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Communications

Induced Electron Transfer in Ammineruthenium Catechol and Quinone Complexes

Sir:

Metal–catechol complexes often exhibit unusual electronic effects due to the ability of both the ligand and metal ion to undergo electron transfer[1-4] and are of major interest since such systems represent models for the biological transport of iron,[3,4] for some enzymes,[5] and for the primary photoelectron donor–acceptor center in bacterial photosynthesis.[6] They may also serve as models for the metal ion interactions with ascorbate in the Udenfriend system and ascorbate oxidase.[7,8]

Complexes derived from catechol (Cat), 2,3-dihydroxynaphthalene (DHN), 3,4-dihydroxybenzoic acid (DHB), and 3-(3,4-dihydroxyphenyl)propanoic acid (DPP) were characterized in solution and as solids. In general, these complexes could be synthesized by heating $[(NH_3)_6Ru]^{3+}$, $[Cl(NH_3)_5Ru]^{2+}$, or *cis*-$[Cl_2(NH_3)_4Ru]^+$ together with the appropriate catechol in aqueous solution adjusted to pH $\simeq$9.5. Regardless of the starting complex ion, the major product obtained (as isolated by ion-exchange chromatography on a carboxylate resin eluted with ammonium formate) was generally the same for reactions run with a given ligand. Elemental analyses of these compounds are consistent with the formulation *cis*-$[L(NH_3)_4Ru]X$, where L is the catechol ligand and X is the counterion (if any). Purity was further verified by a sensitive HPLC method[9] before characterization. When allowed to stand at acidic pH, these complexes generally autooxidize to a magneta-colored species, which often reverts to the reduced form at higher pH. Heating in 1–6 M HCl results in *cis*-$[Cl_2(NH_3)_4Ru]^+$, and variations of this reaction allow for facile syntheses of *cis*-$[X_2(NH_3)_4Ru]^+$, where X = various acido ligands. Titration of the blue catecholato complex to the magenta form with $[IrCl_6]^{2-}$ was complete upon the addition of 1 equiv of the oxidant.

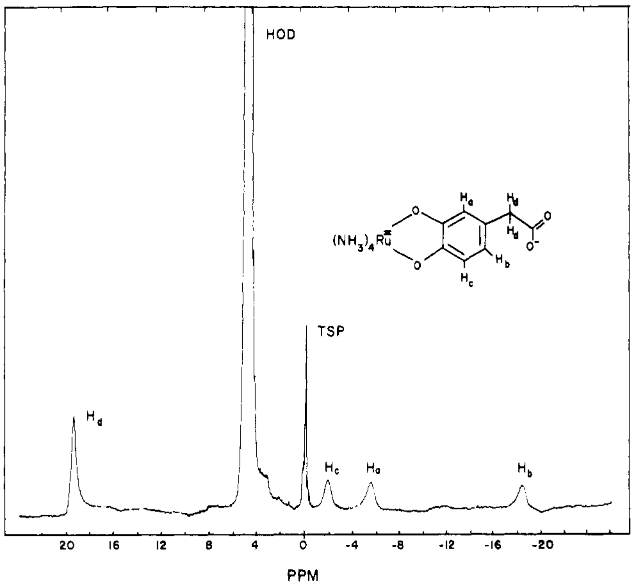

Figure 1. ^1H NMR spectrum of (2-(3,4-dihydroxyphenyl)ethanoato)tetraammineruthenium(III) in D_2O at pD 9.05 (uncorrected) with sodium trimethylsilylpropionate as the reference standard. Peak assignments were made by reference to spectra of the analogous 3-methyl- and 4-methylcatecholato complexes; however, assignments of the two ortho protons remain tentative.

