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Relationship between Reduction Potentials and Mixing Constants of Mixed-Ligand Complexes

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The reduction potential of a mixed-ligand complex is equal to the sum of the weighted average of the reduction potentials of the parent binary complexes plus the term $(2.3RT/nF)\log(K_{m,r}/K_{m,o})$, where $K_{m,r}$ and $K_{m,o}$ are mixing constants of the reduced and oxidized forms, respectively, of the mixed complex. The relationship is derived for a system of the type $(A_aB_bC_cM)_o + ne^- \rightleftharpoons (A_aB_bC_cM)_r$, where A, B, and C are ligands, M is the coordinated metal, and both the oxidized and reduced forms are soluble species. The new relationship is used to explain observed reduction potentials of the mixed-ligand complexes of iron(II) and iron(III) with 1,10-phenanthroline, 4-hydroxy-1,10-phenanthroline, and 4,7-dihydroxy-1,10-phenanthroline.

The concept of ligand additivity predicts that a mixed-ligand complex will exhibit properties that are intermediate between those of the parent binary complexes. In cases for which a chemical property can be quantified, the value for the mixed complex should be approximately equal to the weighted average of the values for the parent binary complexes. This is perhaps most apparent in the treatment of solution equilibria. The logarithm of the formation constant of a mixed complex is commonly compared to the weighted average of the logarithm of the formation constants of the parent binary comlexes, and any difference between the two is attributed to electronic and steric effects.[1] This approach has been used extensively by Sigel and co-workers[2] in studies of mixed complexes of amino acids and similar ligands. Because many metal-containing enzymes have analogies to the simpler mixed-ligand complexes, these studies can offer insights to the understanding of properties of such enzymes.[3]

Another property of a mixed-ligand complex that can be predicted quite well through the concept of ligand additivity is the reduction potential. In many cases for complexes of the type $ML_{n-x}L'_x$ the reduction potential varies in a linear fashion with the number of different ligands added, that is, as one proceeds stepwise from $x = 0$ to $x = n$. In these cases the observed reduction potential of a mixed-ligand complex is equal to the weighted average of the reduction potentials of the parent binary complexes. Such behavior has been observed for complexes of iron(III) and iron(II) with substituted dithiocarbamates[4] and with substituted 1,10-phenanthroline,[5] for complexes of Co(III) and Co(II) with substituted dithiocarbamates,[6] and for complexes of Ni(II) and Ni(I) with dithiocarbamates and phosphines.[7] In other cases the reduction potential does not vary linearly with the number of different ligands added. Such nonlinear variation has been observed for complexes of Mn(II) and Mn(I) with acetonitrile and carbon monoxide[8] and for complexes of Cr(I) and Cr(0) with benzonitrile and carbon monoxide.[9,10] In these cases the observed potentials were explained in terms of a ligand additivity model that considered various molecular parameters.[10] A nonlinear variation has also been reported for the complexes of iron(III) and iron(II) with unsubstituted and hydroxy-substituted 1,10-phenanthrolines.[11]

In none of the cases above has there been an attempt to explain the observed reduction potentials in terms of solution equilibria. In terms of ligand additivity, the topics of reduction potentials and solution equilibria have developed along separate tracks in the chemical literature. The two topics are dealt with simultaneously, however, when the effect of complexation on polarographic half-wave potentials ($E_{1/2}$) is used to determine formation constants of the mixed complexes. Most reports of this nature deal with reversible reduction of cadmium complexes to the metal amalgam,[12-15] for which a single polarographic wave is obtained and the $E_{1/2}$ value varies with the concentrations of the ligands. These systems conform well to the mathematical treatment developed by Schaap and McMasters.[16] The general approach and some special polarographic techniques for irreversible systems have been reviewed by Crow.[17]

In this paper a mathematical relationship is developed that describes exactly the relationship between the reduction potential of a mixed-ligand complex, the reduction potentials of the parent binary complexes, and the mixing constants of the mixed complexes. The treatment is limited to systems in which both the oxidized and reduced forms of the metal are soluble complexes, with specific reference to a system of mixed-ligand complexes of iron and substituted 1,10-phenanthrolines.

