Non-additive Ligand Effects in Series of L-Substituted Ruthenium Halide Complexes (L = CH₃CN, AsMe₃, CO)

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In the series $[RuX_6]^{3-}$, $[RuX_5(CH_3CN)]^{2-}$, *trans*-$[RuX_4(CH_3CN)_2]^{1-}$ (X = Cl, Br), where the ligands are not very contrasting in nature, ruthenium III/II redox couple shifts almost twice further for the first introduction of nitrile than for the second, contrary to recent predictions. Distinct non-additive ligand effects are also demonstrated in the analogous series of arsine complexes. The remarkable electrode potential differences in geometrical isomers of mixed halide/nitrile/carbonyl ruthenium complexes support the non-linear accumulation of ligand electronic effects.

INTRODUCTION

The ligand additivity principle has been considered as one of the foundations of intuitive inorganic chemistry [1]. This concept assumes that the effects exerted by an array of ligands on the electronic properties of a given coordination complex are fundamentally additive. Since the solution redox potentials can be related to the relevant frontier orbital levels, it is of central importance in probing the energetics of a given complex.

It is clearly desirable to codify orderly trends in metal-centered electrode potentials as the ligand complement changes. Empirical approaches to ranking the relative electrochemical effects of individual ligands stem from the pioneering work of Pletcher, Picket, and Chatt [2], who focused initially on the fixed $Cr(CO)_5L$ binding site, to provide a numerical scale of P_L values for numerous ligands

Formal analysis for extended series of the form $MX_{6-n}L_n$ (n = 0 to 6) was provided by Bursten [3], who separated isotropic (i.e. σ and electrostatic) and π-bonding terms, and addressed isomer-specific potential differences by elementary angular-overlap arguments.

Lever [4] has treated additivity phenomena ambitiously, using his own tabulation of redefined ligand parameters, E_L, to predict shifts in redox potentials for an enormous range of organometallic and coordination compounds of a given metal ion bearing any permutation of some 200 ligands.

However, Heath and Humphrey [5] pointed out in 1991 that the simple progression from $[OsBr_6]^{3-}$ to $[OsBr_5(CO)]^{2-}$ and trans-$[OsBr_4(CO)_2]^-$ defies both Bursten's and Lever's expectations, since the shifts in Os(III/II) is 1.9 V for the first Br/CO substitution, but only 0.6 V for the second. They ascribed this discontinuous shift in electrode potential to the mutual influence of strongly π-accepting trans-disposed ligands.

With this in mind, we draw attention to systems ($[RuX_{6-n}L_n]^{z-}$ ($n = 0, 1$, trans-2; X = Cl, Br; L = CH$_3$CN, AsMe$_3$) where the ligands are not very contrasting in terms of their donor-acceptor properties. The truncated series RuX$_6$, RuX$_5$L, trans-RuX$_4$L$_2$, and geometric isomer comparisons are very instructive for testing models of electrochemical ligand-additivity phenomena as illustrated in this work.

EXPERIMENTAL

The electrochemical experiments were conducted in 0.5 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$, by using a Power Macintosh computer-driven PAR 170 electrochemistry instrument via an Echem v1.35β MacLab interface system. The solvent was distilled from P$_2$O$_5$ drying agent under N$_2$ for at least 30 minutes prior to use. The electrolyte was recrystallized twice from ethyl acetate/ether and dried in stages (room temperature to 100°C) under vacuum until a satisfactory voltammetric range was achieved (±2 V in CH$_2$Cl$_2$). The non-aqueous reference electrode was of the form [Ag|AgCl|(0.05 M Bu$_4$NCl, 0.45 M Bu$_4$NBF$_4$/ CH$_2$Cl$_2$)] and was constructed from a Metrohm 24-140 Ag/AgCl assembly and was separated from solution by two porous glass frits. Under these conditions, ferrocene was oxidized to ferrocenium ion at +0.55 V and was maintained reasonably well within the working temperature range of –60 to +20°C.