Magnetic moments of the blue complexes (1.52–1.68 μ_B) are well within the range expected for a single, unpaired electron on a low-spin d^5 metal ion. EPR of the DHB complex in a water/glycerol (1:1) glass at −77 °C yielded a spectrum of axial symmetry with $g_\perp = 2.722$ and $g_\parallel = 1.889$, which indicates the unpaired electron to be largely localized on the Ru(III) ion.[11-13]

The FT ^1H NMR spectrum of the catecholato complex revealed two peaks at −3.85 and −16.4 ppm relative to TSP at pD 6.3.[10] The equivalency of the two adjacent and two distal protons confirms these to be catecholato chelates, and their extreme upfield shifts are consistent with proximity to Ru(III).[5,11-14] The spectrum of the (3,4-dihydroxyphenyl)acetate complex shown in Figure 1 is typical in showing the ring protons to be shifted substantially upfield, while those

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(10) ^1H NMR data were obtained in D_2O on a Varian FT-80 at 37 °C: filter bandwidth 8000 Hz; spectral width 8065 Hz; usually with 600–1000 transients collected with an individual acquisition time of 0.507 s and a pulse delay of 7 s; concentrations 10–20 mM.

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displaced from the catechol plane appear markedly downfield. Comparison of these peak positions with those of the catecholato complex points out the large shifts resulting from ring substitution. Protonation of this complex at pD 2.33 has little effect on the resonance at −5.54 ppm but causes the other three resonances to occur at −3.02, −15.9, and 17.3 ppm. Since small quantities of the magenta forms of these complexes may occur upon standing, an additional redox equilibrium parameter can be easily introduced.

Cyclic voltammetry on all but the DHN complex revealed a single, chemically reversible electrochemical couple occurring in the range 350–650 mV (vs. NHE), when the system is scanned either cathodically or anodically. Separations between the anodic and cathodic peaks were generally similar to those observed for the reversible $(NH_3)_6Ru^{III/II}$ couple, which was used as an internal standard in aqueous solutions adjusted to an ionic strength of 0.1 with LiCl, and approach that for an electrochemically reversible couple ($\Delta E_{pc,pa} = 59$ mV) at slow scan rates. Autooxidation experiments done over a period of 10 min at pH 2 resulted in 20% decomposition during the oxidation or subsequent re-reduction at neutral pH. Plots of E_h vs. pH for the Ru(III) diolato complexes of DHB and DPP exhibited pH-dependent regions of 59 mV/pH unit (consistent with a 1e–1H$^+$ oxidation) and yielded pK_a values of 4.6 and 4.15 (verified by absorbance vs. pH measurements) for the two complexes, respectively.[15] From this it can be estimated that the Ru(III) ion increases the acidity of the carboxyl group by approximately 1 order of magnitude.[16] pK_a values of these two oxidized complexes as determined from E_h–pH plots are 3.3 and 3.7, respectively.[15]

^{1}H NMR studies on the magenta forms are similar to those encountered for diamagnetic complexes with some broadening resulting from the Ru(II) nuclear spin. Magnetic susceptibility studies by both the Evans and the Faraday methods and the complete absence of an ESR signal indicate the oxidized complexes to be diamagnetic Ru(II) complexes. An alternative explanation for the diamagnetism of the 1e-oxidized complexes is that they contain Ru(III) coordinated to the catecholato semiquinone anion. The lack of paramagnetism would then be attributed to antiferromagnetic coupling between ligand and metal portions of the diradical. While this sort of interaction appears to occur with some first-row transition-metal ions,[2] it is unlikely in the case of ruthenium. Reasons for this are as follows: (1) the relative oxidation and reduction potentials of the *o*-semiquinone anion radical and $[(H_2O)_2(NH_3)_4Ru^{III}]^{3+}$ are approximately 230 and 109 mV, respectively,[20,21] so that metal ion oxidation of the semiquinone should be greatly favored; (2) Ru(II) complexes are known to be greatly stabilized with π-acceptor quinone ligands;[22] (3) the oxidized species exhibit carbonyl stretching frequencies (at 1630–1640 cm^{-1}), which are only 20–50 cm^{-1} lower than those exhibited by the free quinone ligands. While the first two arguments are admittedly circumstantial, the final one is compelling. Lowering of the carbonyl stretching frequencies is consistent with retrodative bonding between a metal ion d_π orbital and the lowest unoccupied π^* orbital on the ligand. Therefore, the oxidized forms of these complexes are best formulated as Ru(II) complexes of *o*-quinones.

