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Redox Isomerism for Quinone Complexes of Chromium and Chromium Oxidation State Assignment from X-ray Absorption Spectroscopy

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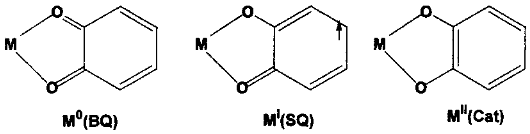
Complexes consisting of redox active metal ions coordinated by one or more ligands that may exist in different charged states offer the potential for redox isomerism. Redox isomers differ in the distribution of charge between electronic levels that remain localized on either metal or ligand in the electronic structure of the complex. Complexes prepared from the ortho-quinone ligands are of recent interest as examples of ambiguous charge distribution.[1] Three isomeric structures may be envisioned for the metal−quinone chelate ring; these are related by successive metal−ligand electron-transfer steps.



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Charge distribution within the chelate ring may be directed by the bonding properties of ancillary ligands also coordinated to the metal and the influence of quinone ligand substituents. Under appropriate thermodynamic conditions, equilibria between redox isomers may be observed, and electrochemical redox processes may take place selectively at either the ligand or metal ion.[2] In cases where orbital mixing is significant, charge delocalization within the chelate ring obscures assignment of the metal and ligand charge. The more highly oxidized complexes of the 1,2-dithiolate/1,2-dithiolene ligands illustrate this feature of electronic structure.[3] A number of probes are available for assessing charge distribution, localized or delocalized, and for making localized charge assignments. Magnetic properties have been particularly helpful in providing insight on charge distribution. Observations on magnetic exchange between radical semiquinonate ligands and paramagnetic metal ions may point to a unique metal spin state.[4] EPR spectra provide information on spin localization, metal or ligand, and on the possibility of spin delocalization over both ligand and metal. For complexes containing localized mixed-charge semiquinonate (SQ) and catecholate (Cat) ligands, intense LL'CT electronic transitions appear in the near infrared.

The reaction between an *o*-benzoquinone and $Cr(CO)_6$ has been reported to give tris(quinone) complexes of general form CrQ_3.[5,6] The view of these complexes as consisting of radical SQ ligands coordinated to Cr(III), $Cr^{III}(SQ^{\bullet})_3$, is based on observations of weak residual paramagnetism and structural features. Radical ligand spins couple antiferromagnetically with metal dπ ($t_{2g}{}^3$) electrons to give temperature-dependent magnetic moments for the molecules that are typically less than 1.0 μ_B.[5,7,8] Mössbauer spectra recorded on the related complexes of iron, $Fe^{III}(SQ^{\bullet})_3$, verify that the metal ion is in the form of high-spin Fe(III) and that temperature-dependent magnetic properties result from similar metal−radical magnetic exchange.[9]

Electrochemical characterization of members of the $Cr^{III}(SQ)_3$ series have shown three-membered oxidation and reduction series. The range of redox potentials is dependent upon quinone substituent effects. This, with other structural, magnetic, and spectral properties obtained for various members of the redox series, has led to the view that the redox couples are ligand based, with the metal remaining in the form of Cr(III) through the series (2).[6,10]

$$[Cr^{III}(BQ)_3]^{3+} \underset{}{\overset{e^-}{\rightleftharpoons}} [Cr^{III}(BQ)_2(SQ)]^{2+} \overset{e^-}{\rightleftharpoons} [Cr^{III}(BQ)(SQ)_2]^{+} \overset{e^-}{\rightleftharpoons} Cr^{III}(SQ)_3$$

$$Cr^{III}(SQ)_3 \overset{e^-}{\rightleftharpoons} [Cr^{III}(SQ)_2(Cat)]^{-} \overset{e^-}{\rightleftharpoons} [Cr^{III}(SQ)(Cat)_2]^{2-} \overset{e^-}{\rightleftharpoons} [Cr^{III}(Cat)_3]^{3-} \quad (2)$$

