Notes

Ligand Additivity in the Oxidation Potentials of Bidentate Mixed-ligand Ruthenium(II) Complexes

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Reversible oxidation half-wave potentials $E_{\frac{1}{2}}^{r}$ have been found to be additive according to the number of ligands x by analysing the potential map of $[Ru(bipy)_{3-x}L_x]^{n+}$ complexes (bipy = 2,2′-bipyridine; L = polypyridine or β-diketone). The slope of plots of $E_{\frac{1}{2}}^{r}$ *vs.* x depends on the kind of ligand L and affords a measure of the π-donor/π-acceptor ability of the bidentate ligands. Ligand parameters, P_L, for various bidentate ligands, are proposed.

Reversible half-wave potentials have been used to estimate the valence electronic energy levels for a number of organic compounds.[1] In recent years, various attempts have been made to evaluate the valence electronic energy of metal complexes from electrochemical data. For instance, the correlation between optical and electrochemical properties of 2,2′-bipyridine (bipy) complexes of ruthenium(II) has been examined in order to estimate the energy of metal-to-ligand charge transfer (m.l.c.t.) absorption and emission processes from the electrochemical potentials.[2] This relation has been found to provide a convenient method for determining the absolute position of the energy levels of ruthenium(II) complexes. Furthermore, a linear correlation between oxidation potentials and the valence electronic energies in both gas and solid phases has been reported.[3]

For the purpose of analysing the electronic effect of ligands on the valence electronic energies quantitatively, Chatt *et al.*[4] defined a ligand parameter, P_L, calculated from the potential difference between $[Cr(CO)_5L]$ and $[Cr(CO)_6]$. Bursten[5] proposed a simple additivity relationship for predicting the oxidation potentials in d^6 $[ML_xL'_{6-x}]^{n+}$ ($M = Cr^0$ or Mn^I; L, L′ = CO or CNR) systems. These ligand parameters for unidentate ligands have been extended to bidentate systems, and P_L for bipy has been determined as $P_{bipy} = -1.14$ V from the redox potentials for $[Ru(bipy)_2L(L')]$ complexes.[6]

We have previously reported the syntheses and electrochemistry of a series of ruthenium complexes containing both bipy and β-diketone as ligands.[7] Here, we report the ligand additivity in the reversible oxidation half-wave potentials of these ruthenium complexes and propose a ligand parameter for bidentate ones such as polypyridines and β-diketones.

Experimental

The mixed-ligand bipy–β-diketone ruthenium complexes were prepared from $[Ru(bipy)_2Cl_2]$ and $[Ru(bipy)Cl_4]$ as reported previously.[7] All the potentials are referred to the saturated calomel electrode (s.c.e.) and calibrated by using ferrocene–ferrocenium as an internal reference.[8]

Table 1. Electrochemical data for the complexes $[Ru(bipy)_{3-x}L_x]^{n+}$ in MeCN at 25 °C

L	$E_{\frac{1}{2}}^{r}(Ru^{III}-Ru^{II})$/V *vs.* s.c.e. $x = 0$	1	2	3	Ref. for $E_{\frac{1}{2}}^{r}$
L^1	+1.26		−0.28	−1.07	*a*
L^2		+0.59	−0.08	−0.77	7, *a*
L^4		+0.70		−0.65	7, *a*
L^3		+0.67		−0.52	7, *a*
L^5			+0.31	−0.09	*a*
L^6		+0.90		+0.10	7, *a*
L^7		+0.93		+0.14[b]	7, *c*
L^8		+1.12		+0.80	*d*
L^9		+1.22	+1.21	+1.17	*e*
L^{10}		+1.40	+1.55	+1.69	2*c*
L^{11}		+1.49	+1.72	+1.98	2*c*
L^{12}		+1.60	+1.88	+2.10	*f*
L^{13}		+1.60	+1.89	+2.23	*f*

