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Excited State Redox Potentials of Ruthenium Diimine Complexes. Correlations with Ground State Redox Potentials and Ligand Parameters

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The relationship between charge transfer emission energies and redox potentials has been investigated for a large and diverse set of ruthenium diimine complexes. An alternative derivation of excited state redox potentials is developed, which relates them directly to the corresponding (observable) ground state potentials and allows them to be estimated when the 0−0′ emission energy is unknown. The difference between the excited state and corresponding ground state potentials, *D*, is shown to be approximately constant for complexes in which the emission and reduction processes involve "bipyridine-like" ligands, provided there are no strong specific solvent-solute interactions. Excited state redox potentials may also be obtained directly by using ligand electrochemical parameters, $E_L(L)$. $E_L(L^-)$ values are calculated here for a number of reduced ligands.

Introduction

Correlations between the charge transfer absorption and emission energies of coordination compounds and their redox potentials have been known for many years.[1−37] In most cases the relationships have been expressed as plots of an optical property, such as the energy of absorption or emission, against a redox potential or difference of potentials, of a couple or couples involved in the optical process. These plots are usually linear or close thereto, and they derive from the earlier analysis by Vlcek,[2] based on work on charge transfer spectra by Rabinowitch[38] and Roothaan.[39]

The equations are generally of the form[2,3,5,23]

$$E(\text{optical}) = \Delta E(\text{redox}) + \sum\nolimits_i a_i \qquad (1)$$

where ΔE(redox) is the difference between the first oxidation and first reduction potentials of the complex, and the term $\sum_i a_i$ collects factors not directly derivable from either of these measurable variables. Since linear plots are normally observed, $\sum_i a_i$ must be approximately constant or effectively a linear function of the redox (or optical) energy. The various factors contributing to the $\sum_i a_i$ term have been discussed by a number of authors.[2,3,5,23,40]

The correlations are based on the fact that the energy of an optical transition is, in a one electron approximation, given by the difference between the energy of the orbital from which the electron is being transferred and the energy of the orbital accepting the electron.[39] This difference is related to the difference in the redox potentials for the oxidation and reduction of the compound in its ground state.[2] For eq 1 to be fulfilled, the pair of orbitals involved in the optical and redox processes must be the same. Furthermore, since charge transfer properties

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(40) The $\sum_i a_i$ term has been broken down in various different ways which are all quite similar, although different terminology is used by different authors. It must include a Coulomb term, a term to correct for the solvation energy differences between the four species, and a term to account for the differences in the relevant orbital energies of the four species. For absorption energies, the vibrational reorganization is also included.

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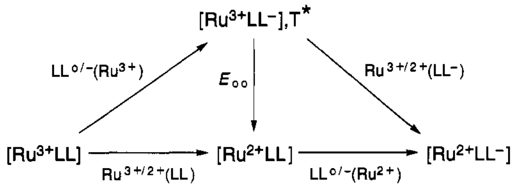
Scheme I



(usually metal to ligand charge transfer, MLCT) are being compared, the orbitals involved in these processes will be primarily localized on different parts of the molecule.[2,41,42]

Previously, the most extensive correlations of redox and electrochemical data have dealt with absorption rather than emission spectra since more absorption data are available. However, if the 0–0′ emission energy (E_{00}) is used, the $\sum_i a_i$ term is simplified because there is no contribution from vibrational reorganization. In this paper we analyze relationship 1 in more detail, using emission data. To test its general validity, it is applied to a much more extended set of data than has been used previously. However, more importantly, we show an alternative derivation of excited state redox potentials which relates them directly to the observable ground state potentials. Thus any relationships derived for ground state potentials may be applied to excited state potentials, and the latter may be estimated without knowledge of E_{00}.

To make any meaningful correlation between the optical and redox properties of a large number of complexes, the sets of orbitals (redox and optical) involved should be closely related within the whole series of compounds investigated, i.e. a series of complexes with similar ligands and the same metal atom. Our analysis is based mainly on data for hexacoordinate ruthenium(II) complexes which contain at least one bidentate diimine ligand, termed LL in the discussion that follows. However, the equations are generally applicable.

Thermodynamic Analysis

The analysis of excited state redox potentials deals with the emitting state, which is believed to be the equilibrated spin triplet of the diimine ligand-centered MLCT state.[41,42] The most useful optical measurable is the 0–0′ emission energy, E_{00}, defined as the energy of the transition from the thermally equilibrated excited state to the zero vibrational level of the ground state.[43] There is some discussion in the literature as to whether a vertical optical transition corresponds with free or internal energy.[44,45] We believe it is correct to treat the optical transition, in solution, as a free energy, and thus that relationships between optical and electrochemical quantities can be drawn.[45]

The entropy terms, though they differ in the optical and electrochemical experiment, are likely to be very small in the optical transition.[44]

Consider Scheme 1 (see e.g. refs 42 and 46). Simple thermodynamic arguments lead to the following equations, which are frequently used to determine the excited state redox potentials:[46,47]

$$E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{3+})) = E(\mathrm{Ru}^{3+/2+}(\mathrm{LL})) - E_{00} \qquad (2)$$

$$E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}^-)) = E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{2+})) + E_{00} \qquad (3)$$

The excited state redox potential $E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{3+}))$ (signifying reduction of the diimine ligand bound to Ru^{3+}) is, however, that of the LL/LL$^-$ couple with LL *ligated to the oxidized form of the metal* in both halves of the redox couple. This potential is related to the potential $E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{2+}))$ which represents the reduction of LL ligated to the *reduced form* of the metal, and, without making any nonthermodynamic assumptions, one may write

$$E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{3+})) = E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{2+})) + D_\mathrm{M} \qquad (4)$$

In an analogous way the excited state redox potential $E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}^-))$, representing the $\mathrm{Ru}^{3+/2+}$ couple for Ru *coordinated to reduced ligand*, LL$^-$, is related to the potential for the $\mathrm{Ru}^{3+/2+}$ couple for Ru coordinated to the *neutral ligand*, and it can be written

$$E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}^-)) = E(\mathrm{Ru}^{3+/2+}(\mathrm{LL})) + D_\mathrm{L} \qquad (5)$$

D_M and D_L are Gibbs free energy changes and are defined as the energy due to replacement of the metal in oxidation state M (Ru^{2+}) by metal in oxidation state M$^+$ (Ru^{3+}), and as the energy due to replacement of the ligand LL by its reduced form LL$^-$, respectively, in both halves of the redox couples. These definitions of D_M and D_L include all possible energy changes caused by the replacement of M by M$^+$ or of LL by LL$^-$, including structural, solvation and entropy changes.

Combining eqs 2 and 4 we obtain

$$E(\mathrm{Ru}^{3+/2+}(\mathrm{LL})) - E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{2+})) = E_{00} + D_\mathrm{M} \qquad (6)$$

Analogously eqs 3 and 5 give

$$E(\mathrm{Ru}^{3+/2+}(\mathrm{LL})) - E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{2+})) = E_{00} - D_\mathrm{L} \qquad (7)$$

Hence $D_\mathrm{M} = -D_\mathrm{L}$; i.e. the thermodynamic treatment shows that both differences in free energies are equal in absolute value, for a given complex. Henceforth we refer to this parameter simply as D, considering only its absolute value.