Variable-temperature voltammetric measurements were carried out in a jacketed cell which was connected to a Lauda model RL6 circulating cryostat bath. In this set up, temperature as low as –70°C was readily attained and with respectable stability at chosen temperatures. The actual solution temperature was precisely monitored by a digital thermometer with the probe placed directly within the cell. Routine scan rates were 100 and 200 mV s^{-1} in cyclic voltammetry and 10 mV s^{-1}, with positive feedback resistance compensation and phase-sensitive detection ($\omega = 205$ Hz), in AC measurements. The measured potentials were corrected for the influence of temperature by cross reference to internal redox standards, either ((Bu$_4$N)$_2$[Ru$^{IV/III}$X$_6$]) or ferrocene, which was added before the end of the experiment.

The voltammetric-scale electrogeneration of sequentially-substituted hexahalide parent complexes were also performed with a PAR 170 potentiostat. The parent [RuX$_6$]$^{2-}$ complex was usually introduced at –60°C to prevent premature substitution. The first reduction (Ru$^{IV} \rightarrow$ Ru^{III})-induced substitution of halide by L occurred in the range –55 to –50°C when the solution is 10^{-3} M in parent complex and with two equivalent moles of L. The disubstituted complexes were generated by either reducing Ru^{IV} directly to Ru^{II} at –60°C or reducing Ru^{III} to Ru^{II} at higher temperatures. Electrochemical routes from [RuX$_6$]$^{-2}$ to [RuX$_4$L$_2$]$^-$ are shown in Fig. 1. The electrochemical synthesis and in situ UV-Vis-NIR spectroscopic characterization of the mixed ligand ruthenium complexes will be detailed elsewhere [6].

RESULTS AND DISCUSSION

The complexes [RuX$_6$]$^{2-}$ and [RuX$_5$L]$^{2-}$ complexes were found to undergo ligand substitution upon reduction in coordinating solvents [7] and this tendency was exploited in generating series of mixed X–L complexes of ruthenium, with careful control of temperature and concentration of ligand L.

Table 1 presents the E$_{1/2}$ data for each of the 17 complexes under consideration, comprising four truncated series ($n = 0$ to 2; L = CH$_3$CN, PMe$_3$; and X = Cl$^-$ or Br$^-$) and a series of mixed halide/nitrile/carbonyl complexes. All couples showed reversible voltammetric response under the conditions given in Table 1 except the Ru$^{III/II}$ couples for RuX$_6$ and RuX$_5$L, in which, their electrode potential values were estimated from half-height of the reduction wave.

Table 1. Electrochemical Data (in V) for [Ru$^{III/II}$X$_{6-n}$L$_n$]$^{z/z-}$, Measured vs. Ag/AgCl^a under the conditions indicated^{b-e}. (Values in parenthesis correspond to the Ru$^{IV/III}$ couple.)

n	L = MeCN		L = AsMe$_3$		L = CO*, MeCN
	X = Cl$^-$	X = Br$^-$	X = Cl$^-$	X = Br$^-$	X = Cl$^-$
0^b	–1.45 (+0.23)	–1.37 (+0.22)	–1.45 (+0.23)	–1.37 (+0.22)	–1.45
1^c	–0.75 (+0.80)	–0.63 (+0.77)	–0.93 (+0.74)	–0.75 (+0.72)	+0.28*
trans-2^d	–0.38 (+1.45)	–0.23 (+1.39)	–0.66 (+1.01)	–0.55 (+1.03)	+0.63
cis-2^e	–0.22	–0.10	–0.51	–0.34	+0.87

