# Additive and Non-additive Ligand Effects in Mixed Halide–Carbonyl–Nitrile Osmium Complexes

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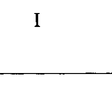
In the series $[\mathrm{OsX_6}]^{3-}$, $[\mathrm{OsX_5(CO)}]^{2-}$, *trans*-$[\mathrm{OsX_4(CO)_2}]^{1-}$ (X = Br) and the series *trans*-$[\mathrm{OsX_4(MeCN)_2}]^{1-}$, *trans*-$[\mathrm{OsX_4(MeCN)(CO)}]^{1-}$, *trans*-$[\mathrm{OsX_4(CO)_2}]^{1-}$, osmium IV/III and III/II redox couples shift two to three times further for the first introduction of CO than for the second, contrary to recent predictions; the corresponding halide to $\mathrm{Os^{III}}$ charge-transfer spectra (X = Cl and Br) confirm the strongly non-linear accumulation of ligand electronic effects, in accord with preliminary X-ray data and near-IR crystal-field spectra.

The principle that the effects exerted by the assembled ligands on the electronic properties of a given coordination complex are fundamentally additive has been described justifiably as one of the cornerstones of intuitive inorganic chemistry.[1]† The nett influence on transition metal electrochemical potentials is of central importance. Sweeping linear relationships between $E^{\circ}_{\mathrm{red}}$ ($\mathrm{d^5/d^6}$) and stoichiometry in $[\mathrm{Mn^I(CO)_{(6-\mathit{n})}(MeNC)_{\mathit{n}}}]^+$ organometallic systems[2] and 'classical' $[\mathrm{Ru^{III}Cl_{(6-\mathit{n})}(PhCN)_{\mathit{n}}}]^{(n-3)}$ complexes[3] (as *n* ranges stepwise from 0 to 6) illustrate that individual ligand effects can accumulate arithmetically. Bursten has provided a formal theoretical analysis of this phenomenon,[4]‡ and an excellent general review of ligand additivity.[1]

In order to rank the nett electron-donor capabilities of various ligands, Pickett and his colleagues established an internally consistent ligand parameter scale ($P_{\mathrm{L}}$),[5] defined by the shift in $E^{\circ}$ as L′ replaces L in $[\mathrm{Cr(CO)_5L}]^+$. Lever has exploited such additivities most ambitiously, using redefined ligand parameters ($E_{\mathrm{L}}$) to predict the redox potentials of an enormous range of organometallic and coordination compounds containing *any permutation* of some 200 ligands.[6,7]§

With this in mind, we draw attention to a seemingly simple system (structure **I**) where the relationship between redox



I

**1**; L = L′ = Br
**2**; L = Br, L′ = MeCN
**3**; L = L′ = MeCN
**4**; L = Br, L′ = CO
**5**; L = L′ = CO
**6**; L = MeCN, L′ = CO

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† For example this concept underlies the establishment of the spectrochemical series of ligands, the analysis of carbonyl stretching frequencies, and the evolution of the angular overlap model (AOM) to describe the Ligand Field.

‡ Bursten's model relates the electrode potential to the Fenske–Hall energy of the HOMO, and is expressly additive in that ligands of a given kind have invariant character regardless of the number introduced or their disposition. See footnote ††.

§ Predicted shifts in $E^{\circ}$ of $\mathrm{ML}_n$ are equated to changes in Lever's summation $S_{\mathrm{M}}\cdot(\Sigma E_{\mathrm{L}})$ where $S_{\mathrm{M}}$ is explicitly a *fixed* scaling factor for a given element–couple (*e.g.* 1.01 for $\mathrm{Os^{III/II}}$, 1.48 for $\mathrm{Tc^{II/I}}$, 1.28 for $\mathrm{Tc^{III/II}}$, and axiomatically unity for $\mathrm{Ru^{III/II}}$). This contrasts sharply with Pickett's analysis where, as the ligand complement changes, the polarisability β is redetermined for each distinct binding site.

