Inorg. Chem. **1995,** *34,* 4281−4283

Thermodynamic Parameters for Cobalt−Quinone Electron Transfer and Spin Transition Steps of the $Co^{III}(bpy)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)/Co^{II}(bpy)(3,5\text{-}DBSQ)_2$ Valence Tautomeric Equilibrium

Cortlandt G. Pierpont* and Ok-Sang Jung[†]

Department of Chemistry and Biochemistry,
University of Colorado, Boulder, Colorado 80309

Received January 5, 1995

Introduction

Complexes that combine quinone ligands with transition metal ions that typically have two or three readily accessible oxidation states have been observed to show metal−quinone electron transfer reactions at unusually low energies.[1] Cobalt and quinone electronic levels remain essentially localized in the electronic structure of members of the Co(N-N)(DBQ)$_2$ series, where DBQ is the semiquinonate or catecholate form of either 3,5- or 3,6-di-*tert*-butyl-1,2-benzoquinone.[2] Qualitatively, the balance of electronic levels is similar to that in $Ru^{II}(bpy)_3^{2+}$, where light excitation results in an intramolecular shift in charge distribution to $Ru^{III}(bpy)_2(bpy^{\bullet -})^{2+}$. With quinone ligands the separation between cobalt and quinone π levels is such that redox isomers differing in charge distribution may be observed in thermal equilibrium (eq 1).[2] With this comes the unique

$$Co^{III}(N\text{-}N)(DBSQ)(DBCat) \rightleftharpoons Co^{II}(N\text{-}N)(DBSQ)_2 \quad (1)$$

opportunity for study of metal−ligand electron transfer under equilibrium conditions. Further, since the complexes that show this effect exhibit changes in charge distribution in the solid state as well as in solution, electron transfer reactions can be studied in both media.

Experimental Section

Co(bpy)(3,5-DBSQ)(3,5-DBCat) was prepared by procedures described previously.[2a] Equilibrium measurements in toluene solution were made using a Perkin-Elmer Lambda 9 spectrophotometer equipped with a RMC-Cryosystems cryostat.

Results and Discussion

The equilibrium shown in eq 1 was first observed for a complex prepared with 2,2′-bipyridine (bpy).[2a] Characteristic electronic spectra may be observed for the $Co^{III}(bpy)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)$ and $Co^{II}(bpy)(3,5\text{-}DBSQ)_2$ redox isomers in solution, and shifts in band intensity have been used to determine constants for the tautomeric equilibrium in toluene at several temperatures.[2c] Magnetic properties of the two isomers differ with the change in metal ion charge and spin state. The low-spin Co^{III} form has a single unpaired electron on the radical SQ ligand; the high-spin Co^{II} isomer exhibits more complicated behavior due to magnetic coupling between the $S = {}^3/_2$ metal ion and the two radical ligands. Magnetic measurements carried out in toluene-d_8 solution and on solid samples indicate that $Co^{II}(bpy)(3,5\text{-}DBSQ)_2$ has a magnetic moment of 4.33(2) μ_B. Changes in magnetism recorded in solution at different temperatures for the Co(III)/Co(II) equilibrium follow changes in electronic spectra. The results of both solution measurements have been used to calculate values for ΔG, and the plot shown in Figure 1 has been used to determine values for ΔH and ΔS of 33.9(1) kJ mol^{-1} and 124(1) J mol^{-1} deg^{-1}.[3] Both thermodynamic parameters contain contributions from solvation effects, but given the structural features of the molecule, contributions to both ΔH and ΔS in toluene should be small.[4] High-spin Co(II) has Co−N and Co−O bond lengths that are typically 0.2 Å longer than corresponding lengths of low-spin Co(III) due the presence of electrons in antibonding dσ orbitals.[2] Structural features of complex molecules with the $Co^{III}(N\text{-}N)(SQ)(Cat)$ and $Co^{II}(N\text{-}N)(SQ)_2$ charge distributions show this difference, and light-induced shifts in charge distribution have used the associated change in molecular volume to produce photomechanical effects in the solid state.[2d,5] Smaller changes in C−O and C−C lengths occur for the quinone ligand, and the enthalpy change associated with the equilibrium reflects the collective differences in metal and quinone bond energies that occur with electron transfer and spin transition.

