.; Bill, E.; Weyhermüller, T.; Wieghardt, K.; Chaudhuri, P. *Chem. Commun.* **1999**, 1747.

(33) Palit, C. M.; Boles, K.; Kelly, J.; Pierpont, C. G. Manuscript in preparation.

(34) (a) Buchanan, R. M.; Downs, H. H.; Shorthill, W. B.; Pierpont, C. G.; Kessel, S. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 4318. (b) Buchanan., R. M.; Kessel, S. L.; Downs, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894.

(35) Attia, A. S.; Conklin, B. J.; Lange, C. W.; Pierpont, C. G. *Inorg. Chem.* **1996**, *35*, 1033.

(36) Kelly, J.; Hawkey, N.; Nelson, P.; Pierpont, C. G. Submitted for publication.

(37) Raymond, K. N.; Isied, S. S.; Brown, L. D.; Fronczek, F. R.; Nibert, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 1767.

(38) Attia, A. S.; Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1995**, *34*, 4427.

(39) Jung, O.-S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227.

(40) Bhattacharya, S.; Gupta, P.; Basuli, F.; Pierpont, C. G. *Inorg. Chem.* **2002**, *41*, 5810.

(41) Ray, K.; Weyhermüller, T.; Goossens, A.; Craje, M. W.; Wieghardt, K. *Inorg. Chem.* **2003**, *42*, 4082.

(42) (a) Pierpont, C. G.; Downs, H. H. *J. Am. Chem. Soc.* **1975**, *97*, 2123. (b) deLearie, L. A.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1988**, *27*, 3842.

(43) deLearie, L. A.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 817.

(44) (a) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1995**, *34*, 1172. (b) Caneschi, A.; Dei, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 3005. (c) Kiriya, D.; Nakamura, K.; Chang, H.-C.; Kitagawa, S. *Chem. Commun.* **2009**, 4085.