Theory

Consider the following redox couples involving only soluble species (ignoring charges)

$$OA_x + ne^- \rightarrow RA_x \quad E°_A$$

$$OB_y + ne^- \rightarrow RB_y \quad E°_B$$

$$OC_z + ne^- \rightarrow RC_z \quad E°_C$$

where A, B, and C are ligands, O = oxidized form of the metal ion, R = reduced form of the metal ion, and $E°_A$, $E°_B$, and $E°_C$ are the standard reduction potentials of the simple metal complex couples. Then for

$$OA_aB_bC_c + ne^- \rightarrow RA_aB_bC_c \tag{1}$$

we define

$$E°_{calcd} = \frac{a}{x}E°_A + \frac{b}{y}E°_B + \frac{c}{z}E°_C \tag{2}$$

In the special case where $x = y = z = a + b + c$

$$E°_{calcd} = \frac{aE°_A + bE°_B + cE°_C}{a + b + c} \tag{3}$$

In the following treatment we will assume that the coordination

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numbers of O and R are equal to some value N regardless of the ligand and that the fraction of the coordination sphere occupied by the ligands in any complex is unity. In this case a/x represents the fraction of the coordination sphere that is occupied by A, b/y for that by B, and c/z for that by C. This leads to the relation

$$\frac{a}{x} + \frac{b}{y} + \frac{c}{z} = 1 \tag{4}$$

The formation constants of the oxidized and reduced mixed complexes can be approximated by the weighted averages of the binary complexes.[1] Thus for

$$\mathrm{O} + a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \rightleftarrows \mathrm{OA}_a\mathrm{B}_b\mathrm{C}_c \tag{5}$$

$$\log \beta_{\mathrm{calcd,o}} = \frac{a}{x} \log \beta_{\mathrm{OA}_x} + \frac{b}{y} \log \beta_{\mathrm{OB}_y} + \frac{c}{z} \log \beta_{\mathrm{OC}_z} \tag{6}$$

and for

$$\mathrm{R} + a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \rightleftarrows \mathrm{RA}_z\mathrm{B}_b\mathrm{C}_c \tag{7}$$

$$\log \beta_{\mathrm{calcd,r}} = \frac{a}{x} \log \beta_{\mathrm{RA}_x} + \frac{b}{y} \log \beta_{\mathrm{RB}_y} + \frac{c}{z} \log \beta_{\mathrm{RC}_z} \tag{8}$$

where, for example, β_{OA_x} is the cumulative formation constant for OA_x. The weighted-average formation constant is rarely identical with the observed value, and this difference is accounted for by a mixing constant K_{m}, such that

$$\log \beta_{\mathrm{o}} = \log \beta_{\mathrm{calcd,o}} + \log K_{\mathrm{m,o}} \tag{9}$$

$$\log \beta_{\mathrm{r}} = \log \beta_{\mathrm{calcd,r}} + \log K_{\mathrm{m,r}} \tag{10}$$

where β_{o} and β_{r} are the observed cumulative formation constants for $\mathrm{OA}_a\mathrm{B}_b\mathrm{C}_c$ and $\mathrm{RA}_a\mathrm{B}_b\mathrm{C}_c$, respectively, and $K_{\mathrm{m,o}}$ and $K_{\mathrm{m,r}}$ are mixing constants. The mixing constant accounts for the increased (or decreased) stability that results from mixed complex formation, and it includes a statistical factor as well as electronic and steric factors.