The two D values are equal because they both involve differences between two redox potentials, i.e. differences of differences, and the same four states are involved in both. Thus D is also equal to the energy of quenching of the excited state, by the ground state, to generate the oxidized and reduced species, i.e. for a tris-LL ruthenium species the energy of

$$[\mathrm{Ru(LL)_3}]^{2+*} + [\mathrm{Ru(LL)_3}]^{2+} \rightarrow [\mathrm{Ru(LL)_3}]^{3+} + [\mathrm{Ru(LL)_3}]^{+} \qquad (8)$$

In a simple one-electron approximation D is equal to the Coulomb repulsion energy, $J_{\mathrm{a,x}}$, between an electron in the ligand orbital (x) and one in the metal valence level (a), plus the appropriate solvation energy differences.[2,3] DeArmond has previously commented that the linearity between E_{00} and

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Table 1. Redox and Emission Data for Ruthenium Complexes (V)

complex[a,b]	E_1[c]	E_2[d]	E_3[e]	E_4[f]	$E_L(LL^-)$[g]	D	ΔE(red)	E_{00}	complex[a,b]	E_1[c]	E_2[d]	E_3[e]	E_4[f]	$E_L(LL^-)$[g]	D	ΔE(red)	E_{00}
Tris-LL Species																	
Ru(bt)$_3$	1.49	−0.71	−0.09	0.87	−0.06	0.62	2.20	1.58	Ru(biq)$_3$	1.71	−0.49	−0.02	1.24	0.05	0.47	2.20	1.73
Ru(hpiq)$_3$	1.47	−0.83	−0.22	0.86	−0.06	0.61	2.30	1.69	Ru(44dcebpy)$_3$	1.78	−0.65	−0.18	1.31	0.06	0.47	2.43	1.96
Ru(azpy)$_3$	2.34	0.11	0.72	1.73	0.08	0.61	2.23	1.62	Ru(terpy)$_2$	1.50	−1.05	−0.58	1.03	0.09	0.47	2.55	2.08
Ru(33mbpy)$_3$	1.39	−1.22	−0.69	0.86	−0.01	0.53	2.61	2.08	Ru(hphen)$_3$	1.44	−1.15	−0.69	0.98	0.01	0.46	2.59	2.13
Ru(44mbpy)$_3$	1.37	−1.13	−0.61	0.85	−0.03	0.52	2.50	1.98	Ru(5Clphen)$_3$	1.63	−0.98	−0.53	1.18	0.05	0.45	2.61	2.16
Ru(4tepbpy)$_3$	1.76	−0.72	−0.21	1.25	0.04	0.51	2.48	1.97	Ru(phen)$_3$	1.51	−1.11	−0.68	1.08	0.04	0.43	2.62	2.19
Ru(tmbpy)$_3$	1.30	−1.25	−0.75	0.80	−0.03	0.50	2.55	2.05	Ru(4Clbpy)$_3$	1.66	−0.82	−0.41	1.25	0.08	0.41	2.48	2.07
Ru(bpm)$_3$	1.93	−0.67	−0.17	1.43	0.07	0.50	2.60	2.10	Ru(66mbpm)$_3$	1.73	−0.54	−0.14	1.33	0.09	0.40	2.27	1.87
Ru(bpz)$_3$	2.10	−0.56	−0.06	1.60	0.08	0.50	2.66	2.16	Ru(44dbbpy)$_3$	1.35	−1.20	−0.81	0.96	0.03	0.39	2.55	2.16
Ru(bpy)$_3$	1.50	−1.11	−0.62	1.01	−0.02	0.49	2.61	2.12	Ru(pynapy)$_3$	1.32	−0.75	−0.37	0.94	0.03	0.38	2.07	1.69
Ru(L1)$_3$	1.64	−1.01	−0.52	1.15	0.03	0.49	2.65	2.16	Ru(dinapy)$_3$	1.21	−0.59	−0.27	0.89	0.04	0.32	1.80	1.48
Ru(BL)$_3$	1.94	−0.36	0.12	1.46	0.12	0.48	2.30	1.82	Ru(taphen)$_3$	1.84	−0.46	−0.15	1.53	0.15	0.31	2.30	1.99
Ru(dmch)$_3$	1.50	−0.66	−0.19	1.03	0.02	0.47	2.16	1.69									
Other LL-Emitting Complexes																	
Ru(bpy)(azpy)$_2$	2.12	0.03	0.62	1.53	0.11	0.59	2.09	1.50	Ru(bpy)$_2$(HL0)	1.54	−0.99	−0.56	1.11	0.04	0.46	2.56	2.10
Ru(bpy)$_2$(biq)	1.57	−0.67	−0.12	1.02	−0.01	0.55	2.24	1.69	Ru(bpy)$_2$(47pphen)	1.48	−1.08	−0.63	1.03	−0.01	0.45	2.56	2.11
Ru(bpy)$_2$(dmch)	1.49	−0.76	−0.23	0.96	−0.04	0.53	2.25	1.72	Ru(bpy)$_2$(44dpbpy)	1.47	−1.07	−0.63	1.03	−0.01	0.44	2.54	2.10
Ru(bpy)(biq)$_2$	1.64	−0.58	−0.05	1.11	0.01	0.53	2.22	1.69	Ru(bpy)$_2$(bpz)	1.73	−0.67	−0.23	1.29	0.13	0.44	2.40	1.96
Ru(bpy)(terpy)py	1.45	−1.02	−0.50	0.93	0.05	0.52	2.47	1.95	Ru(bpy)(terpy)CN	1.32	−1.09	−0.66	0.89	0.12	0.43	2.41	1.98
Ru(bpy)$_2$(HL3)	1.53	−0.98	−0.47	1.02	−0.01	0.51	2.51	2.00	Ru(bpy)(BL)$_2$	1.77	−0.42	−0.01	1.37	0.11	0.41	2.19	1.79
Ru(bpy)$_2$(pq)	1.54	−0.87	−0.36	1.03	−0.01	0.51	2.41	1.90	Ru(bpy)$_2$(BL)	1.63	−0.54	−0.14	1.23	0.10	0.40	2.17	1.77
Ru(bpy)(pq)$_2$	1.54	−0.83	−0.32	1.03	0.00	0.51	2.37	1.86	Ru(bpy)(terpy)Cl	1.05	−1.11	−0.74	0.68	0.13	0.37	2.16	1.79
Ru(bpy)(dmch)$_2$	1.49	−0.68	−0.19	1.00	0.00	0.49	2.17	1.68	Ru(bpy)(taphen)$_2$	1.72	−0.50	−0.21	1.43	0.15	0.29	2.22	1.93
Ru(bpy)(hphen)$_2$	1.45	−1.13	−0.67	0.99	0.00	0.46	2.58	2.12	Ru(bpy)$_2$(L2)	1.55	−0.85	−0.60	1.30	0.13	0.25	2.40	2.15
2,2′-Bipyridine Emitting Complexes																	
Ru(bpy)$_2$(bbzimH$_2$)	1.36	−1.36	−0.65	0.65	−0.11	0.71	2.72	2.01	Ru(bpy)(33mbpy)$_2$	1.42	−1.17	−0.68	0.93	−0.01	0.49	2.59	2.10
Ru(bpy)$_2$(pzH)$_2$	1.42	−1.28	−0.57	0.71	−0.10	0.71	2.70	1.99	Ru(bpy)(44dbbpy)$_2$	1.44	−1.15	−0.66	0.95	−0.01	0.49	2.59	2.10
Ru(bpy)$_2$(bimH$_2$)	1.28	−1.42	−0.73	0.58	−0.10	0.70	2.70	2.00	Ru(bpy)$_2$(MeCN)$_2$	1.62	−1.15[h]	−0.67	1.14	−0.03	0.48	2.77	2.29
Ru(bpy)$_2$(dppene)	1.99	−1.04	−0.40	1.35	0.06	0.64	3.03	2.39	Ru(bpy)(44mbpy)$_2$	1.42	−1.17	−0.69	0.94	−0.02	0.48	2.59	2.11
Ru(bpy)$_2$(pbzimH)	1.41	−1.25	−0.66	0.82	−0.04	0.59	2.66	2.07	Ru(bpy)$_2$(ibiq)	1.46	−1.14	−0.66	0.98	0.02	0.48	2.60	2.12
Ru(bpy)$_2$(pimH)	1.38	−1.28	−0.70	0.80	−0.03	0.58	2.66	2.08	Ru(bby)$_2$(hphen)	1.48	−1.12	−0.64	1.00	0.02	0.48	2.60	2.12
Ru(bpy)$_2$(diars)	1.69	−1.12	−0.56	1.13	0.00	0.56	2.81	2.25	Ru(bpy)(ibiq)$_2$	1.41	−1.18	−0.71	0.94	0.00	0.47	2.59	2.12
Ru(bpy)$_2$(dppe)	1.64	−1.14	−0.59	1.09	−0.07	0.55	2.78	2.23	Ru(bpy)$_2$(phen)	1.47	−1.12	−0.67	1.02	−0.01	0.45	2.59	2.14
Ru(bpy)$_2$(hpiq)	1.49	−0.93	−0.39	0.95	−0.05	0.54	2.42	1.88	Ru(bpy)$_2$(py)Cl	1.03	−1.27	−0.85	0.62	0.04	0.42	2.30	1.88
c-Ru(bpy)$_2$(mpp)$_2$	1.79	−1.04	−0.51	1.26	0.03	0.53	2.83	2.30	Ru(bpy)$_2$(en)	1.17	−1.24	−0.83	0.76	0.05	0.41	2.41	2.00
Ru(bpy)$_2$(33mbpy)	1.46	−1.13	−0.62	0.95	−0.01	0.51	2.59	2.08	Ru(bpy)$_2$(L0)	1.19	−1.20	−0.82	0.81	0.07	0.38	2.39	2.01
Ru(bpy)$_2$(3aep)	1.26	−1.20	−0.69	0.75	−0.01	0.51	2.46	1.95	Ru(bpy)$_2$(L3)	1.16	−1.20	−0.82	0.78	0.07	0.38	2.36	1.98
t-Ru(bpy)$_2$(mpp)$_2$	1.70	−1.06	−0.56	1.20	0.00	0.50	2.76	2.26	Ru(bpy)$_2$Cl$_2$	0.55	−1.43	−1.10	0.22	0.09	0.33	1.98	1.65
Ru(bpy)$_2$(py)$_2$	1.49	−1.11	−0.62	1.00	−0.01	0.49	2.60	2.11	Ru(bpy)$_2$(CN)$_2$	1.08	−1.32	−1.06	0.82	0.13	0.26	2.40	2.14
Ru(bpy)$_2$(nmi)$_2$	1.18	−1.24	−0.75	0.69	0.00	0.49	2.42	1.93									