^{a}The $E_{1/2}$ values listed here, recorded as described in CH$_2$Cl$_2$ vs. Ag/AgCl, can be compared with electrode potentials measured vs. common reference electrodes in CH$_3$CN at ambient temperature, as follows: ~65 mV more positive when referred to the NHE, ~180 mV less positive when referred to SCE, and ~600 mV less positive when referred to Fc/Fc$^+$. ^{b}CH$_2$Cl$_2$ at -60 °C. ^{c}10% MeCN/CH$_2$Cl$_2$ or 2 equiv moles of L at -50 °C. *Prepared by Menglet (Ref. 10). ^{d}10% MeCN/CH$_2$Cl$_2$ or 2 equiv moles of L at -30 °C. ^{e}10% MeCN/CH$_2$Cl$_2$ at or two equiv moles of L -60 °C and upon reduction of Ru^{IV} directly to Ru^{II}.
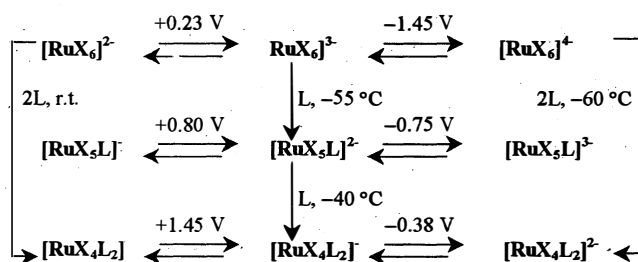
Fig. 1. Synthetic scheme showing the stepwise substitution of a ruthenium hexahalide by a neutral ligand, yielding pentahalo and tetrahalo complexes of ruthenium, including all electrochemically accessible species and the pathways between them. The potentials shown apply to complexes where $X = Cl$, $L = MeCN$, and trans-X_4L_2 isomer.

Fig. 2. Voltammetry of $[Bu_4N][RuCl_4(MeCN)_2]$ at 230 K, and the location of $Ru^{III/II}$ couples (vs Ag/AgCl) for comparable complexes.

Figure 2 shows a representative low-temperature cyclic voltammogram of trans-$[RuCl_4(MeCN)_2]^-$ in CH_2Cl_2, related to the overall pattern of $Ru^{III/II}$ couples for the binary chloride-MeCN and mixed chloride-MeCN-CO complexes. The general trend of the $Ru^{III/II}$ electrode potentials with varying stoichiometry is illustrated in Fig. 3 and Fig. 4. In the $[RuCl_{6-n}L_n]^{n-3}$ series ($n = 0, 1$, trans-2), the $Ru^{III/II}$ couple moves anodically by about 0.70 V at the first substitution of Cl by MeCN, and then by just 0.37 V at the second substitution. For the corresponding bromo series, the effect was essentially similar, the electrode potential having shifted by 0.74 V upon the first replacement and by only 0.40 V on the second.

In the series $[RuX_6]^{3-} \rightarrow [RuX_5(AsMe_3)]^{2-} \rightarrow$ trans-$[RuX_4(AsMe_3)_2]^-$, the $Ru^{III/II}$ couple moved by roughly twice on the first introduction of $AsMe_3$ than on the second. For X = Br, the $Ru^{III/II}$ couple shifted by +0.62 V for the first substitution and by only +0.20 V on the second step. For the chloro series, the anodic movement was +0.52 V and +0.27 V for the first and second substitution, respectively. The irregular movement of electrode potential upon successive substitution is also evident in the corresponding $Ru^{IV/III}$ series.

The consequences of geometric isomerism are also evident in disubstituted complexes, the electrode potential of cis-X_4 being more positive than that of the trans isomer by an average of 125 mV. For the bis(acetonitrile) complex, $RuX_4(MeCN)_2$, the $Ru^{III/II}$ electrode potential difference between cis and trans isomers are 180 mV when X = Cl⁻ and 200 mV when X = Br⁻.