For the reduction of a metal complex involving only soluble species, in which there is no loss or gain of ligands, as in eq 1, it can be shown that

$$E^\circ_{\mathrm{c}} = E^\circ_{\mathrm{s}} + \frac{2.3RT}{nF} \log \frac{\beta_{\mathrm{r}}}{\beta_{\mathrm{o}}} \tag{11}$$

where E°_{c} = standard reduction potential of the complex couple and E°_{s} = standard reduction potential of the simple metal aquo ion couple. Combining the log term in (11) with (9) and (10) yields

$$E^\circ_{\mathrm{c}} = E^\circ_{\mathrm{s}} + \frac{2.3RT}{nF}(\log \beta_{\mathrm{calcd,r}} - \log \beta_{\mathrm{calcd,o}}) + \frac{2.3RT}{nF}(\log K_{\mathrm{m,r}} - \log K_{\mathrm{m,o}}) \tag{12}$$

Expressing each of the terms in (2) in the form of (11) yields

$$\frac{a}{x}E^\circ_{\mathrm{A}} = \frac{a}{x}E^\circ_{\mathrm{s}} + \frac{a}{x}\,\frac{2.3RT}{nF}(\log \beta_{\mathrm{RA}_x} - \log \beta_{\mathrm{OA}_x}) \tag{13}$$

$$\frac{b}{y}E^\circ_{\mathrm{B}} = \frac{b}{y}E^\circ_{\mathrm{s}} + \frac{b}{y}\,\frac{2.3RT}{nF}(\log \beta_{\mathrm{RB}_y} - \log \beta_{\mathrm{OB}_y}) \tag{14}$$

$$\frac{c}{z}E^\circ_{\mathrm{C}} = \frac{c}{z}E^\circ_{\mathrm{s}} + \frac{c}{z}\,\frac{2.3RT}{nF}(\log \beta_{\mathrm{RC}_z} - \log \beta_{\mathrm{OC}_z}) \tag{15}$$

Combining (13), (14), and (15) with (2)

$$E^\circ_{\mathrm{calcd}} = E^\circ_{\mathrm{s}}\left(\frac{a}{x} + \frac{b}{y} + \frac{c}{z}\right) + \frac{2.3RT}{nF}\left(\frac{a}{x} \log \beta_{\mathrm{RA}_x} + \frac{b}{y} \log \beta_{\mathrm{RB}_y} + \frac{c}{z} \log \beta_{\mathrm{RC}_z}\right) - \frac{2.3RT}{nF}\left(\frac{a}{x} \log \beta_{\mathrm{OA}_x} + \frac{b}{y} \log \beta_{\mathrm{OB}_y} + \frac{c}{z} \log \beta_{\mathrm{OC}_x}\right) \tag{16}$$

Noting that the coefficient of E°_{s} is unity and substituting (6) and (8) into (16), we obtain

$$E^\circ_{\mathrm{calcd}} = E^\circ_{\mathrm{s}} + \frac{2.3RT}{nF}(\log \beta_{\mathrm{calcd,r}} - \log \beta_{\mathrm{calcd,o}}) \tag{17}$$

which on combination with (9) and (10) yields

$$E^\circ_{\mathrm{calcd}} = E^\circ_{\mathrm{s}} + \frac{2.3RT}{nF} \log \frac{\beta_{\mathrm{r}}}{\beta_{\mathrm{o}}} - \frac{2.3RT}{nF} \log \frac{K_{\mathrm{m,r}}}{K_{\mathrm{m,o}}} = E^\circ_{\mathrm{c}} - \frac{2.3RT}{nF} \log \frac{K_{\mathrm{m,r}}}{K_{\mathrm{m,o}}} \tag{18}$$

Rearranging gives

$$E^\circ_{\mathrm{c}} = E^\circ_{\mathrm{calcd}} + \frac{2.3RT}{nF} \log \frac{K_{\mathrm{m,r}}}{K_{\mathrm{m,o}}} \tag{19}$$

Thus, the reduction potential of a mixed-ligand complex couple involving only soluble species, in which the coordination number of the metal does not vary, is shown to be equal to the weighted average of the reduction potentials of the binary complexes plus a term that involves the mixing constants for the oxidized and reduced forms of the mixed complex.