[a] Each group is ordered according to *D*. Data were collected from refs 30−34, 42, and 49. [b] Overall charges omitted for clarity. [c] $E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}))$. [d] $E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{2+}))$. [e] $E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{3+}))$. [f] $E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}^-))$. [g] $E_L(\mathrm{LL}^-)$ parameter, for the reduced form of the ligand involved in the emitting state in the given species. [h] This work.

ΔE(redox) depends, in a series of ruthenium bipyridine complexes, upon the constancy of $J_{a,x}$ plus the solvation term, which he suggested were the major contributors to *D*.[3] He also estimated the sum of these to be about 0.5 eV.

It is not possible to factorize the contributions to *D* accurately in detail without being able to calculate the exact energies of the above species and their solvation energies. Thus in this contribution, our emphasis is not to factorize *D* but rather to explore how the sum of all these contributions varies over a large data set.

Results and Discussion

To test these results, data for about 70 ruthenium diimine complexes and a smaller number of osmium complexes have been analyzed. We discuss the ruthenium data in more detail because the data set is larger, but the trends are similar for both sets of complexes.

Ruthenium(II) has a fairly weak interaction with most diimine ligand π^*-orbitals,[48] particularly when more than one diimine is present in the complex. Consequently the LUMO can be regarded as a mainly ligand orbital and the HOMO is essentially a localized ruthenium d-orbital; thus, the conditions under which the fundamental equation was derived[2,39] are closely met.

Most data for $E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}))$ and $E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{2+}))$ have been collected in acetonitrile; only those reported as being reversible are used here. Many E_{00} values are available (e.g. data collected in ref 42). All the complexes analyzed are reported as having the same orbitals involved in their redox and optical processes.

***D* Values.** Values of *D* were obtained by subtracting the E_{00} energy from ΔE(redox), the difference between the observed oxidation and first reduction potentials of the complexes (eqs 6 and 7). These values are listed in Table 1. The entire group of complexes gives an average D of 0.48 V with a standard deviation (σ) of 0.09 V. This lies close to DeArmond's estimate of 0.5 V.[3] Thus it appears that *D* does not vary greatly for quite a wide variety of ruthenium diimine complexes. 80% of the data (in any data set) lie within $\pm 1.29\sigma$. The horizontal dotted lines in Figure 1 show these limits.