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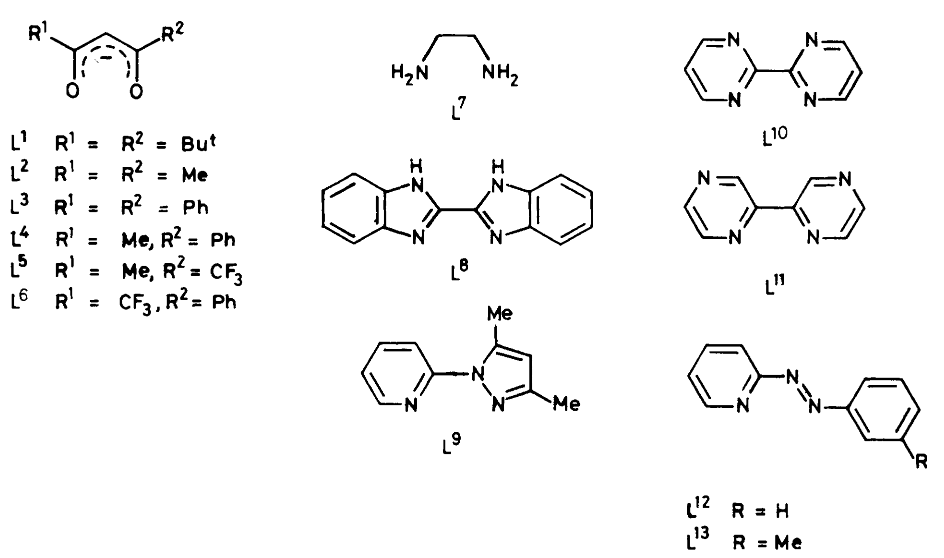
Results and Discussion

Each of the $[Ru(bipy)_{3-x}L_x]^{n+}$ complexes showed a reversible one-electron oxidation process over a wide range of potential (+2.2 to −1.1 V), which corresponds to removal of an electron from the highest occupied molecular orbital (h.o.m.o.) of ruthenium(II) to form the d^5 low-spin ruthenium(III) state. These oxidation potentials vary with the ligand L and its number x as listed in Table 1. Plots of $E_{\frac{1}{2}}^{r}$ *vs.* x give straight lines, which intersect at the $E_{\frac{1}{2}}^{r}$ value for $[Ru(bipy)_3]^{2+}$, as shown in the Figure. The slopes of these lines, $dE_{\frac{1}{2}}^{r}/dx$, depend on the ligand L and increase in the order of $L^1 < L^2 < L^4 < L^3 < L^5 < L^6 < L^7 < L^8 < L^9 < L^{10} < L^{11} < L^{12} < L^{13}$. The complex $[Ru(bipy)_3]^{2+}$ and its derivatives have a filled d_π symmetry orbital as the h.o.m.o. and an empty π^*_L orbital as the lowest occupied molecular orbital (l.u.m.o.). As the reversible oxidation half-wave potentials $E_{\frac{1}{2}}^{r}$ are considered to be a measure of the energy level of the h.o.m.o., the linear plots indicate that this energy level is raised or lowered by the



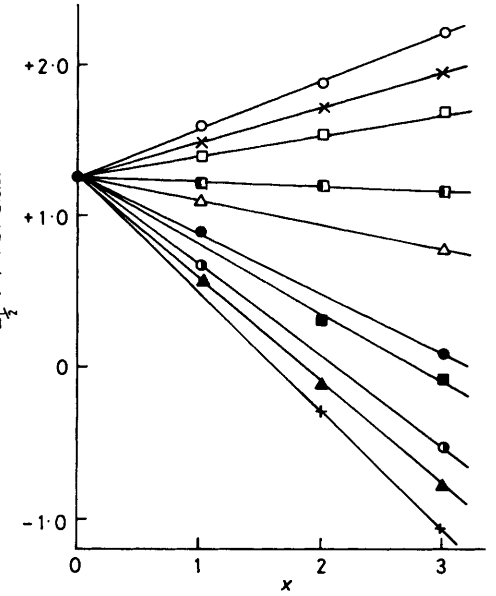


Figure. Plots of the oxidation potentials $E_{\frac{1}{2}}$ *vs.* the number of ligands x for $[\mathrm{Ru(bipy)}_{3-x}\mathrm{L}_x]^{n+}$ complexes. Ligands: (+) L^1; (▲) L^2; (◑) L^3; (■) L^5; (●) L^6; (△) L^8; (◧) L^9; (□) L^{10}; (×) L^{11}; (○) L^{13}