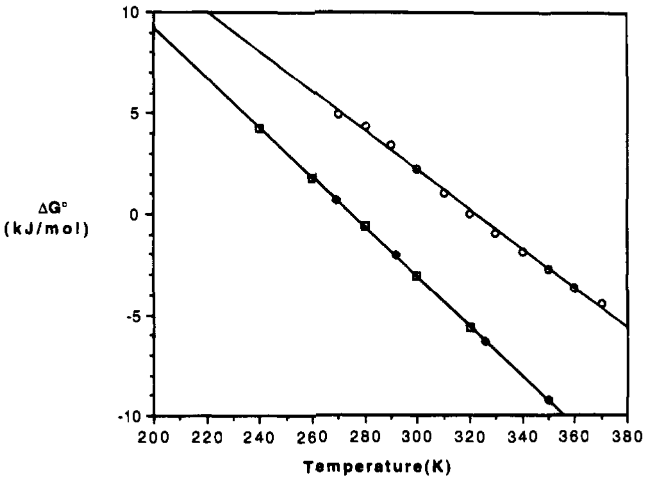

Figure 1. Plots of ΔG vs T for the Co(III)/Co(II) equilibrium described in eq 1 for Co(bpy)(3,5-DBQ)$_2$. Measurements made in toluene solution were obtained from changes in either magnetic moment (◆) or optical band intensities (□). Magnetic measurements were used to obtain relative concentrations of Co(III) and Co(II) isomers in a solid microcrystalline sample (○).

Entropy changes (ΔS_{rc}) of Co(III/II) redox reactions are typically large, and contributions from solvation are often

---

[†] Permanent address: Korea Institute of Science and Technology, Cheongryang, Seoul, Korea.

(1) (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45. (b) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1993**, *41*, 381.

(2) (a) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951. (b) Jung, O.-S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 1127. (c) Jung, O.-S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227. (d) Abakumov, G. A.; Cherkasov, V. K.; Bubnov, M. P.; Ellert, O. G.; Dobrokhotova, Z. B.; Zakharov, L. N.; Struchkov, Y. T. *Dokl. Akad. Nauk SSSR* **1993**, *328*, 12. (e) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 8221. (f) Attia, A. S.; Jung, O.-S.; Pierpont, C. G. *Inorg. Chim. Acta* **1994**, *226*, 91.

(3) Relative concentrations of $Co^{III}(bpy)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)$ and $Co^{II}(bpy)(3,5\text{-}DBSQ)_2$ were calculated from magnetic data using the relationship $\mu_{meas}{}^2 = (\mu_{Co(III)})^2\chi_{Co(III)} + (\mu_{Co(II)})^2(1 - \chi_{Co(III)})$ where $\mu_{Co(III)} = 1.73\ \mu_B$, $\mu_{Co(II)} = 4.33\ \mu_B$, and $\chi_{Co(III)}$ is the mole fraction of $Co^{III}(bpy)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)$. Relative concentrations of the two complexes present in toluene solution at various temperatures were determined by monitoring changes in spectral intensity at 580 nm for $Co^{III}(bpy)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)$ and 810 nm for $Co^{II}(bpy)(3,5\text{-}DBSQ)_2$.

(4) Samples of Co(bpy)(3,5-DBSQ)(3,5-DBCat) obtained from toluene solution were found to contain a toluene solvate molecule well-separated from the complex molecule.[2a] Solvent interactions in toluene are effectively blocked by the quinone *tert*-butyl substituents, and solvation effects are weak.

(5) Jung, O.-S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 2229.