In all series considered here, the ruthenium III/II couple shifted anodically by no less than twice on the first substitution of a halide by a modest π-acceptor ligand L than on the second. This remarkable observation is in frank disagreement with the predictions of the prevailing models [1-4]. In particular, Bursten's ligand additivity model [1, 3] predicts that each successive replacement has the same effect regardless of how many ligands have been substituted.
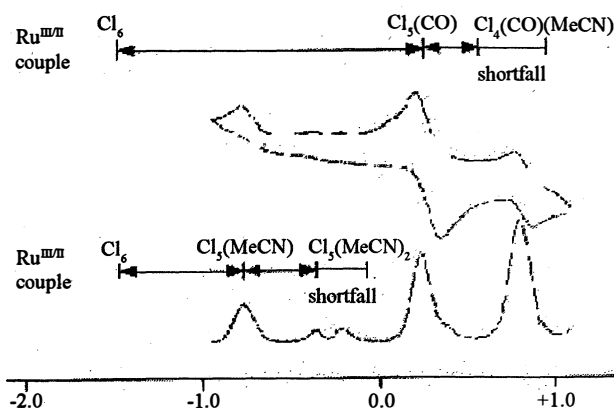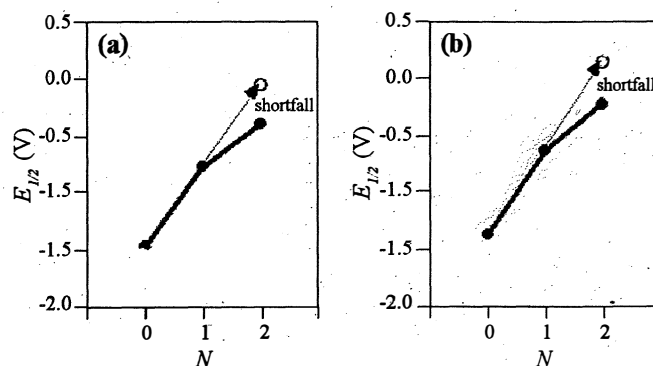

Fig. 3. Electrode potential (in V vs Ag/AgCl) ($Ru^{III/II}$ vs. composition for $[RuX_{6-n}(MeCN)_n]^z$ complexes, $n = 0, 1$, trans-2; (a) X = Cl, (b) X = Br. The empty circle locates the expected position for trans-2 in a strictly additive ligand effect.
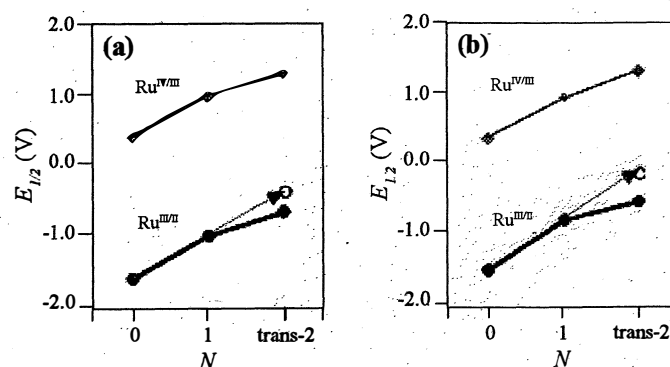

Fig. 4. Plot of $E_{1/2}$ (in V vs Ag/AgCl) ($Ru^{IV/III}$ and $Ru^{III/II}$) vs n for $[RuX_{6-n}(AsMe_3)_n]^{z/z-}$ ($n = 0, 1$, trans-2). (a) X = Cl, (b) X = Br.

Let us examine closely the Bursten model [1, 3] in order to illustrate the serious implication of these overwhelming empirical observations on the widely accepted ligand-additivity models. Bursten's model separates isotropic (combination of σ and electrostatic) and π-bonding terms and address isomer-specific potential differences by elementary angular overlap arguments. For a binary complex $[MX_{6-n}L_n]$, the model expresses the energy ε of a particular $d\pi$ orbital as a linear sum of three effects (Equation 1): a) the identity of the metal ion itself (the invariant A_M term); b) isotropic contributions of all six ligands (the B_L and B_X terms); and, c) the π-bonding contribution of each of the four ligands coplanar with the d-orbital in question (the C_L and the C_X terms).