Since only one electron is extracted from the blue Ru(III) complexes by external oxidizing agents, a second electron must be transferred intramolecularly to yield a Ru(II) species containing *o*-benzoquinone ligands. As such, these represent the first *o*-benzoquinone complexes that are stable in aqueous solution for extended periods.[2] Dissociation of the oxidized complexes to yield *cis*-$(H_2O)_2(NH_3)_4Ru^{II}$ and the reduced species to yield free catechols upon large pH changes accounts for the observed reversion to the blue forms at higher pH, since these species are capable of reducing the *o*-benzoquinone complexes in basic media.

Since chelation eliminates the requirement for proton transfer to the quinone oxygens upon reduction of simple 1,2-benzoquinone complexes, reductions of the Cat and DHN complexes are independent of pH.[17,18] While the presence of metal ions generally stabilizes the *semiquinone* form and so facilitates the addition of the first electron to *o*-benzoquinones,[20] stabilization of *quinone* species by retrodative bonding from $(NH_3)_4Ru^{II}$ has previously been observed with flavins and *o*-benzoquinone mono- and diimine ligands.[19,22,23] The presence of a visible charge-transfer band (~520 nm) is also consistent with retrodative bonding, which joined with the normal substitution inertness of Ru(II) is probably responsible for the unusual stability of these complexes.

The Ru(III) diolato complexes exhibit intense absorbances at substantially lower energies (610–675 nm) than the corresponding oxalato or carboxylato complexes.[24] Since these transitions shift toward lower energy with decreasing oxidation potential for a series of ligands or with deprotonation of a given ligand, they can be assigned to a ligand to metal charge transfer, which probably arises from a $\pi \rightarrow d_\pi$ electronic transition.

The spectroscopic and electrochemical similarities between the catecholato complexes and new Ru(III) ascorbato complexes now under investigation[8] suggest that the former are good models for the latter and that 1e transfer from these complexes is also likely. Analogous complexes with the catecholamine family of neurotransmitters also provide for reversible, 1e oxidation at potentials similar to those of the free ligands at neutral pH.[8] Finally, the facility with which catecholate displaces ammines from the metal ion lends credence to the suggestion that transferrin plays an important role in the biodistribution of some ruthenium chemotherapeutic and radiodiagnostic agents.[25]

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Registry No. $[(Cat)(NH_3)_4Ru]Br$, 88288-70-4; $[(DHN)(NH_3)_4Ru]Br$, 88288-71-5; $[(DHB)(NH_3)_4Ru]$, 88288-72-6; [(DP-

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(15) The NLIN procedure of SAS statistical analysis program (SAS Instruments, Cary, NC) was used to fit reduction potential data as a function of pH according to the following equation: $E_h = E° - (RT/nF) \ln\{([H^+] + K_1)/([H^+] + K_2)\}$, where E_h is the potential at a given pH, K_1 is the proton ionization constant for the magenta form, and K_2 is that for the blue form.

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P)$(NH_3)_4$Ru], 88288-73-7; [(1,2-benzoquinone)$(NH_3)_4Ru^{II}]^{2+}$, 88288-74-8; [(DHB)$(NH_3)_4Ru^{III}]^+$, 88288-77-1; [$(DHB^-)(NH_3)_4Ru^{III}$], 88288-75-9; $[(NH_3)_6Ru]^{3+}$, 18943-33-4; $[Cl(NH_3)_5Ru]^{2+}$, 21560-19-0; *cis*-$[Cl_2(NH_3)_4Ru]^+$, 25604-36-8; (2-(3,4-dihydroxyphenyl)ethanoato)tetraammineruthenium(III), 88288-76-0.