It can also be shown that the statistical portion of the mixing constants can be factored out. The mixing constants are defined as[1]

$$\log K_{\mathrm{m,r}} = \log K_{\mathrm{s,r}} + \log S_{\mathrm{r}}$$

$$\log K_{\mathrm{m,o}} = \log K_{\mathrm{s,o}} + \log S_{\mathrm{o}}$$

where K_{s} is the stabilization constant, which accounts for the electronic and steric factors that contribute to the increased or decreased stability of the mixed complex over that predicted by β_{calcd}, and S is a statistical factor. If the total number of ligands in the mixed complex is defined as Q, then $a + b + c = Q$, and

$$S = \frac{Q!}{a!\ b!\ c!}$$

The values of a, b, c, and Q are identical for the oxidized and reduced forms of the mixed complex, so that $S_{\mathrm{o}} = S_{\mathrm{r}}$, and

$$\log (K_{\mathrm{m,r}}/K_{\mathrm{m,o}}) = \log (K_{\mathrm{s,r}}/K_{\mathrm{s,o}}) \tag{20}$$

Equation 19 may now be rewritten as

$$E^\circ_{\mathrm{c}} + E^\circ_{\mathrm{calcd}} + \frac{2.3RT}{nF} \log \frac{K_{\mathrm{s,r}}}{K_{\mathrm{s,o}}} \tag{21}$$

The use of K_{s} to describe the electronic and steric contributions to the stability of a mixed complex is widely accepted, and the various contributions to K_{s} have been studied.[2,18] In cases where experimental measurement of E°_{c} is impossible, eq 21 can be used to calculate the reduction potential if E°_{calcd}, $K_{\mathrm{s,r}}$, and $K_{\mathrm{s,o}}$ are known. If only E°_{calcd} can be determined, a reasonable estimate of E°_{c} can be made from knowledge of the factors that influence K_{s}.

Discussion

The derivation of eq 19 and 21 assumes that each of the half-reactions for the appropriate binary and mixed complexes involves only a single oxidized form and a single reduced form. In recent years there have been numerous reports of redox couples in which the oxidized and reduced forms differ in electronic spin state or in which either the oxidized or reduced form may exist in more than one electronic spin state.[4,19-23] In cases where a

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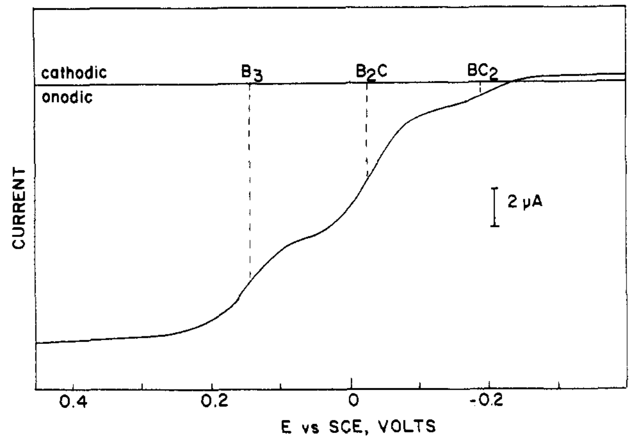

Figure 1. Voltammetry of B_3Fe^{II}, B_2CFe^{II}, and BC_2Fe^{II} at a rotated-platinum-wire electrode. Conditions: pH 11.0 ammonia/ammonium chloride buffer; ionic strength 1.0; 25 °C; $C_B = 2.0 \times 10^{-3}$ M; $C_C = 5.5 \times 10^{-4}$ M; $C_{Fe(II)} = 5.0 \times 10^{-4}$ M; scan rate 1.0 mV/s.

spin equilibrium exists, the observed reduction potential may deviate from the reduction potentials for both the low-spin and high-spin forms of the complex.[4] A general treatment for the electrochemistry of a couple in which either or both forms of a couple are in equilibrium with other species has been reported.[24] If the possibility exists that the oxidized and reduced forms of a couple differ in spin state, or if a spin equilibrium exists, eq 19 and 21 must be applied with caution.