$$\varepsilon = A_M + \Sigma(B \text{ terms}) + \Sigma(C \text{ terms}) \qquad [1]$$
$$\text{metal} \quad \sigma\text{-effects} \qquad \pi\text{-effects}$$

It also assumed the individual ligand terms are constant, that is, indifferent to overall stoichiometry and mutual disposition. For cis- and trans-X_4L_2 considered here:

$$\varepsilon_{(HOMO)}(cis\text{-}X_4) = A_M + (4B_X + 2B_L) + (3C_X + C_L) \qquad [2]$$

$$\varepsilon_{(HOMO)}(trans\text{-}X_4) = A_M + (4B_X + 2B_L) + (4C_X) \qquad [3]$$
$$\qquad\qquad\qquad\qquad\quad \sigma\text{-effects} \qquad \pi\text{-effects}$$

For geometric isomers, the isotropic B terms must cancel and only the differentiated π-bonding C terms can contribute to the resultant electrode potential differences between the isomers. For the two isomers of the formula $[RuX_4L_2]^z$, where L is a stronger π-acceptor than X, it follows from Equation 2 and Equation 3 that:

$$\varepsilon_{(HOMO)}(cis\text{-}X_4) - \varepsilon_{(HOMO)}(trans\text{-}X_4) = C_L - C_X \qquad [4]$$

For MX_4L_2 systems, the relative stabilities of the respective HOMO's (and therefore the redox potentials) will depend on the difference between C_L and C_X which is a measure of the difference in the π-donor/π-acceptor ability of the co-ligands L and X.

However, on the same basis, for the complementary MX_2L_4 systems, the cis/trans differentiation in electrode potentials is explicitly predicted to be zero:

$$\varepsilon_{(HOMO)}(cis\text{-}X_2) = \varepsilon_{(HOMO)}(trans\text{-}X_2)$$

$$= A_M + (2B_X + 4B_L) + (2C_X + 2C_L) \qquad [5]$$

Although we saw no cis-$X_2(RCN)_4$ here, several other systems demonstrate that the magnitude of cis/trans differentiation in MX_2L_4 may equal or exceed that of their MX_4L_2 counterparts. For example, our fresh electrochemical data for cis- and trans-$[RuCl_4(AsMe_3)_2]$ differ by only 150 mV whereas the difference for the isomeric pair of $[RuCl_2(AsMe_3)_4]$ is 250 mV [9].

$$[MX_6]^{3-} \qquad [MX_5]^{2-} \qquad trans\text{-}[MX_4L_2]^- \qquad cis\text{-}[MX_4L_2]^-$$
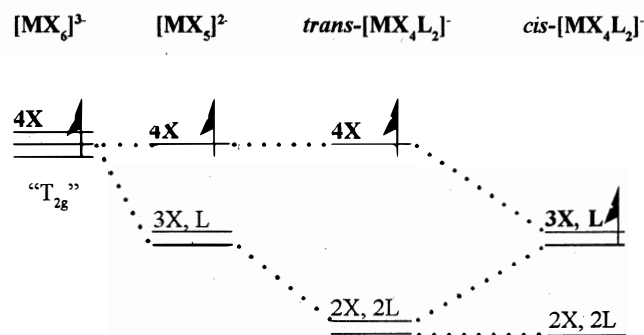

Fig. 5. π-effects on the redox-active frontier orbital level of $Ru^{III/II}$ (d^5/d^6) complexes.

The distinct non-linear trend in electrode potential in the series RuX_6 through RuX_5L to RuX_4L_2, and the notable difference in electrode potential values for isomeric complexes demonstrate the limitations of Bursten's model. Bursten's success in predicting the cis/trans differentiation at the X_4L_2 level has to be set against a failure at the corresponding X_2L_4 level. The current observations show that, firstly, the operative C_L value is actually less stabilizing for two mutually trans π-acid ligands in the X_2L_2 plane, compared to the same two ligands mutually cis and therefore each trans to a π-donor halide ligand. Secondly, the weaker charge-withdrawal by competing π-acceptor axial ligands, that characterizes the trans-arrangement, has an indirect effect on the overall 'isotropic' stabilization of all three metal d-orbitals, making Bursten's B term isomer-sensitive as well.