0020-1669/95/1334-4281$09.00/0

significant.[6] Recent efforts have attempted to separate intermolecular (ΔS_{solv}) and intramolecular ($\Delta S_{\mathrm{intra}}$) contributions to ΔS_{rc}.[7] Changes in spin and orbital degeneracy contribute significantly to $\Delta S_{\mathrm{intra}}$ as an electronic entropy change (ΔS_{elec}), but the largest contribution arises from the increase in low-frequency vibrational activity (ΔS_{vib}) associated with the weakened metal−ligand bonds of Co(II).[7a] In the absence of a significant contribution from ΔS_{solv}, much of the entropy change of reaction 1 is derived from ΔS_{elec} and ΔS_{vib}. The experimental value of 124 J mol^{-1} deg^{-1} obtained for Co(bpy)(3,5-DBSQ)(3,5-DBCat) is large, and it is responsible for the strong temperature dependence of the tautomeric equilibrium. A contribution from ΔS_{elec} is included in this value, but the change in orbital degeneracy is small due to the low symmetry of the complex molecule and the contribution from the change in spin that occurs at both the metal and the radical ligands can be estimated to be no greater than 12 J mol^{-1} deg^{-1}.[8] Therefore, the shift to low-frequency vibrational modes is primarily responsible for the large value of ΔS. An interchange between octahedral and trigonal prismatic structures may occur in solution for the Co(II) isomer, and the entropic contribution from the dynamic change in structure may be ascertained from equilibrium measurements on crystalline samples. Temperature-dependent magnetic data recorded on solid $\mathrm{Co^{III}(bpy)(3,5\text{-}DBQ)_2}$ show the same qualitative appearance of solution magnetic measurements as the Co(III)/Co(II) (eq 1) transition takes place.[2c] The transition temperature is about 50 °C higher in the solid state, and values for $\Delta G_{\mathrm{solid}}$ are plotted in Figure 1.[10] $\Delta H_{\mathrm{solid}}$ obtained from the plot is 32(1) kJ mol^{-1}, close to the value obtained from solution measurements. Bond length distortions associated with electron transfer are apparently no different in the solid state than in solution, and the assumption that changes in solvation effects in solution are small appears valid. The calculated entropy change in the solid state ($\Delta S_{\mathrm{solid}}$) is 98(2) J mol^{-1} deg^{-1}, 26 J mol^{-1} deg^{-1} less than the solution value. Assuming that ΔS_{elec} and other contributions to ΔS_{vib} are unchanged in solid and solution, the difference between $\Delta S_{\mathrm{solid}}$ and ΔS_{soln} is the entropy gain associated with the octahedral/trigonal prismatic interchange. Structural characterizations of $\mathrm{Co^{II}(NO_2\text{-}phen)(3,6\text{-}DBSQ)_2}$ and $\mathrm{Co^{II}(dafl)(3,6\text{-}DBSQ)_2}$ have shown TP coordination geometries, and it is not unreasonable that Oh/TP interchange should occur with facility in toluene solution.[2c,9]

Equation 1 can be divided into separate electron transfer (eq 2) and spin transition (eq 3) steps. With the results of spin

$$\begin{array}{ccc} \mathrm{Co^{III}(N\text{-}N)(SQ)(Cat)} & \rightleftarrows & \mathrm{Co^{II}(N\text{-}N)(SQ)_2} \\ (t_{2g})^6(e_g)^0(\pi_{Q1})^2(\pi_{Q2})^1 & & (t_{2g})^6(e_g)^1(\pi_{Q1})^1(\pi_{Q2})^1 \end{array} \qquad (2)$$

$$\begin{array}{ccc} \mathrm{Co^{II}(N\text{-}N)(SQ)_2} & \rightleftarrows & \mathrm{Co^{II}(N\text{-}N)(SQ)_2} \\ (t_{2g})^6(e_g)^1(\pi_{Q1})^1(\pi_{Q2})^1 & & (t_{2g})^5(e_g)^2(\pi_{Q1})^1(\pi_{Q2})^1 \end{array} \qquad (3)$$

transition studies on octahedral Co(II) complexes, it is possible to estimate enthalpic and entropic contributions for both processes. Zarembowitch has reported thermodynamic changes for the $\mathrm{Co(H_2(fas)_2en)L_2}$ series (L = $\mathrm{H_2O}$, py, 4-*t*-Bupy) that range from 1.4 to 2.4 kJ/mol for ΔH and from 11 to 23 J/(mol K) for ΔS.[12] A recent study on $\mathrm{[Co(dmvi)(phen)_2]^+}$ has produced similar values of ΔH = 1.7 kJ/mol and ΔS = 16 J/(mol K) for the low-spin/high-spin transition.[13] Comparing these values with the enthalpy and entropy changes obtained experimentally for reaction 1, it is clear that the spin transition step makes only a small contribution to the values of ΔH and ΔS. Changes in bond energy and vibrational frequency associated with the electron transfer step are the primary contributors to the thermodynamic changes of the equilibrium.