Although eq 19 and 21 are based directly on established thermodynamic relationships, it would be desirable to test these equations with data for a chemical system that have been obtained by independent methods. Such a comparison would require knowledge of the reduction potentials of the binary and corresponding mixed-ligand complex couples, as well as the formation constants of the binary and mixed-ligand complexes of the oxidized and reduced forms, all under the same experimental conditions. There appears to be no system for which all of the required data have been measured. Studies on mixed complex equilibria generally focus on the complexes of a single oxidation state[1,2] or deal with polarographic reduction of a soluble complex to the metal amalgam.[12-15]

With the consideration about spin equilibrium in mind, eq 19 and 21 will be applied to the analysis of reduction potentials for the system of mixed-ligand complexes of iron(III) and iron(II) with 1,10-phenanthroline (A), 4-hydroxy-1,10-phenanthroline (B), and 4,7-dihydroxy-1,10-phenanthroline (C). Although formation or mixing constants of the individual complexes are not available, it is possible to draw some general conclusions about the relative enhancement in stability of the oxidized and reduced forms of a single mixed complex. Furthermore, it is known that substituted 1,10-phenanthrolines form stable low-spin complexes with iron(III) and iron(II) provided there are no substituents in the 2-position and there are no strongly electron-withdrawing groups in other positions.[25,26] Therefore, it may be safely assumed that the spin-state-related complications discussed above are not present in this system. The redox reaction for this system may be written

$$A_aB_bC_cFe^{III} + e^- \rightarrow A_aB_bC_cFe^{II}$$

where A, B, and C are the phenanthrolines as defined above and $a + b + c = 3$. Previous studies (see ref 6 and articles cited therein) have shown the following: (1) A, B, and C form stable binary and mixed complexes with iron(II) at pH 10–11, but the iron(III) derivatives in general are less stable, undergoing hydrolysis over a period of hours; (2) the binary and mixed complexes undergo reversible oxidation at a platinum electrode with $E_{1/2} = E^{\circ\prime}$ (conditional reduction potential);[27] (3) the reduction potentials of the binary complexes are pH-independent; (4) a solution containing several forms of $A_aB_bC_cFe^{II}$ in equilibrium yields a series of voltammetric waves with $E_{1/2}$ values corresponding to the individual complexes present. Figure 1 shows a voltammogram for a solution containing several mixed complexes of iron(II) with 4-hydroxy-1,10-phenanthroline and 4,7-dihydroxy-1,10-phenanthroline obtained under conditions similar to those reported in ref 6. Waves are observed for the oxidation of three complexes, marked B_3 for tris(4-hydroxy-1,10-phenanthroline)iron(II) and marked similarly for the other two waves. Figure 1 is typical of the voltammograms obtained for the mixed-ligand complexes in this series.

Table I. Reduction Potentials and Ratios of Stabilization Constants for Mixed-Ligand Iron–Phenanthroline Complexes

complex[a]	$E^\circ{}_c$,[b] V	$E^{\circ\prime}{}_{calcd}$, V	$E^\circ{}_c - E^\circ{}_{calcd}$, V	log $(K_{s,o}/K_{s,r})$
A_3Fe	1.06			
A_2BFe	0.78	0.84	−0.06	+1.0
AB_2Fe	0.60	0.61	−0.01	+0.2
B_3Fe	0.39			
B_2CFe	0.22	0.23	−0.01	+0.2
BC_2Fe	0.06	0.06	0.00	0.0
C_3Fe	−0.10			
C_2AFe	0.21	0.29	−0.08	+1.4
CA_2Fe	0.58	0.67	−0.09	+1.5

[a] Abbreviations: A = 1,10-phenanthroline; B = 4-hydroxy-1,10-pnenanthroline; C = 4,7-dihydroxy-1,10-phenanthroline. [b] Conditional reduction potential for the iron(III)/iron(II) complex couple from ref 11.