Figure 1 shows a plot of *D* versus $E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}))$. Although this plot is quite scattered,[50] there appears to be a tendency for *D* to increase as $E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}))$ increases, described by

$$D = -D_M = 0.11(\pm 0.04)E(\mathrm{Ru}^{3+/2+}(\mathrm{LL})) + 0.32(\pm 0.09) \tag{9}$$

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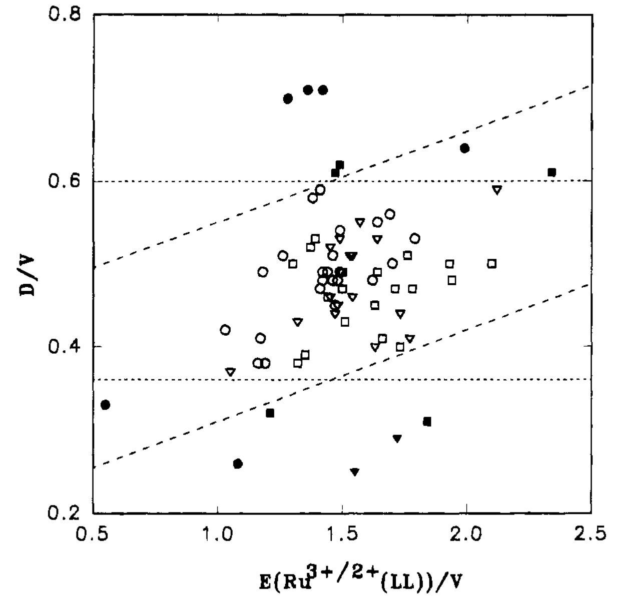

Figure 1. Plot of D against $E(\text{Ru}^{3+/2+}(\text{LL}))$. In this and subsequent figures, the open symbols are "bipyridine-like" and closed symbols are "non-bipyridine-like". In all figures, the tris-LL complexes are squares, bipyridine emitting complexes are circles, and other Ll-emitting complexes are triangles. See Table 1 for details.

The standard deviations of the slope and intercept are shown in parentheses (74 complexes). The hatched lines (Figure 1) are drawn at distances of 1.29σ above and below the intercept (using the σ value of the intercept). Due to the clustering of D values around the center of the plot almost the same group of complexes lie outside the two sets of limits.

Although the dependence upon $E(\text{Ru}^{3+/2+})$ is slight, with a rather low correlation coefficient, this correlation is included because a tendency for D to increase with an increase in the electron accepting ability of the diimine ligands might be expected. Following eq 4, D is equal to the shift in the LL/LL$^-$ potential when Ru^{2+} is replaced by Ru^{3+}. Considering the value of $J_{\text{a,x}}$, this would be expected to be larger for complexes in which there is a stronger metal–ligand interaction.[2] The strongly electron accepting ligands (generally those with more positive $E(\text{Ru}^{3+/2+}(\text{LL}))$, will tend to couple more strongly with the ruthenium center and hence give rise to slightly larger values of D, as is observed. However, more data (especially for complexes with more extreme Ru$^{3+/2+}$ potentials) are needed in order to justify the use of eq 9.

Note that in all the figures different symbols are used for bipyridine emitting species and non-bipyridine emitting species, for comparison purposes. Those complexes whose D values lie between the dotted lines in Figure 1 are largely those which have "bipyridine-like" ligands involved in their reduction and charge transfer processes. The term "bipyridine-like" is used to describe substituted bipyridines, phenanthrolines, and closely related ligands, i.e. those in which redox/optical (π^*) orbital is very similar to that of bipyridine. Complexes lying outside the ±1.29σ range are termed "non-bipyridine-like" (Table 2) and most of them have some special characteristic which makes them fall outside the range of bipyridine-like complexes. Such characteristics are discussed below.

Table 2. Species with D Values Lying Outside the 1.29σ Range (V)

complex	$E(\text{Ru}^{3+/2+}(\text{LL}))$	D	diff[a]
$\text{Ru(bpy)}_2(\text{bbzimH}_2)^{2+}$	1.36	0.71	−0.23
$\text{Ru(bpy)}_2(\text{CN})_2$	1.08	0.26	0.22
$\text{Ru(bpy)}_2\text{Cl}_2$	0.55	0.33	0.15
$\text{Ru(bpy)}_2(\text{bimH}_2)^{2+}$	1.28	0.70	−0.22
$\text{Ru(bpy)}_2(\text{pzH})_2^{2+}$	1.42	0.71	−0.23
$\text{Ru(bpy)}_2(\text{dppene})^{2+}$	1.99	0.64	−0.16
Ru(bt)_3^{2+}	1.49	0.62	−0.14
Ru(hpiq)_3^{2+}	1.47	0.61	−0.13
Ru(dinapy)_3^{2+}	1.21	0.32	0.16
Ru(azpy)_3^{2+}	2.34	0.61	−0.13
Ru(taphen)_3^{2+}	1.84	0.31	0.17
$\text{Ru(bpy)(taphen)}_2^{2+}$	1.72	0.29	0.19
$\text{Ru(bpy)}_2(\text{L2})^{2+}$	1.55	0.25	0.23

[a] Deviation of D from the average of 0.48 V. The first six entries, only, emit from a charge transfer state involving 2,2′-bipyridine.

The excited state reduction potentials, should, if charge is the important factor, lie close to the potentials of the corresponding LL$^{0/-}$(Ir^{3+}) couples. Taking the value of −1.33 V vs SCE for $E(\text{LL}^{0/-}(\text{Ru}^{3+}))$ for $[\text{Ru(bpy)}_3]^{2+}$ and adding the average value of D (0.48 V) we obtain −0.85 V, a value very close to that reported for the $[\text{Ir(bpy)}_3]^{3+}$ complex (−0.83 V)[51] and compared with −0.81 V for the Ru complex from quenching data.[52] While the agreement is reasonable we recall that Ru^{3+} value is for the triplet spin state, forming a doublet reduced species, whereas the Ir^{3+} value is for the ground (singlet) state, also forming a doublet reduced product.

Recently excited state potentials of some ruthenium diimine complexes have been measured directly by Fox and coworkers.[53] The values obtained are in reasonable agreement with those obtained from eqs 2 and 3.

Data for osmium complexes are less plentiful[35–37] (Table 3). The entire osmium data set gives an average D value of 0.54 V with a standard deviation of 0.10 V, i.e. the data are slightly more scattered than those for the ruthenium complexes. Alternatively, the data can be described by the regression line

$$D = -D_{\text{M}} = 0.24(\pm 0.06)E(\text{Os}^{3+/2+}(\text{LL})) + 0.23(\pm 0.08) \qquad (10)$$

As in the case of ruthenium, more data are needed in order to judge the significance of this correlation.

Note that the value of D for $[\text{Os(bpy)}_3]^{2+}$ is close (within experimental error) to the value for $[\text{Ru(bpy)}_3]^{2+}$ (0.44 and 0.49 respectively). The higher average D value for the Os complexes, compared to Ru, is thus probably a reflection of the different set of complexes used to generate it, especially if the dependence on the M$^{3+/2+}$ potential is real (there is a greater percentage of strongly π-accepting ligands in the Os data set).

Correlation between Excited State and Ground State Redox Potentials. To test the basic equations 4 and 5 against experimental data, $E(\text{LL}^{0/-}(\text{Ru}^{3+}))$ values for all Ru-diimine complexes in this study, derived from eq 2, have been plotted against $E(\text{LL}^{0/-}(\text{Ru}^{2+}))$ (Figure 2), and $E(\text{Ru}^{3+/2+}(\text{LL}^-))$ values derived from eq 3 have been plotted against $E(\text{Ru}^{3+/2+}(\text{LL}))$ (Figure 3). In both cases very good linear correlations are obtained (see Table 4 for regression parameters), confirming the basic relationships involved. In most cases the slopes are close to unity.