It becomes of interest to extend the results of the analysis on Co(bpy)(3,5-DBSQ)(3,5-DBCat) to other quinone complexes that exhibit valence tautomerism and, further, to those that fail to show tautomeric equilibria. Manganese complexes that are related to the members of the cobalt series show two one-electron-transfer steps (eq 4) associated with the Mn(IV,III) and

$$\mathrm{Mn^{IV}(N\text{-}N)(Cat)_2} \rightleftarrows \mathrm{Mn^{III}(N\text{-}N)(SQ)(Cat)} \qquad (4a)$$

$$\mathrm{Mn^{III}(N\text{-}N)(SQ)(Cat)} \rightleftarrows \mathrm{Mn^{II}(N\text{-}N)(SQ)_2} \qquad (4b)$$

Mn(III,II) tautomeric equilibria.[2f,14] Many of the observations made concerning the cobalt complexes apply also to the manganese analogs. Reduction of metal from Mn(IV) by intramolecular electron transfer from a Cat ligand has much the same effect on Mn−N and Mn−O bond lengths as observed for the Co(III,II) reduction. As a d^3 metal ion, Mn(IV) resembles d^6 low-spin Co(III). Reduction to high-spin Mn(III) results in an axial distortion, and further reduction to high-spin Mn(II) gives a general lengthening of all Mn−L bonds. Structural studies on $\mathrm{Mn(N\text{-}N)(Q)_2}$ complexes of all three charge distributions clearly show these effects.[2f,14] Distortions in bond length that accompany the addition of charge to the e_g $d\sigma$ antibonding orbital result in an increase in low-frequency vibrational modes, as with Co(II), and changes in spin degeneracy further add to the positive entropy change for the electron transfer steps. Structural characterization on $\mathrm{Mn^{II}(NO_2\text{-}phen)(3,6\text{-}DBSQ)_2}$ has indicated a trigonal prismatic coordination geometry, and Oh/TP interchange may also contribute to ΔS for the Mn complexes.

Changes in the occupancy of strongly antibonding $d\sigma$ orbitals are responsible for the large entropy changes that give the temperature-dependent shifts in valence tautomeric equilibria for the Co and Mn complexes. Related complexes of iron, $\mathrm{Fe^{III}(N\text{-}N)(SQ)(Cat)}$, fail to show evidence for tautomerism.[2f,15]

$$\mathrm{Fe^{III}(N\text{-}N)(DBSQ)(DBCat)} \rightleftarrows \mathrm{Fe^{II}(N\text{-}N)(DBSQ)_2} \qquad (5)$$

Positive contributions to ΔS from changes in spin degeneracy and low-frequency shifts in vibrational modes would not offset

---

(6) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.

(7) (a) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1991**, *30*, 1412. (b) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1993**, *32*, 1809.

(8) The entropy change associated with the change in spin degeneracy is $\Delta S_{\mathrm{spin}} = R \ln[(2S + 1)_{\mathrm{Co(II)}} - (2S + 1)_{\mathrm{Co(III)}}]$. Spin multiplicity of the Co(III) isomer is 2. For the Co(II) isomer a coupled $S = {}^5/_2$ state may be used to estimate maximum spin multiplicity. With these values, ΔS_{spin} = 11.5 J/(mol K).

(9) Bhattacharya, S.; Boone, S. R.; Fox, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 1088.

(10) Using magnetic data to determine the relative concentrations of Co(III) and Co(II) species for both solid and solution measurements assumes that Co(II)−SQ and SQ−SQ exchange interactions contribute negligibly over the temperature range and that the magnetic moment of $\mathrm{Co^{II}(bpy)(3,5\text{-}DBSQ)_2}$ is constant. Characterization of $\mathrm{Co_4(3,5\text{-}DBSQ)_8}$ supports this assumption as temperature-dependent exchange interactions appear significantly only at temperatures below 200 K.[11]

(11) Lynch, M. W.; Buchanan, R. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1038.

(12) Zarembowitch, J. *New J. Chem.* **1992**, *16*, 255.

(13) Faus, J.; Julve, M.; Lloret, F.; Real, J. A.; Sletten, J. *Inorg. Chem.* **1994**, *33*, 5535.

(14) (a) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041. (b) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1995**, *34*, 1172.

the positive enthalpy change associated with reaction 5 at an experimentally accessible temperature. Both $\Delta H_{\mathrm{intra}}$ and $\Delta S_{\mathrm{intra}}$ would be smaller for the iron equilibrium than for those of the complexes of Co and Mn, and contributions from solvation effects become proportionately more significant.

Acknowledgment. Support for this research was provided by the National Science Foundation through Grant CHE 90-23636. The early contributions of Dr. Robert M. Buchanan (University of Louisville) to this project are most gratefully acknowledged.

IC950013R

---

(15) (a) Cohn, M. J.; Xie, C.-L.; Tuchagues, J.-P. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 5028. (b) Zirong, D.; Bhattacharya, S.; McCusker, J. K.; Hagen, P. M.; Hendrickson, D. N.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 870. (c) Attia, A. S.; Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.*, in press.