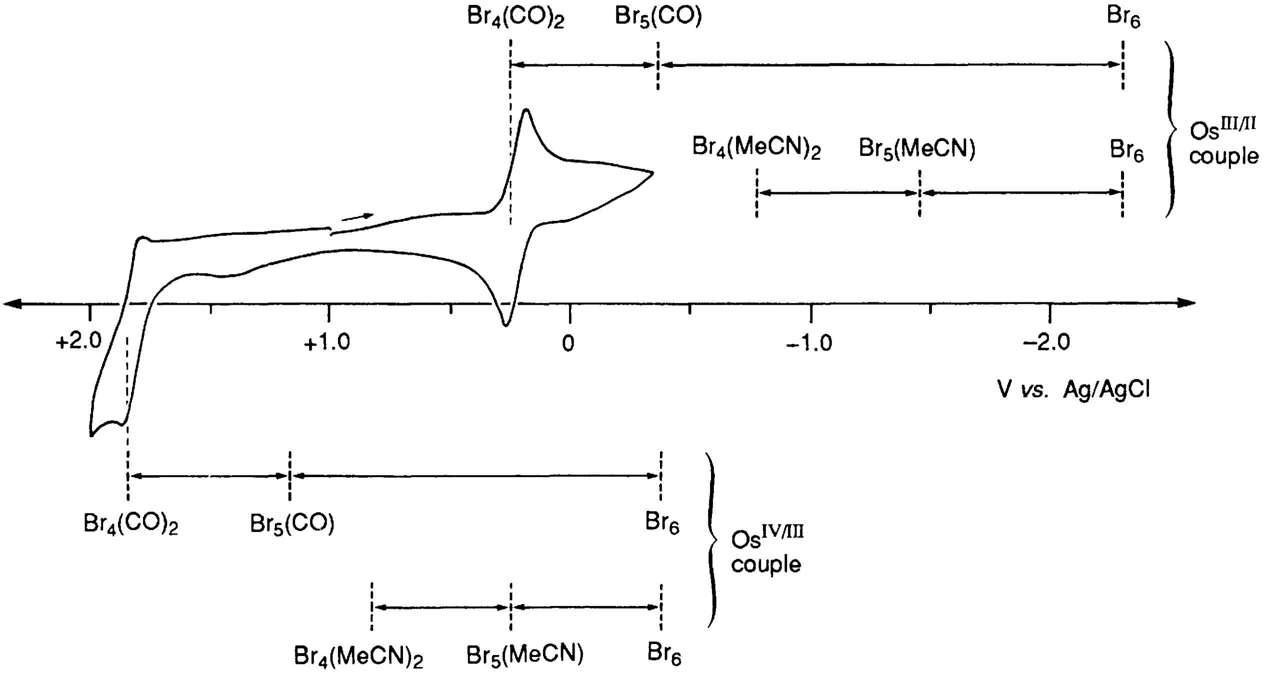

**Fig. 1** Voltammetry of $[\mathrm{Bu^n_4N}][\mathrm{OsBr_4(CO)_2}]$ at 220 K, and the location of the IV/III and III/II couples for comparable complexes of structure **I**. Conditions as in Table 1.

**Table 1** Voltammetric and spectroscopic data

| **I** | Complex | $E_{1/2}$/V[a] IV/III | $E_{1/2}$/V[a] III/II | $h\nu$/cm$^{-1}$ [b] Br→Os$^{\rm III}$CT |
|---|---|---|---|---|
| **1** | $[\mathrm{OsBr_6}]^{3-}$ | −0.37 | −2.28[c] | 28700 ($\mathrm{T_{1u}}$)[d] |
| **2** | $[\mathrm{OsBr_5(MeCN)}]^{2-}$ | +0.25 | −1.45 | 26530 (E)[d] |
| **3** | $[\mathrm{OsBr_4(MeCN)_2}]^{1-}$ | +0.82 | −0.77 | 24190 ($\mathrm{E_u}$) |
| **4**[e] | $[\mathrm{OsBr_5(CO)}]^{2-}$ | +1.16 | −0.36 | 20360 (E) |
| **5**[e] | $[\mathrm{OsBr_4(CO)_2}]^{1-}$ | +1.84 | +0.27 | 19320 ($\mathrm{E_u}$) |
| **6**[e] | $[\mathrm{OsBr_4(CO)(MeCN)}]^{1-}$ | +1.53 | −0.08 | 20390 (E) |