Structural characterization of members of the reduction series support this view of localized charge distribution. Metal−oxygen bond lengths are typical of Cr(III), and structural features of the quinone ligands support the catecholate and semiquinonate charges of $[Cr^{III}(Cat)_3]^{3-}$, $Cr^{III}(Cl_4SQ)_3$, and Cr^{III}(3,5-DBSQ)$_3$.[6,11,12] Semiquinonate features include C−O bond lengths of 1.29 Å, intermediate between catecholate (1.34 Å) and unreduced benzoquinone (1.23 Å) values, and a pattern of ring C−C lengths that shows slight contraction at positions that would contain double bonds for the BQ form of the ligand. The correlation between structure and ligand charge has been confirmed by Carrugo in a 1992 survey of complexes containing quinone ligands,[13] and by the results of many subsequent structural studies.[1,2,4] Intermediate members of the redox series with charges of −1 and −2 are viewed as Cr(III) complexes containing mixed-charge SQ and Cat ligands.[7,14] Strong antiferromagnetic coupling between radical SQ ligands and the $S = 3/2$ Cr(III) ion results in $S = 1/2$ and 1 spin ground states for the $[Cr^{III}(SQ)_2(Cat)]^-$ and $[Cr^{III}(SQ)(Cat)_2]^{2-}$ ions, respectively. These conclusions have been confirmed recently in a report on the magnetic, structural, and spectral properties of complexes containing the $[Cr^{III}(X_4SQ)_2(X_4Cat)]^-$ and

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$[Cr^{III}(X_4SQ)(X_4Cat)_2]^{2-}$ (X = Cl, Br) anions.[7] These ions typically show intense electronic transitions in the 4000−5000 cm^{-1} region of the NIR that have been assigned as LL'CT bands between the mixed-charge SQ and Cat ligands.

It was surprising to see a recent report on the electronic structure of "$K[Cr(3,5\text{-}DBQ)_3]$" which concluded that the metal is Cr(V) and the ligands are catecholate, $K[Cr^{V}(3,5\text{-}DBCat)_3]$.[15] This view was based on the position and intensity of the Cr K-edge and pre-edge peaks in the X-ray absorption spectrum. Other features of the complex anion that were given in support of this charge assignment include the narrow line width of the EPR spectra of both the −1 and +1 ions, which is atypical of $S = 3/2$ Cr(III) species and more similar to d^1 Cr(V), and a pattern of structural features that have been interpreted as reflecting increased π donation to the metal with oxidation of the complex from the −3 trianion to the neutral members of the series. Detailed ligand structural features derived from a multiple-scattering model gave semiquinone-like values for the bond lengths of $K[Cr^{V}(3,5\text{-}DBCat)_3]$ in agreement with structures reported by Kitagawa.[7] However, in Lay's report, these values are viewed as resulting from strong π donation from Cat ligands to the high oxidation state metal ion. This latter point discredits the notion that ligand charge can be deduced from a consistent set of structural features. In this view, quinone ligands of all complexes may be considered to be catecholate, with structural differences arising from varying degrees of π donation to the metal.

EPR spectra for both the $[Cr^{III}(SQ)_2(Cat)]^-$ and $[Cr^{III}(SQ)_2(BQ)]^+$ redox isomers are associated with $S = 1/2$ spin ground states.[7,14] Recent magnetic measurements on the $[Cr^{III}(X_4SQ)_2(X_4Cat)]^-$ anions confirm this result,[7] and there is no reason to expect that EPR spectra should show the broadening commonly observed for $S = 3/2$ Cr(III) species. Spectra obtained on both the cation and anion show exceptionally strong ^{53}Cr hyperfine coupling, pointing to spin localization on the metal and, specifically, partial population of a metal d level of a_1 symmetry in the Gordon and Fenske molecular orbital model.[14,16] Consequently, it is not surprising that sharp EPR signals are observed for the anions in either the $[Cr^{III}(SQ)_2(Cat)]^-$ or $[Cr^{V}(Cat)_3]^-$ charge distributions.