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(50) The scatter is not surprising since the experimental error in redox potentials recalculated from various sources to a common standard, amounts to about ±0.03 V. E_{00} values also tend to vary somewhat from one laboratory to another, for the same species, and certainly exhibit some solvent dependence (see discussion of deviations from average D values). Data originating from one laboratory give a much smaller scatter than those compiled from several different sources.

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Table 3. Redox and Emission Data for Osmium Complexes (V)

Complex[a,b]	E_1[c]	E_2[d]	E_3[e]	E_4[f]	D	ΔE(red)	E_{00}
$Os(44mbpy)_2(dppb)$	1.49	−1.14	−0.45	0.80	0.69	2.63	1.94
$Os(44mbpy)_2(dppene)$	1.50	−1.13	−0.45	0.82	0.68	2.63	1.95
$Os(tmphen)_2(dppene)$	1.49	−1.27	−0.60	0.82	0.67	2.76	2.09
$Os(bpy)_2(dppb)$	1.58	−1.02	−0.37	0.93	0.65	2.60	1.95
$Os(tmphen)_2(PPh_3)_2$	1.00	−1.44	−0.79	0.35	0.65	2.44	1.79
$Os(44mbpy)_2(dppm)$	1.44	−1.11	−0.47	0.80	0.64	2.55	1.91
$Os(bpy)_2(dppene)$	1.58	−1.03	−0.39	0.94	0.64	2.61	1.97
$Os(5Clphen)_2(dppm)$	1.48	−1.12	−0.49	0.85	0.63	2.60	1.97
$Os(56mphen)_2(dppm)$	1.55	−1.05	−0.43	0.93	0.62	2.60	1.98
$Os(bpy)_2(dppm)$	1.51	−1.02	−0.42	0.91	0.60	2.53	1.93
$Os(tmphen)_2(dppm)$	1.44	−1.21	−0.61	0.84	0.60	2.65	2.05
$Os(55mbpy)_2(dppm)$	1.48	−1.11	−0.52	0.89	0.59	2.59	2.00
$Os(phen)_2(dppm)$	1.56	−1.00	−0.43	0.99	0.57	2.56	1.99
$Os(44mbpy)_2(diars)$	1.23	−1.15	−0.58	0.66	0.57	2.38	1.81
$Os(tmphen)_2(MeCN)_2$	1.03	−1.39	−0.83	0.47	0.56	2.42	1.86
$Os(bpy)_2(diars)$	1.35	−1.03	−0.47	0.79	0.56	2.38	1.82
$Os(phen)_2(dppene)$	1.60	−0.99	−0.44	1.05	0.55	2.59	2.04
$Os(44mbpy)(mmp)_2$	1.14	−1.18	−0.65	0.61	0.53	2.32	1.79
$Os(55mbpy)_2(CO)Cl$	1.37	−1.20	−0.68	0.85	0.52	2.57	2.05
$Os(bpy)_2(CO)Cl$	1.42	−1.05	−0.53	0.90	0.52	2.47	1.95
$Os(phen)_2(dppb)$	1.47	−1.00	−0.49	0.96	0.51	2.47	1.96
$Os(phen)_2(diars)$	1.35	−1.02	−0.51	0.84	0.51	2.37	1.86
$Os(tmbpy)_2(CO)Cl$	1.28	−1.29	−0.79	0.78	0.50	2.57	2.07
$Os(tmphen)_2(py)_2$	0.86	−1.36	−0.86	0.36	0.50	2.22	1.72
$Os(44mbpy)_2(CO)Cl$	1.33	−1.14	−0.65	0.84	0.49	2.47	1.98
$Os(44eabpy)_2(CO)Cl$	0.84	−1.54	−1.07	0.37	0.47	2.38	1.91
$Os(44mbpy)_3$	0.90	−1.14	−0.69	0.45	0.45	2.04	1.59
$Os(44Clbpy)_2(CO)Cl$	1.49	−0.81	−0.36	1.04	0.45	2.30	1.85
$Os(bpy)_2(py)_2$	0.99	−1.07	−0.62	0.54	0.45	2.06	1.61
$Os(bpy)_3$	1.05	−1.05	−0.61	0.61	0.44	2.10	1.66
$Os(phen)_2(py)_2$	0.98	−1.06	−0.68	0.60	0.38	2.04	1.66
$Os(44mobpy)_2(CO)Cl$	1.22	−1.19	−0.85	0.88	0.34	2.41	2.07
$Os(phen)_3$	1.06	−0.97	−0.66	0.75	0.31	2.03	1.72

[a] Data ordered according to D. Data collected from refs 35−37. [b] Overall charges omitted for clarity. [c] $E(Os^{3+/2+}(LL))$. [d] $E(LL^{0/-}(Os^{2+}))$. [e] $E(LL^{0/-}(Os^{3+}))$. [f] $E(Os^{3+/2+}(LL^{0/-}))$.

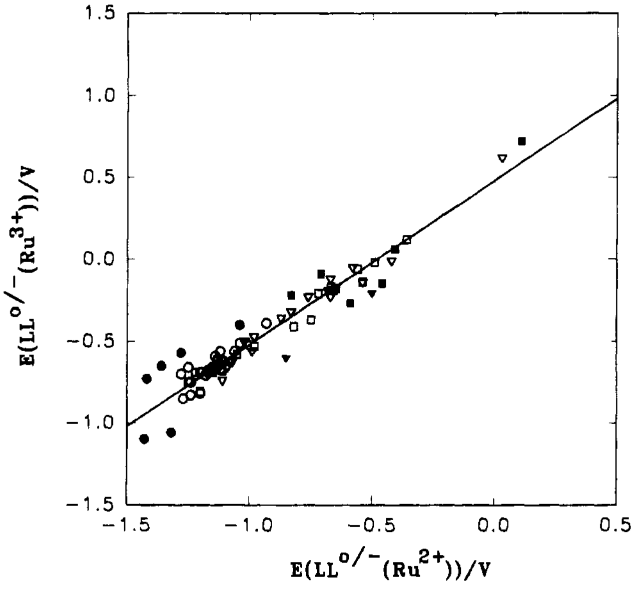

Figure 2. Plot of $E(LL^{0/-}(Ru^{3+}))$ versus $E(LL^{0/-}(Ru^{2+}))$. See legend to Figure 1.

The regression lines with *unit slope* are shown in Figures 2 and 3. The use of eqs 4 and 5 with a slope of one, rather than the least squares data shown in Table 4, provides a much simpler approach without giving significantly larger standard deviations when the observed and calculated values from each equation are compared. Note that, in both Figures 2 and 3, the "non-bipyridine-like" complexes, indicated by open squares, follow the same general pattern, although most of them are displaced a little from the unity line.