[a] At a Pt electrode in $\mathrm{CH_2Cl_2}$–0.5 mol dm$^{-3}$ $\mathrm{Bu^n_4NPF_6}$ solutions under reversible conditions, referred to Ag/AgCl such that $E_{1/2}$ = +0.55 V for $[\mathrm{Fe(C_5H_5)_2}]^{+/0}$. Scan rates $n$ = 20 (acV) and 100 (CV) mV s$^{-1}$. [b] For $\mathrm{CH_2Cl_2}$ solutions. Band assignments in parentheses. Energies refer to centres of $\mathrm{T_{1u}}$, E or $\mathrm{E_u}$. The splitting is about 2000 cm$^{-1}$ for X=Br (*cf.* Fig. 3). [c] Requires evacuable superdry cell. [d] By reduction in an optical semi-thin layer electrogenerative (OSTLE) cell. [e] IR data (KBr discs): $\nu_{\rm CO}$ 1953, 2043 and 2006 cm$^{-1}$ for **4**, **5** and **6** respectively.

properties and composition ranges from linear to sharply non-linear, depending upon the nature of the ligands (L) occupying the axial sites of the *trans*-$\mathrm{OsX_4(L)_2}$ chromophore. These six complexes (spanning every combination of L and L′ = Br, MeCN, CO) were isolated and characterised as their organosoluble $\mathrm{Bu^n_4N^+}$ salts.[8–10]¶

We have studied the chloride analogues of **1**–**6** as well, with fully consistent results, though structural and electrochemical data are as yet incomplete. Isomer-sensitive deviations from linear additivity due to π-covalency are not expected for **I**,[11]|| since the redox-active orbital lies orthogonal to the ligands being substituted.

Fig. 1 shows a representative low-temperature cyclic voltammogram of *trans*-$[\mathrm{OsBr_4(CO)_2}]^-$ in $\mathrm{CH_2Cl_2}$, related to the overall pattern of Os$^{\rm IV/III}$ and Os$^{\rm III/II}$ couples for the binary halide–CO and halide–MeCN complexes. In the $[\mathrm{OsBr}_{6-n}(\mathrm{MeCN})_n]^z$ series ($n$ = 0, 1, 2), the III/II couple moves by *ca.* 0.8 V and then by 0.68 V. The corresponding step-wise shifts in the IV/III couple are 0.62 and 0.57 V. Such shifts are typical for replacement of halide by neutral moderate π-acceptor ligands.[3,12,13]

In contrast, in the $[\mathrm{OsBr}_{6-n}(\mathrm{CO})_n]^z$ series the III/II couple shifts anodically by a remarkable 1.8 V upon the first substitution of bromide by a carbonyl ligand, but by only 0.63 V at the second step,** and this strongly non-additive effect is parallelled in the IV/III couple. *This observation is in frank disagreement with the predictions of prevailing models*,†† and is especially pertinent given the general prominence of CO ligands in additivity studies.

The rational correlation expected between halide-to-metal charge-transfer (LMCT) energies and metal-based reduction

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¶ All have been appropriately characterized by elemental analysis, IR spectroscopy and negative-ion FAB mass spectrometry. Complexes **3** and **6** are new. As isolated, **1** and **2** are Os$^{\rm IV}$ compounds and **3**–**6** are Os$^{\rm III}$. We prepared **2**[8] by action of Ag$^+$ on **1** in warm MeCN, **5**[9] by action of Ag$^+$ and CO on **1** in $\mathrm{CH_2Cl_2}$, and **4**[10] by treating **5** with $\mathrm{Bu^n_4NBr}$. Reduction of **2** with $\mathrm{Bu^n_4NBH_4}$ in MeCN yielded **3**. The dicarbonyl **5** readily forms **6** when dissolved in MeCN. A full report is in preparation.