Supplementary Material Available: Listings of elemental analyses and representative UV-vis spectral data (1 page). Ordering information is given on any current masthead page.

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Articles

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Osmium(V): Synthesis, Characterization, and Spectral Examination of Hexahalogeno Complexes

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Two new complex ions of osmium(V), $OsCl_6^-$ and $OsBr_6^-$, have been generated by oxidation in acidic acetonitrile with PbO_2 of the corresponding hexahalogenoosmate(IV) complex ions. The very stable $(Ph_4P)OsCl_6$ salt has been isolated and fully characterized. The $OsCl_6^-$ ion was found to be substitution inert and behaved as a potent one-electron oxidant. Its solution d-d spectral properties indicate a very low nephelauxetic ratio, β_{55}, and a correspondingly high covalency must be attributed to the complex. Examination of its ligand to metal charge-transfer spectrum has led to the reinstatement of Jørgensen's selection rule based on *j-j* coupling in modified form for $5d^3$ ions. The major features of the charge-transfer spectrum were predicted by using a single energy variable, representing the lowest energy Laporte-allowed transition, by mapping onto the d-d spectrum of the $5d^4$ $OsCl_6^{2-}$ ion. The optical electronegativity of Os(V) was found to be 2.45. The charge-transfer spectrum of the less stable $OsBr_6^-$ confirmed the selection rule and optical electronegativity for Os(V). This complex decomposed by a redox process in acetonitrile to afford the $[OsBr_5(NCCH_3)]^-$ ion.

Introduction

The chemistry of osmium in the V oxidation state has not been extensively studied, and only a handful of well-characterized compounds have been reported.[1] Information about such important properties as substitution rates, redox behavior, precise bond lengths, and electronic structure is very limited. The literature preparative routes to Os(V) are challenging at best. Reaction of $F_2(g)$ with osmium metal affords OsF_6, which may be used as a synthetic intermediate. Reduction of the hexafluoride with Si formed OsF_5, and the recently reported osmium pentachloride dimer, Os_2Cl_{10}, has been obtained from reaction of OsF_6 with BCl_3.[2-4] Alternatively, $OsCl_4$ may be oxidized to the OsF_6^- ion by treatment with BrF_3.[5] Most of the Os(V) complexes are prone to hydrolysis and decompose either by disproportionation or oxidation of water, so that handling of the compounds has also hindered the development of the chemistry of Os(V). This has led to the generally accepted belief that this oxidation state is inherently unstable.[6]

Although the spectral properties of hexahalogeno transition-metal complexes have been well studied, there still remain unresolved issues. In particular, the ligand to metal charge-transfer selection rules for metals with strong spin-orbit coupling are unclear. Jørgensen has suggested that the similarity of charge-transfer spectra of $5d^4$ and $5d^5$ ions may be the result of *j-j* coupling in the charge-transfer state.[7] On the other hand, it has been pointed out that a pure electrostatic limit also yields only one term for the excited state.[8] For $5d^3$ ions it was necessary to introduce both electrostatic and spin-orbit influences to rationalize the spectral properties of the Re^{4+} ion in cubic chloride and bromide host crystals. However, the transitions for Re^{4+} that could give insight to the selection rule dilemma are expected to occur in inaccessible or cluttered high-energy regions.[8-10]

Herein is reported the facile, bench-top synthesis of the stable $OsCl_6^-$ complex ion and its less stable bromo analogue. The chloro complex is particularly suited for study of the $5d^3$ charge-transfer bands because of their low energy and the availability of extensive information about the electronic structure of the one-electron-reduced $OsCl_6^{2-}$ ion. A previous claim[11] has been made for the pulse radiolytic generation of the $OsCl_6^-$ ion with Cl_2^-; however, the reported spectrum differs substantially from the findings here. A single-crystal X-ray structural determination has been carried out on $(Ph_4P)OsCl_6$ and will be reported subsequently.[12]

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