With regard to the claim that strong π donation results in semiquinonate-like structural features for the quinone ligands, it is instructive to look at the features of complex molecules and ions where high oxidation state metals are stabilized by strong catecholate donation. The structures of $[V^{IV}(Cat)_3]^{2-}$, formally isoelectronic with the chromium monoanion, and d^0 $[V^{V}(3,5\text{-}DBCat)_3]^-$ have appeared and clearly show the expected catecholate features for the ligands.[17,18] Similarly, the $[M^{VI}(Cl_4Cat)_3]_2$ (M = Mo, W) dimers have been reported. Lengths between the metals and oxygen atoms of bridging ligands are quite short, due to strong π donation, and yet the ligands retain their catecholate structure.[1,19] There is no structural evidence suggesting that strong catecholate π donation leads to contracted C−O lengths or SQ-like features. Further, features of the catecholate ligand of the strongly nucleophilic $[Mn(CO)_3(3,5\text{-}DBCat)]^-$ anion, as an example of a case where π donation contributes little to metal coordination, are no different from those of the V(V) and Mo(VI) complexes.[20] Among the complexes cited in support of the claim of contracted Cr−O lengths with complex oxidation, $[Cr^{III}(Cat)_3]^{3-}$ (Cr−O 1.986(9) Å)[11] has lengths longer than $[Cr^{III}(Br_4SQ)(Br_4Cat)_2]^{2-}$ (1.943(6) Å), $[Cr^{III}(Cl_4SQ)_2(Cl_4Cat)]^-$ (1.941(2)), $Cr^{III}(Cl_4SQ)_3$ (1.949(7) Å), and $Cr^{III}(3,5\text{-}DBSQ)_3$ (1.933(8) Å), Cr−O bond lengths that are, within error, the same.[6,7,12] The crystal structure of $K_3[Cr^{III}(Cat)_3]$ shows potassium cations located at sites close to the chelated catecholate oxygens.[11] The presence of strong K−O interactions serves to lengthen the Cr−O bonds over values that would be normal for Cr(III). Values of 1.910(4) Å reported by McCusker for the $Cr^{III}-O^{Cat}$ lengths of $[Cr^{III}(tren)(3,6\text{-}DBCat)]^+$ are more representative and show little change with ligand oxidation to $[Cr^{III}(tren)(3,6\text{-}DBSQ)]^{+2}$ (1.919(4) Å).[21] Consequently, the lengthening of Cr−O lengths with complex oxidation observed by Lay appears only for $K_3[Cr^{III}(Cat)_3]$, and in this case, it is the consequence of strong cation bonding. Lengths for the series of complexes ranging in charge from −2 to 0 are essentially constant as would be expected for a ligand-based redox series with the metal remaining as Cr(III). Taken together, the structural, spectral, and magnetic properties of the $[Cr^{III}(SQ)_2(Cat)]^-$ and $[Cr^{III}(SQ)(Cat)_2]^{-2}$ anions, the neutral $Cr^{III}(SQ)_3$ molecules, the $[Cr^{III}(SQ)_2(BQ)]^+$ cations, and the other members of the redox series all point uniquely to ligand-based redox processes with the metal remaining as Cr(III) throughout the series (2). It is further relevant to examine Cr−O lengths in complexes of Cr(V). Few structure determinations have appeared for the metal in this oxidation state, but Lay has reported the characterization of the $[CrO(ehba)_2]^-$ anion.[22] Bond lengths to the metal are 1.547(5) Å for the oxo ligand, 1.793(3) Å for alkoxide oxygens, and 1.903(3) Å for carboxylate oxygens. As expected, all lengths are significantly shorter than values that appear for the SQ and Cat complexes.

Lay's optimized multiple-scattering model gave features for the inner coordination sphere that agree reasonably well with the crystallographic structure determinations on the monoanions. Multiple scattering may be used to obtain reasonable structural features, but their comparative interpretation of K-edge and pre-edge energies in this case has led to an unreasonable assignment for metal oxidation state. The example of Cr(V), $[CrO(ehba)_2]^-$, used in their analysis contains oxo and alkoxo ligands, both strong σ and π donor ligands. It is more reasonable to assume that strong donation from the oxygens of these ligands contributes to an apparently lower charge for the Cr of $[CrO(ehba)_2]^-$ than to view members of the $[Cr(Q)_3]^n$ series as containing metal ions of a charge that is inconsistent with the results of all other structural, spectral, and magnetic characterization on the compounds.

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