|| Bursten's model is isomer-specific through AOM-type summation of ligand effects on the redox-active $d_\pi$ orbital (his C term). This concept stems from the fruitful analysis of *cis*- and *trans*-$[\mathrm{Mo(CO)_2(diphos)_2}]^{+/0}$ by Bond *et al.*[11]

** The mean shift for *twofold* introduction of CO is *ca.* 1.2 V per Br ligand, in deceptive accord with $P_{\rm L}$ or $E_{\rm L}$ values; this emphasises the importance of the intervening complexes.

†† 'The ligand additivity model predicts that each successive replacement has the same effect regardless of how many ligands have been substituted. This non-intuitive result is well supported by Fenske–Hall MO calculations' (ref. 1, p. 429).

Lever reports that carbonyl species generally fit rather well (ref. 6, p. 1284), and that the $E_{\rm L}$ plot for Os$^{\rm III/II}$ shows an excellent correlation (ref. 6, p. 1275).

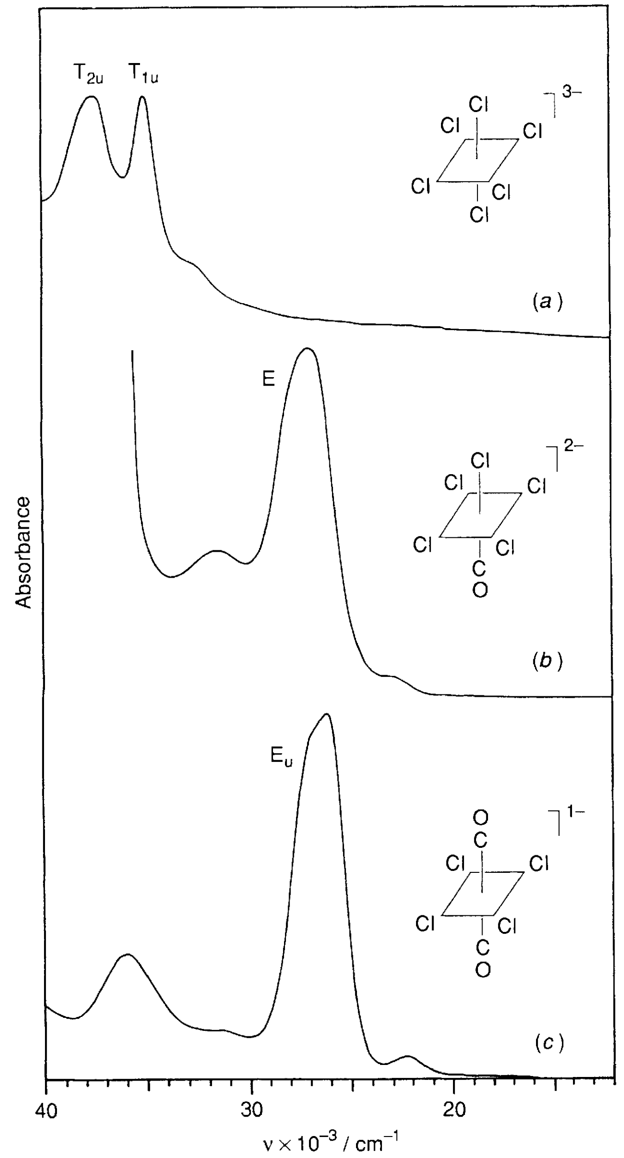

Fig. 2 Electronic absorption spectra in $CH_2Cl_2$ of (*a*) $[OsCl_6]^{3-}$, (*b*) $[OsCl_5(CO)]^{2-}$, (*c*) *trans*-$[OsCl_4(CO)_2]^{1-}$. LMCT manifolds are systematically *ca.* 6000 $cm^{-1}$ lower for the bromides than for the corresponding chlorides, in accord with optical electronegativity differences.