The appearance of separate waves for the individual complexes, as observed in Figure 1, is not a common occurrence in voltammetry of mixed-ligand complexes. In polarographic studies on the mixed complexes of cadmium(II)[12-15] a single wave is obtained for which $E_{1/2}$ vaies with the concentration of the ligands. In such systems the various metal complexes are presumed to be in rapid equilibrium at the electrode surface. In some cases it has been shown that a single species undergoes extremely rapid reduction at the electrode surface and that the kinetics of the solution equilibria are fast enough to maintain the equilbirium concentration of the active species at the electrode surface. A general treatment of these cases has been given by Crow.[17] The appearance of more than one wave in the present study indicates that equilibrium between the various mixed complexes in solution is not maintained at the electrode surface, making it possible to measure the half-wave potentials of the individual mixed complexes. Furthermore, since the half-wave potentials of the binary complexes are pH-independent, it is reasonable to conclude that equilbrium with hydrolysis products is not a complicating factor.

The half-wave potentials of the complexes and the corresponding $E^\circ{}_{calcd}$ values for the mixed complexes in Table I are taken from ref 11. From these data it is a simple matter to determine the ratio of mixing constants (K_m) or stabilization constants (K_s) for the oxidized and reduced forms of the mixed complexes from eq 19 and 21 at 25 °C:

$$\log (K_{m,o}/K_{m,r}) = \log (K_{s,o}/K_{s,r}) = (E_c - E_{calcd})/0.0591 \quad (22)$$

Because the entropic contributions to K_m are identical for the oxidized and reduced forms (i.e., $S_r = S_o$), it is appropriate to discuss here the ratio of stabilization constants. These values have been calculated from eq 22 and are listed in Table I.

The values of log $(K_{s,o}/K_{s,r})$ listed in Table I reflect an enhancement in stability of the mixed complexes of iron(III) relative to those of iron(II). The lack of absolute values of K_s makes interpretation of these results difficult, but the situation is sim-

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(27) The reduction potentials and equilibrium constants in this section are conditional constants. While eq 19 and 21 are written in terms of the standard reduction potentials and thermodynamic equilibrium constants, conditional reduction potentials and equilibrium constants may be substituted, provided all constants are referenced to the same conditions, which in this case are unit ionic strength at pH 11 and 25 °C.

plified somewhat because, due to the structural similarities of these ligands and the absence of steric effects, K_s must be due entirely to electronic effects. Let us consider the effects of electrostatic attraction and repulsion on bond length between the positively charged iron and ligand A, B, or C. Ligand A is neutral whereas B and C carry negative charges. No electrostatic interactions exist between A and Fe nor between A and the neighboring ligands, so the A–Fe bond lengths should be nearly identical in all of the mixed complexes for a single oxidation state of iron. However, the C–Fe bond length should increase (or the bond strength should decrease) in going from A_2CFe to AC_2Fe to C_3Fe because of the increasing electrostatic repulsion between the negatively charged C ligands. For the mixed complexes A_2CFe and AC_2Fe, this results in stabilities that are greater than would be predicted from simple ligand additivity and entropic effects, and positive values of log K_s are anticipated for both the iron(II) and iron(III) derivatives. The data in Table I, however, give us only the *ratio* of stabilization constants. The positive values for log $(K_{s,o}/K_{s,r})$ show that the stabilization effect is greater for the iron(III) derivatives, which is not surprising given that a negatively charged ligand C should interact more strongly with iron(III) than with iron(II). The same arguments apply to the A–B–Fe system. For the B–C–Fe complexes, however, no significant stability enhancement is anticipated for either the iron(II) or the iron(III) complex because all ligands in these complexes are negative charged. This would result in values of $K_{s,o}$ and $K_{s,r}$ that are both close to unity. The values of log $(K_{s,o}/K_{s,r})$ for B_2CFe and BC_2Fe in Table I are both approximately zero, which is consistent with this argument.