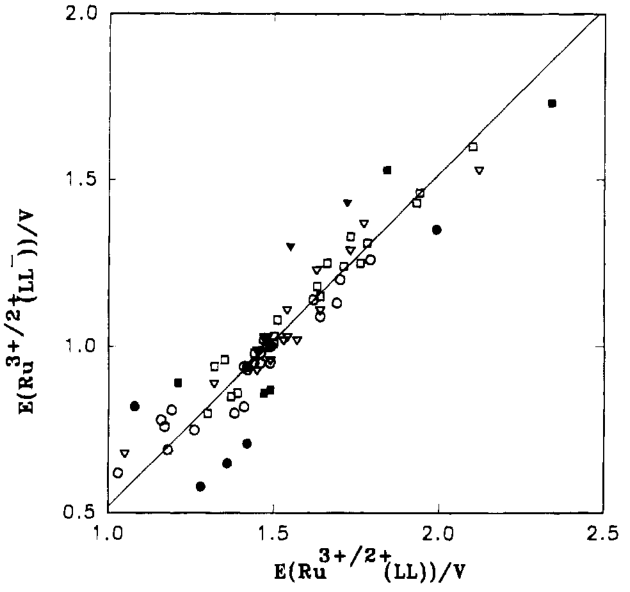

Figure 3. Plot of $E(Ru^{3+/2+}(LL^-))$ versus $E(Ru^{3+/2+}(LL))$. See legend to Figure 1.

Relationships between ΔE(redox) and E_{00}. Equations 6 and 7 require that a plot of ΔE(redox) against E_{00} should be linear with a slope of one and an intercept equal to D, assuming D to be independent of the ligand. Plots of this kind have been reported in the literature for limited series of complexes (e.g. see refs 28, 31−34, and 37). Figure 4 shows data for over 70 ruthenium complexes, a much larger number than has previously been correlated. Linear correlations and slopes near unity are found for the various groups of complexes as described in Table 4.

While these plots are influenced by the experimental errors inherent in each measurement which may be increased by recalculating the data from different sources to a common standard, they show unambiguously the relationship between ΔE(redox) and E_{00}, expressed in eqs 6 and 7. This dependence is valid for the whole group of compounds, albeit being structurally related diimine complexes. Once again, however, the "non-bipyridine-like" species lie off the line, though the deviation from the line is relatively less than for the plots in Figures 2 and 3 (y axis scales are different). The ΔE(redox) term tends to cancel some of the errors in the individual potentials.

Factorization of Excited State Potentials. The alternative definition of excited state redox potentials, eqs 4 and 5, relating the couples involved to the analogous couples in the ground state of the complexes, allows them to be analyzed in terms of the component ligands without necessarily knowing E_{00}. A fairly good estimate of the excited state potentials, $E(Ru^{3+/2+}(LL^-))$ and $E(LL^{0/-}(Ru^{3+}))$, may be obtained from the observable ground state potentials, $E(Ru^{3+/2+}(LL))$ and $E(LL^{0/-}(Ru^{2+}))$, by adding and subtracting D respectively (eqs 4 and 5). Note here that the excited state *reduction* potential is obtained from the ground state *oxidation* potential and vice versa. The simple relationship to the ground state potentials allows us to derive the excited state redox potentials directly from the ligand electrochemical parameters, $E_L(L)$.[54]

(a) The $E(Ru^{3+/2+}(LL^-))$ Value. Alternatively we may factorize the excited state redox potentials showing the contribution of each ligand to the potential. This factorization has been carried out for ground state $Ru^{3+/2+}$ couples[54] and recently for some diimine reduction potentials using the concept of a redox

Table 4. Linear Regression Parameters for Bipyridine-like Ruthenium Complexes[a]

plot (x,y)	type of compound[a]	slope	intercept	R[b]	no.[c]
$E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}))$, $E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}^-))$	all diimines	0.92(0.03)	−0.35(0.05)	0.97	61
	tris diimines	0.96(0.04)	−0.40(0.04)	0.98	20
	bipyridine	0.82(0.05)	−0.24(0.05)	0.96	23
	LL-emitting[d]	0.92(0.04)	−0.35(0.05)	0.97	38
$E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{2+}))$, $E(\mathrm{LL}^{0/-}(\mathrm{Ru}^{3+}))$	all diimines	1.01(0.02)	0.49(0.05)	0.98	61
	tris diimines	0.98(0.04)	0.45(0.04)	0.99	20
	bipyridine	1.16(0.15)	0.68(0.06)	0.86	23
	LL-emitting[d]	1.04(0.03)	0.50(0.05)	0.99	38
E_{00}, ΔE(redox)	all diimines	0.91(0.04)	−0.25(0.05)	0.96	61
	tris diimines	0.90(0.50)	−0.22(0.04)	0.97	20
	bipyridine	0.76(0.06)	0.14(0.04)	0.94	23
	LL-emitting[d]	0.98(0.05)	−0.41(0.05)	0.96	38

[a] Excludes species with D values differing from the average (0.48 V) by more than 1.29σ. [b] Regression coefficient. [c] Number of species in the set. [d] All bipyridine-like complexes other than those emitting from MLCT state involving bipyridine.

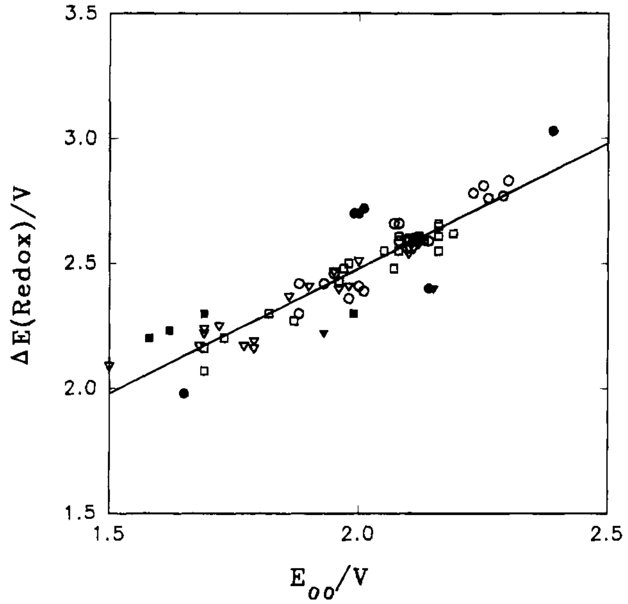

Figure 4. Plot of ΔE(redox) versus E_{00}. See legend to Figure 1.

active fragment.[55] In a similar manner, for a complex, [Ru(LL)WXYZ], we can write

$$E(\mathrm{Ru}^{3+/2+}(\mathrm{LL}^-)) = \sum E_\mathrm{L}(\mathrm{L}) = \sum E_\mathrm{L}(\mathrm{WXYZ}) + 2E_\mathrm{L}(\mathrm{LL}^-) \quad (11)$$

where the right-hand side of eq 11 reflects the sum of the E_L(L) parameters of the four unreduced ligands (W, X, Y and Z) plus twice the $E_\mathrm{L}(\mathrm{LL}^-)$ parameter for the reduced diimine. Table 1 contains these $E_\mathrm{L}(\mathrm{LL}^-)$ values and average values (where several data are available for the same ligand) are given in Table 5.