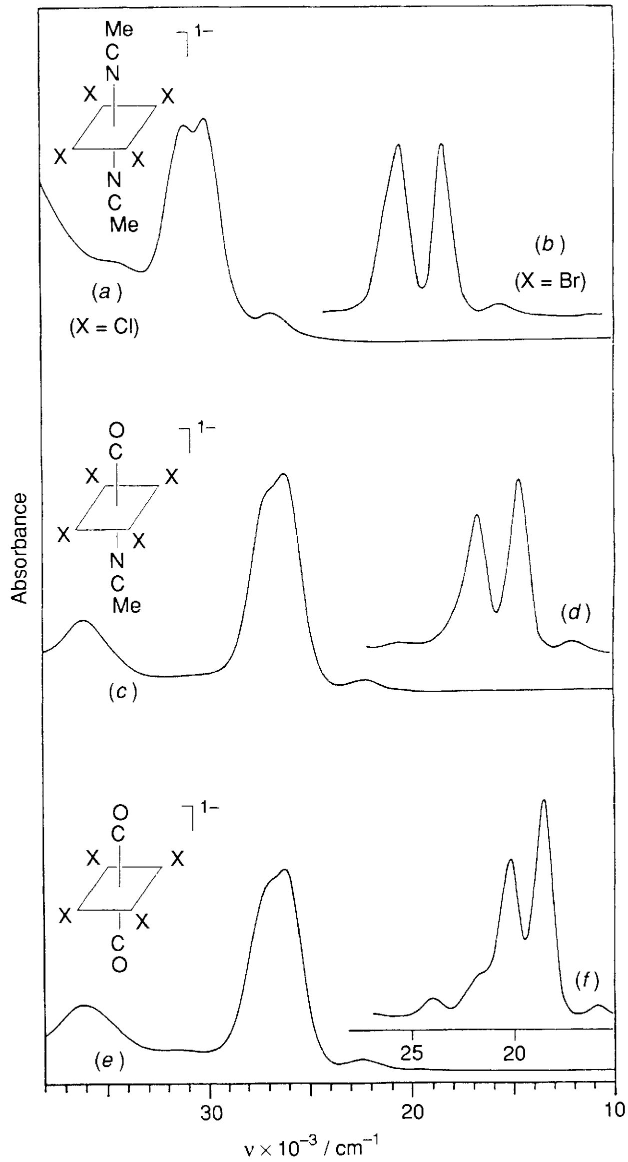

Fig. 3 Electronic absorption spectra of *trans*-$[OsX_4(L)_2]^{1-}$ complexes in $CH_2Cl_2$: (*a*) $[OsCl_4(MeCN)_2]^{1-}$; (*b*) $[OsBr_4(MeCN)_2]^{1-}$; (*c*) $[OsCl_4(CO)(MeCN)]^{1-}$; (*d*) $[OsBr_4(CO)(MeCN)]^{1-}$; (*e*) $[OsCl_4(CO)_2]^{1-}$; (*f*) $[OsBr_4(CO)_2]^{1-}$. The frequency scale for the bromides (*b*, *d* and *f*) is offset by 5000 $cm^{-1}$, as shown below *f*.

potentials in low-spin $d^5$ systems[3] suggests a fresh means of assessing the cumulative influence of the axial ligands in the present context. Fig. 2 traces the optical spectra of $[OsCl_6]^{3-}$, $[OsCl_5(CO)]^{2-}$ and $[OsCl_4(CO)_2]^{1-}$, where the non-linear movement of the $Cl(\pi)\rightarrow Os^{III}(d_\pi)$ charge-transfer bands is clearly evident. As with the bromo complexes **1**, **4** and **5** (Table 1), the manifold is red-shifted by *ca.* 8000 $cm^{-1}$ at the first substitution (CO replacing X), but by 1000 $cm^{-1}$ or less at the second. The corresponding MeCN complexes behave very differently; the leading $Cl(\pi)\rightarrow Os^{III}(d_\pi)$ band moves by *ca.* 2300 $cm^{-1}$ at each stage, and $Br\rightarrow Os^{III}$ likewise, in accord with the regular progression of the $Os^{III/II}$ redox couple.‡‡