It should be emphasized that the arguments presented above are based on the assumption that only electrostatic interactions contribute to K_s for the mixed complexes and, as a corollary to this assumption, that values of log K_s are positive for mixed complexes containing at least one neutral ligand and at least one negatively charged ligand. While the values of log $(K_{s,o}/K_{s,r})$ are consistent with these assumptions, knowledge of the absolute values of K_s for the mixed complexes is desirable. Due to the kinetic instability of the iron(III)–phenanthroline complexes to hydrolysis, direct determination of the formation constants of the complexes (from which the mixing constants are readily calculated) would be extremely difficult. If, however, the formation constants of the iron(II) derivatives were measured, eq 11, 19, and 21 could then be applied to calculate the formation constants, mixing constants, and stabilization constants of the iron(III) derivatives.

Conclusion

The relationship between the reduction potential of a mixed-ligand complex and the reduction potentials of the parent binary complexes, in which the electronic spin states of all complexes are the same and no significant spin equilibrium exists, has been established. As demonstrated by the discussion on the mixed complexes of iron phenanthrolines, the relationships involving K_m and K_s provide a convenient and sound basis to account for the observed reduction potentials of the mixed-ligand-complex couples. These relationships also provide a means to calculate the mixing constants and stabilization constants for one oxidation state of a mixed-ligand complex couple, provided that the corresponding constants for the other oxidation state are known.

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Synthesis and Excited-State Properties of Rhodium(III) Terpyridine Complexes

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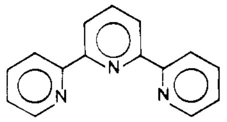
Reported are the photophysical properties of several previously known and newly synthesized rhodium(III) complexes of 2,2′:6′,2″-terpyridine: $Rh(trpy)_2^{3+}$, $Rh(trpy)(bpy)(py)^{3+}$, and $Rh(trpy)(bpy)Cl^{2+}$ (bpy = 2,2′-bipyridine; py = pyridine). The absorption spectrum of each of these complexes in aqueous solution is dominated by intraligand π_L–π_L* transitions that obscure the regions where ligand field (LF) bands would be expected. However, the luminescence spectra both in ambient-temperature fluid solutions and in 77 K glasses show broad, Gaussian-shaped bands interpreted to be the result of emission from the lowest energy triplet ligand field states. Photolysis of $Rh(trpy)(bpy)Cl^{2+}$ in aqueous solution leads to photolabilization of Cl^-, as seen with other Rh(III) chloro amine complexes; however, the quantum yield proved to be quite small (0.002 mol/einstein), a feature that can be attributed to an unusually small rate constant for Cl^- labilization from the $^3LF^*$ state.

The polypyridyl complexes of d^6 metal ions have been the subjects of considerable interest in recent years, especially with regard to their extraordinarily rich photochemical and photophysical properties. Much of this attention has focused on complexes of 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and their substituted derivatives; however, some examples of 2,2′:6′,2″-terpyridine (trpy) complexes have also been the objects of photochemical/physical investigations.[3-5] The present investigation is concerned with such properties of rhodium(III) trpy complexes, the goals being to compare these to similar Rh(III) complexes of other amines and to characterize the manner in which changes in ligand fields influence the energies and dynamics of relevant excited states (ES).



trpy

Experimental Section

Syntheses. Trichloro(terpyridine)rhodium(III), $Rh(trpy)Cl_3$, was prepared from $RhCl_3 \cdot xH_2O$ plus terpyridine (Aldrich) according to the

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[1] Taken in part from the Ph.D. dissertations of M.E.F. (1984) and S.D.S. (1984), University of California, Santa Barbara.

[2] On leave (1983) from the University of New South Wales, Kensington, NSW 2023, Australia.

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