Table 2. The slope $(\mathrm{d}E_{\frac{1}{2}}{}^{\mathrm{r}}/\mathrm{d}x)_{\mathrm{L}}$ for a series of bidentate ligands in $[\mathrm{Ru(bipy)}_{3-x}\mathrm{L}_x]^{n+}$ and ligand parameter P_{L}

L	$(\mathrm{d}E_{\frac{1}{2}}{}^{\mathrm{r}}/\mathrm{d}x)_{\mathrm{L}}{}^{a}$/V	$P_{\mathrm{L}}{}^{b}$/V
L^1	−0.78	−1.92
L^2	−0.68	−1.82
L^4	−0.64	−1.78
L^3	−0.59	−1.73
L^5	−0.45	−1.59
L^6	−0.39	−1.53
L^7	−0.38	−1.52 (−1.57)^{c}
L^8	−0.15	−1.29
L^9	−0.03	−1.17
bipy	0	−1.14
L^{10}	+0.14	−1.00
L^{11}	+0.24	−0.90
L^{12}	+0.28	−0.86 (−0.76)^{c}
L^{13}	+0.32	−0.82

[a] Obtained from the plots of the oxidation potentials $E_{\frac{1}{2}}{}^{\mathrm{r}}$ *vs.* the number of ligands x. [b] Calculated from the equation $P_{\mathrm{L}} = (\mathrm{d}E_{\frac{1}{2}}{}^{\mathrm{r}}/\mathrm{d}x)_{\mathrm{L}} - 1.14$ V. [c] The values in parentheses are quoted from ref. 6.

stepwise substitution of bipy with another ligand L. The extent of stabilization of the h.o.m.o. level is determined by whether the ligand acts as an electron donor or acceptor; in the case of a π-acceptor ligand, the h.o.m.o. energy is lowered and thus the oxidation potential shifts in the anodic direction with increasing number of ligands. Thus, the values of the slopes in Table 2 can be considered to be a electrochemical series of ligands, and afford a measure of π-donor/π-acceptor ability of the bidentate ligands; a ligand with a negative slope has a stronger π-donor property compared to bipy, while a ligand with a positive slope has a stronger π-acceptor property.

Chatt *et al.*[4] proposed the ligand parameter P_{L}, defined by equation (1); P_{L} can be related to the value $(\mathrm{d}E_{\frac{1}{2}}{}^{\mathrm{r}}/\mathrm{d}x)_{\mathrm{L}}$ for $[\mathrm{M(CO)}_{6-x}\mathrm{L}_x]^{n+}$.[4]

$$P_{\mathrm{L}} = E_{\frac{1}{2}}{}^{\mathrm{r}}[\mathrm{Cr(CO)}_5\mathrm{L}] - E_{\frac{1}{2}}{}^{\mathrm{r}}[\mathrm{Cr(CO)}_6] \qquad (1)$$

Here we can extend these ligand parameters to the bidentate ligands by using the ligand additivity in the reversible oxidation half-wave potentials for $[\mathrm{Ru(bipy)}_{3-x}\mathrm{L}_x]^{n+}$. The parameters P_{L} derived from the value of the slope, $(\mathrm{d}E_{\frac{1}{2}}{}^{\mathrm{r}}/\mathrm{d}x)_{\mathrm{L}}$, are summarized in Table 2, in which the P_{L} value for bipy is taken as −1.14 V. Our P_{L} values for L^{12} and L^7 are in fair agreement with those obtained by Datta[6] (Table 2).

In conclusion, we report here the additivity in the oxidation potentials based on the potential map of $[\mathrm{Ru(bipy)}_{3-x}\mathrm{L}_x]^{n+}$, and propose ligand parameters P_{L} for bidentate ligands. Both the potential map and the ligand parameter are very useful for prediction of the properties of metal complexes and for the design of new ones.

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