Particularly interesting are the distinctive charge-transfer spectra of the six *trans*-$[OsX_4(MeCN)_{2-n}(CO)_n]^{1-}$ complex anions (Fig. 3). Optical and voltammetric electron-transfer processes both probe the same redox-active orbital ($d_{xy}$ or $b_{2g}$) lying in the $MX_4$ plane. The doublet principal absorption arises from the favoured in-plane $X(\pi)\rightarrow M(d_\pi)$ ($e_u\rightarrow b_{2g}$) transition,[14] split by halide-based spin–orbit coupling ($\zeta_{\text{free ion}}$ = 650 $cm^{-1}$ for Cl, 2200 $cm^{-1}$ for Br). Clearly, the essential chromophore is conserved despite radical changes in axial ligation and $E^\circ$(III/II). A non-linear progression in charge-transfer energy is observed in this sequence as well; the manifold moves by *ca.* 3800 $cm^{-1}$ and then 1000 $cm^{-1}$ or less while $E^\circ$ moves by 0.7 and 0.35 V.

In summary, the discontinuous shifts in Fig. 2 and Fig. 3 emphasise both the strong effect of the first axial carbonyl ligand on the chromophore and the remarkably attenuated (*i.e.* non-additive) electronic influence of dual substitution. Lately we have shown that the complementary isonitrile

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‡‡ In all cases, there is a simultaneous increase in the effective ionisation energy of the halide ligands in the $MX_4$ chromophore as axial substitution proceeds; this moderates the movement of the charge-transfer band.[3]

complexes (**I**; L, L′ = all permutations of Bu$^t$NC, CO, Br) exhibit similar non-linear trends in behaviour.[15]§§

Crystal structures of **2**, **5** and **6** have been determined.[15] The latter are *trans*-isomers as is consistent with the spectroscopic data. The mean Os–CO bond length in the dicarbonyl is significantly greater than in *trans*-$[OsBr_4(CO)(MeCN)]^{1-}$ [194.3(1.0) *vs.* 184.3(1.5) pm] although $Os^{III}$–Br distances are unchanged [averaging 249.55(10) pm in **5** *vs.* 249.70(15) pm in **6**]. This is consistent with the marked lability of **5**,¶ and with the diminished electronic effect of two mutually *trans* CO ligands demonstrated here.

Finally, we have detected the weak ($d_{xz}$, $d_{yz}$) to $d_{xy}$ transition that directly maps the tetragonal distortion of the ligand field in **I**. This band has two spin-orbit components ($\Gamma_6$ and $\Gamma_7$) *ca.* 1500 $cm^{-1}$ apart, centred near 5500, 7900 and 8200 $cm^{-1}$ in **3**, **6** and **5** respectively in a non-additive progression.

In the instructive cases presented here, electrochemical observations are augmented by clear optical and structural evidence. That the mutual influence of strongly π-accepting *trans*-disposed ligands can result in attenuated ligand additivity effects is in our view not surprising.¶¶ Our purpose is to draw attention to the shortcomings of parameterised models which insist that this is not so.

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§§ *Added in proof*: In the $[OsX_{6-n}(Bu^tNC)_n]^{n-3}$ sequence ($n$ = 0,1,2; X = Cl or Br) the IV/III and III/II couples shift in parallel by 1.0 V then 0.3 V. The *overall* shifts between $[RuX_6]^{3-}$ and *trans*-$[RuX_4(Bu^tNC)_2]^{1-}$ for the same couples were recently reported to be in the range 1.2 to 1.4 V, as above, but the pentahalide complexes were unavailable, see, C. M. Duff and R. J. Schmid, *Inorg. Chem.*, 1991, **30**, 2938.

¶¶ In a study demonstrating the widespread utility of linear ligand additivity relationships, Heath has already stressed that they need not prevail in inappropriate systems (ref. 3, p. 2534).