The $E_\mathrm{L}(\mathrm{LL}^-)$ values were calculated with the assumption that the extra electron is localized on *one* ligand with the other ligands remaining unreduced. This provides a more useful analysis than assuming, in a $[\mathrm{Ru(LL)_3}]^{2+}$ species for example, the possibility of delocalization of the electron over all three ligands.[56,57] Calculated in this latter manner, the parameters could not be usefully transferred to species containing less than three LL ligands.

Table 5. $E_\mathrm{L}(\mathrm{LL}^-)$ Values for Reduced Diimine Ligands

ligand	$E_\mathrm{L}(\mathrm{LL}^-)(\sigma)$[a]	no.[a,b]
33mbpy	−0.01	
44dbbpy	0.03	
44dcebpy	−0.06	
44dpbpy	−0.01	
44mbpy	−0.03	
47pphen	−0.01	
4Clbpy	0.07	
4tepbpy	−0.04	
5Clphen	0.05	
66mbpm	0.09	
azpy	0.10	2
BL	0.11 (0.01)	3
biq	0.02 (0.02)	3
bpm	0.07	
bpy	0.00 (0.05)	29
bpz	0.10	2
bt	−0.06	
dinapy	0.04	
dmch	0.01 (0.02)	3
HL0	0.04	
HL3	−0.01	
hphen	0.01	2
hpiq	−0.06	
ibiq	0.01	2
L1	0.03	
L2	0.13	
phen	0.04	
pq	0.00	2
pynapy	0.03	
taphen	0.15	2
terpy	0.10 (0.03)	4
tmbpy	−0.03	

[a] Where there is no entry in the number (no.) column, the datum is for a single complex. For an average derived from 3 or more complexes, a standard deviation (σ) is noted in parentheses. [b] Number of complexes used to derive an average.

The $E_\mathrm{L}(\mathrm{LL}^-)$ values for these anionic ligands are, on average, about 0.24 V lower than those for neutral ligands and are close to zero (hence the two coordination sites of LL^- require a correction of 0.48 V (D) to the ground state potentials). These newly observed values of $E_\mathrm{L}(\mathrm{LL}^-)$ for anionic diimine ligands indicate that the reduction to the anionic form causes loss of π-accepting properties since simple, non-π amines, such as ammonia and ethylenediamine, have E_L(L) values near 0 V. Apparently the increase in electron density caused by reduction of diimines is not sufficiently large to make them π-donors.

The average value of $E_\mathrm{L}(\mathrm{bpy}^-)$ is 0.00 V (NHE), with a standard deviation of 0.05 V. There does not appear to be any systematic dependence upon the other ligands. The deviations for $E_L(\mathrm{bpy}^-)$ are larger than the expected experimental error and probably reflect subtle inter-ligand interactions which are not included in the E_L(L) values. A similar value for $E_\mathrm{L}(\mathrm{bpy}^-)$ can be obtained by substituting the second reduction potential of $[\mathrm{Ru(bpy)_3}]^{2+}$ into eq 12,[55] assuming the validity of this

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equation for the second reduction potential. However this is not an accurate procedure since an error of only 0.01 V in the second reduction potential leads to a variation in $E_L(\text{bpy}^-)$ of 0.02 V.

(b) The $E(\text{LL}^{0/-}(\text{Ru}^{3+}))$ Value. The $E(\text{LL}^{0/-}(\text{Ru}^{3+}))$ value can be related to factors describing the contribution of the ligands to the reduction potential $E(\text{LL}^{0/-}(\text{Ru}^{2+}))$ recently reported[55] to be related to $\sum E_L(\text{L})$:

$$E(\text{LL}^{0/-}(\text{Ru}^{2+})) = S_L \sum E_L(\text{L}) + I_L \qquad (12)$$

In eq 12 $\sum E_L(\text{L})$ is the sum over all the ligands around the ruthenium atom, *excluding* the ligand which is being reduced. The S_L value is characteristic of the given redox active fragment (e.g. Ru(bpy)) and represents its sensitivity towards other components of the coordination sphere. I_L is a constant related to the reduction potential of the relevant free ligand and the degree of interaction between the metal center and ligand.

Equation 4 then provides the simple result that, for the "bipyridine-like" species, $E(\text{LL}^{0/-}(\text{Ru}^{3+}))$ is just 0.48 V more positive than $E(\text{LL}^{0/-}(\text{Ru}^{2+}))$. This simple calculation provides a fit for $E(\text{LL}^{0/-}(\text{Ru}^{3+}))$ which deviates no more than 0.07 V from the value calculated by using eq 2. Thus the factorization of $E(\text{LL}^{0/-}(\text{Ru}^{3+}))$, using eqs 4 and 12 can be carried out using the same set of parameters as for the ground state couples.

Deviations from Average *D* Values. There are systems which do not exactly fit the correlations described above, the so-called "non-bipyridine like" complexes. These are listed in Table 2. Deviations may be expected for various reasons, such as differences in the nature of the redox orbital, steric effects and solvent effects.

Since there are a large number of substituted bipyridines and other closely related ligands in the data set, the average D (0.48 V) is very close to that for the $[\text{Ru(bpy)}_3]^{2+}$ complex (0.49 V). Deviations from the average D might be expected to increase as the ligand redox orbital (i.e. the LUMO of the complex) becomes more different from the lowest π^*-orbital of bipyridine. For example, the π^* orbitals of phenylazopyridine (azpy) and dipyridopyridazine (taphen) are mainly localized on the respective N=N groups of these two ligands,[21,58,59] making them different in nature from the LUMO of bipyridine. In addition, the azo group in phenylazopyridine is very close to the Ru atom which may cause the large D values observed for azpy complexes. In contrast, in taphen the ligand reduction orbital is localized further from the ruthenium atom, which may explain the small D values for taphen complexes. Alternatively, if the dependence of D on $E(\text{Ru}^{3+/2+}(\text{LL}))$ shown in eq 9 is real then azpy may have a large D value due to its low π^* energy and consequent stronger interaction with the metal.

The π^* orbitals may also differ from that of bipyridine due to partial saturation of the aromatic system, which limits the degree of delocalization and may cause steric strain. Steric effects on the Ru−LL bonds could also alter D, as in ligands which are substituted in the equivalent of the 6,6′-position of 2,2′-bipyridine, e.g. 6,6′-dimethylbipyridine, dinapy[60] and biquinoline, although biquinoline complexes have quite "normal" D values.