The second point is demonstrated by the effect of stepwise axial substitution on $[RuX_6]^{3-}$ to form $[RuX_5L]^{2-}$ and trans-$[RuX_4L_2]^-$. In this short series, the redox active orbital (d_{xy}) lies orthogonal to the location of progressive substitution (on the z-axis). The π term is therefore equal to $4C_X$ throughout the series. Figure 5 illustrates the π-bonding effects on the redox-active orbital. It is easy to see that the π-effects on the frontier level is constant throughout the set ($n = 0 - trans$-2). Thus, in the progression from X_6 to X_5L to trans-X_4L_2, Bursten's expression predicts a linear shift in ε_{HOMO}, governed only by the stepwise change in the isotropic term from ($6B_X$) through ($5B_X + B_L$) to ($4B_X + 2B_L$). In contrast the notable non-linearity of the observed electrode potential progression in both acetonitrile and trimethylarsine series makes it clear that introduction of the second (mutually trans) L has lesser effect than the first. Hence, contrary to the fundamental assumption, the effective value of ($B_L - B_X$) must diminish significantly between RuX_5L and trans-RuX_4L_2. In fact, this effect has been exaggerated in extreme combinations of ligands, such as π-donor halides with very strong π-acceptor carbony and nitrosyl co-ligands [5, 10].

In the eyes of a descriptive chemist the apparent failure of trans-oriented second substitution to exert twice the effect of the first is not surprising since the two trans-disposed π-

acceptor ligands are competing for the same metal electron pairs, and are less withdrawing than the two *cis* ones. This is also demonstrated by comparison of series of mixed-L complexes: [RuCl$_6$]$^{3-}$, [RuCl$_5$(CO)]$^{2-}$, [RuCl$_5$(MeCN)]$^{2-}$, and *trans*-[RuCl$_4$(CO)(MeCN)]$^-$. When a carbonyl replaces a chloride in an RuCl$_5$ binding site, the electrode potential shifted by 1.73 V, whereas with MeCN the shift was 0.70 V. When an MeCN replaces the chloride which is *trans* to CO in the monocarbonyl complex, the shift was just 0.35 V instead of 0.70 V. Similarly, when CO replaces the chloride *trans* to MeCN in [RuCl$_5$(MeCN)]$^{2-}$, the potential shift was reduced from 1.73 V to only about 1.0 V (Fig. 2). Although MeCN is a much weaker π-accepting ligand than CO, in a *trans* geometry both ligands compete for the same electron density, thus their individual effects are mutually attenuated, though, the effect of CO on MeCN being stronger than that of MeCN on CO. In the *cis* isomer, this competition is relieved and the potential is shifted to a more positive value.

CONCLUSION

Although Bursten's formulation for each individual species is valuable and enlightening, its limitation lies in the basic assumption of invariant numerical values of the various terms. The non-additive ligand effects observed in the series [RuX$_6$]$^{3-}$ through [RuX$_5$L]$^{2-}$ to *trans*-[RuX$_4$L$_2$]$^-$ indicate that Bursten's σ and π terms change from case to case making the expressions incommensurate and inappropriate for arithmetic combination. Both the directed π-bonding contributions and the *isotropic* σ-bonding contributions are open to quantitative deviations. This effect is discernable even in cases where L and L' (or X) co-ligands differ less dramatically in their nature (as with MeCN vs. X and AsMe$_3$ vs. X).

The electrochemical observations presented here demonstrate our contention that the mutual influence of π-accepting *trans*-disposed ligands can result in attenuated ligand additivity effects. Our purpose is to draw attention to the limitations of Bursten's theorem or even Lever's simplistic compendium which insists that this is not so.

ACKNOWLEDGEMENT

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