Strong specific interactions with the solvent, shown by solvatochromism in absorption or emission spectra and/or solvent-dependent electrochemistry (e.g. in $\text{Ru(bpy)}_2(\text{CN})_2$),[61−63] $\text{Ru(bpy)}_2\text{Cl}_2$[64] and[65,66] $[\text{Ru(bpy)}_2(\text{bimH}_2)]^{2+}$), may also cause extreme D values. The thermodynamic relationships (eqs 2−8) assume all species to be equilibrated thermally and with respect to solvent. This will be true for all species except the emitting excited state (at low temperature) where the frozen solvent is ordered around the ground state configuration. Thus there is a small solvent reorganization energy which increases the apparent magnitude of E_{00} in all species, and decreases D. This reorganization energy will be larger for the complexes which have stronger interactions with the solvent. More importantly, most of the electrochemical data are collected in acetonitrile whereas the low temperature emission spectra are mostly collected in ethanol/methanol glasses. Complexes that interact strongly with the alcohols will be stabilized in this solvent mixture significantly more than they are in acetonitrile. Thus there will be differences between the energies of the solvated ground state species that are larger than for most other complexes. The most likely result of this is that E_{00} will be increased compared to ΔE(redox), and therefore D will appear to be smaller, as is observed for the dicyano and dichloro complexes.

For the biimidazoles and bis(pyrazole) which are H-bond donors, it appears that the opposite effect may occur; there is evidence[67] that ΔE(redox) may be decreased in MeOH compared to CH_3CN, and thus ΔE(redox) is large compared to E_{00}, and D is large. Note that the *N*-Me−imidazole complex, which lacks the acidic proton, shows normal "bipyridine-like" behavior. The corresponding pyridylimidazole ligands also show "bipyridine-like" behavior within experimental error. Detailed solvent-dependence studies have not been reported for the biimidazole species.

However, while suggesting this explanation, we do note that the reported electrochemical behavior for the biimidazole series of complexes is unusual with respect to shifts upon protonation/deprotonation, and other explanations are being considered.

All of the "non-bipyridine-like" species, with usually small values of D, fall into one of the above categories and are therefore "predictably" different, as are some of the complexes with large values of D, such as $[\text{Ru(azpy)}_3]^{2+}$ and the biimidazole and pyrazole-containing species. The other remaining complex with a large value of D is the dppene complex, which however, is "bipyridine-like" if eq 9 is used to calculate D; i.e. it also has a high $\text{Ru}^{3+/2+}(\text{LL})$ potential. Finally, emission spectra for a few species, such as the pyrazine−triazole complexes (ligands L0−L3[49]) are uncorrected. This may explain the rather low D values of most of these species.

Conclusions

The alternative approach to excited state redox potentials presented here emphasizes the relationship of the excited state couples to the corresponding ground state couples (eqs 4 and 5). For the series of diimine complexes explored here, the excited state redox potentials can be obtained from the related ground state potentials simply by adding or subtracting the quantity D, which is approximately a constant (0.48 V) for these species.

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Further, excited state redox potentials can be obtained directly by using the ligand electrochemical parameters, $E_L(L)$, making use of the newly obtained $E_L(L^-)$ values for reduced ligands.

The quantity D has been defined by a simple thermodynamic procedure, reflecting the difference in the redox potentials induced by the presence of the electron in the redox orbital of the ligand or by the existence of a hole in the redox orbital of the central metal atom. This difference essentially reflects the Coulomb interaction ($J_{a,x}$) between an electron on the metal and one in the diimine π^* orbital.

The linearity of the $\Delta E(\text{redox}) - E_{00}$ plots forms a very sound basis for predictive purposes. If both $E(\text{Ru}^{3+/2+}(\text{LL}))$ and $E(\text{LL}^{0/-}(\text{Ru}^{2+}))$ are known, E_{00} can be predicted with a tolerance of about 0.1 V. If only one potential is known then E_{00} can be predicted by adding the corresponding value of D. In all these cases the ligand redox orbital must be clearly specified as belonging to the bipyridine-like group of complexes. While this methodology is used primiarly to describe ruthenium systems, osmium appears to behave in a similar manner.

Abbreviations

33mbpy = 3,3′-dimethyl-2,2′-bipyridine; 3aep = 3-(2-aminoethyl)pyridine; 4Clbpy = 4-chloro-2,2′-bipyridine; 44Clbpy = 4,4-dichloro-2,2′-bipyridine; 44dcebpy = 4,4′-dicarboxyethyl-2,2′-bipyridine; 44dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; 44mbpy = 4,4′-dimethyl-2,2′-bipyridine; 44mobpy = 4,4′-dimethoxy-2,2-bipyridine; 44eabpy = 4,4′-bis(N,N-diethylamino)-2,2′-bipyridine; 44dpbpy = 4,4′-diphenyl-2,2′-bipyridine; 4tepbpy = 4-(triethylphosphonio)bipyridine; 47pphen = 4,7-diphenyl-1,10-phenanthroline; 5Clphen = 5-chloro-1,10-phenanthroline; 56mphen = 5,6-dimethyl-1,10-phenanthroline; 66mbpm = 6,6′-dimethyl-4,4′-bipyrimidine; azpy = 2-(phenylazo)pyridine; bbzimH_2 = 2,2′-dibenzoimidazole; bimH_2 = 2,2′-biimidazole; biq = 2,2′-biquinoline; BL = 2,3-bis(2-pyridyl)quinoxaline; bpm = 2,2′-bipyrimidine; bpy = 2,2′-bipyridine; bpz = 2,2′-bipyrazine; bt = 2,2′-bi-2-thiazoline; diars = o-phenylenebis(dimethylarsine); dmch = 5,6-dihydro-4,7-dimethylbenzo[3,2-*b*:2′,3′-*j*][1,10]phenanthroline; dp = dipyrido[3,2-*a*:2′,3′-*c*]phenazine; dinapy = 5,6-dihydro-dipyrido[3,2-*b*:2′,3′-*j*][1,10]phenanthroline; dpah = Bis(2-pyridyl)amine; dppb = 1,2-bis(diphenylphosphino)benzene; dppe = cis-1,2-bis(diphenylphosphino)ethane; dppene = cis-1,2-bisdiphenylphosphino)ethene; dppm = 1,2-bis(diphenylphosphino)methane; en = ethylenediamine; HL0 = 3-(pyrazin-2-yl)-1,2,4-triazole; hpiq = 3,4-dihydro-1-(2-pyridyl)isoquinoline; hphen = 5,6-dihydro-1,10-phenanthroline; ibiq = 3,3′-biisoquinoline; L0 = deprotonated HL0; L1 = 1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole; L2 = 1-methyl-5-(pyrazin-2-yl)-1,2,4-triazole; L3 = 3-methyl-5-(pyrazin-2-yl)-1,2,4-triazole; MeCN = acetonitrile; mmp = dimethylphenylphosphine; mpp = methyldiphenylphosphine; nmi = *N*-methylimidazole; pbzimH = 2-(2-pyridyl)benzimidazole; pimH = 2-(2-pyridyl)imidazole; phen = 1,10-phenanthroline; PPh_3 = triphenylphosphine; pq = 2-(2-pyridyl)quinoline; py = pyridine; pyd = pyridazine; pynapy = 2-(2-pyridyl)-1,8-naphthyridine; pz = pyrazole anion; pzH = pyrazole; taphen = dipyrido[3,2-*c*:2′3′-*e*]pyridazine; terpy = 2,2′:6′,2″-terpyridine; tmbpy = 4,4′,5,5′-tetramethyl-2,2′-bipyridine; tmphen = 4,5,6,7-tetramethyl-1,10-phenanthroline.

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