Chatt's Ligand Constants: Applicability and Correspondence with Bursten's Ligand Additivity

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Recently Chatt has assigned a parameter P_L, closely analogous to the Hammett σ, for each of the common monodentate ligands L to indicate its electron-donating power. These P_L values correlate linearly with the oxidation potential E^0_L of various low-spin d^6 complexes, where L can be varied through a three-parameter relation of the type $E^0_L = E_s + \beta P_L$ (E_s and β are two constants). Considering low-spin d^6 complexes where two ligands can be varied, I have shown that these P_L constants are almost additive in nature. The concept of P_L is extended to bidentate ligands. P_L values for ethylenediamine (en), 2,2′-bipyridyl (bipy), and 2-phenylazopyridine are found to be −1.57, −1.14, and −0.76 V respectively; interestingly, $P_{en} \approx 2P_{NH_3}$ and $P_{bipy} \approx 2P_{py}$ (py = pyridine). The additivity of P_L does not hold if one (or both) of the substituting ligands is (are) strongly electron-withdrawing or -donating in nature. Possible applicability of P_L to d^8 systems is indicated by the observed variation of the rate of the substitution of L in $[Pt(dien)L]^{2+}$ (dien = diethylenetriamine) by py with P_L. Bursten has recently given a semiempirical relationship for predicting the oxidation potentials of low-spin d^6 complexes of type $[ML_nL'_{6-n}]$.
A correspondence between the two approaches of Chatt and Bursten towards parameterisation of the ligand effect is established. Meanings of P_L, E_s, and β in the light of Bursten's model of ligand additivity are explored. It is observed that Chatt's P_L values should be applicable only in cases where the substituting ligand(s) is (are) much less π acidic than the ligands constituting the unchanged (core) fragments of the complexes.

The properties of metal complexes depend mostly on the electronic nature of the ligands bound to the metal centre. Therefore if the electronic properties of the ligands can be parameterised, it may be possible to predict the effect of ligand substitution *a priori.* Though the Hammett σ parameter helps in this direction, its use is limited as aromatic substitution is not readily achieved in metal complexes, unless the ligand is suitably designed. Extension of the Hammett σ concept to 'common inorganic' ligands has been attempted recently by Chatt.[1] He has designated a constant quantity P_L for every monodentate ligand L in order to indicate its electron-releasing or -withdrawing power. These quantities (units are V) are obtained from the changes in redox potentials (E^0) of Cr^0/Cr^I couple in $[Cr(CO)_5L]$ with various L [equation (1)].

$$P_L = E^0[Cr(CO)_5L] - E^0[Cr(CO)_6] \qquad (1)$$

The more negative is the value of P_L, the more electron releasing (or weaker π acceptor) is the ligand concerned. Those constants are observed to correlate linearly with metal oxidation potentials of several low-spin d^6 metal complexes through a simple three-parameter relation of type (2). The other two

$$E^0_L = E_s + \beta P_L \qquad (2)$$

parameters E_s and β represent respectively the metal centre's electron richness and sensitivity (polarisability) towards ligand substitution.

The work of Chatt has been restricted to the effects of monosubstitution and to d^6 systems only. Herein I show, taking new examples from the literature, that these constants are almost additive in nature, and it may be possible to assign such useful P_L values to bidentate ligands as well. That these constants may be applicable to square-planar d^8 systems is discussed.

Recently there have been several empirical or semiempirical approaches[2,3] to quantify the notion of ligand additivity in relation to a variety of physical measurements. Only metal carbonyls and their derivatives have been used to test this. The most successful example is the prediction of the metal oxidation potentials of low-spin d^6 complexes of type $[M(CO)_n(CNR)_{6-n}]$ by Bursten's model.[3] This model, which does not take into account the interaction between the ligands, helps to express the oxidation potential of $[ML_nL'_{6-n}]$ (M = low spin d^6) as in equation (3). Here A^0_M is a characteristic of M, B^L_M or

$$E^0_M = A^0_M + nB^L_M + (6-n)B^{L'}_M + n'C^L_M + n''C^{L'}_M \qquad (3)$$

$B^{L'}_M$ represents the ability of L or L′ to stabilise each d orbital of M electrostatically through net electron donation,* C^L_M or $C^{L'}_M$ denotes the power of L or L′ to stabilise the d_π orbital involved in forming the highest occupied molecular orbital (h.o.m.o.) of the complex through π interaction, and n' and n'' are respectively the numbers of L and L′ interacting with the highest occupied d_π orbital.

A correspondence between Chatt's approach and Bursten's model of ligand additivity is established. This allows us to examine critically the applicability of Chatt's ligand constants.

Results and Discussion

Additivity of P_L *and Application of the Concept of* P_L *to Chelating Ligands.*—In the case of the octahedral ruthenium(II) complexes of 2,2′-bipyridyl (bipy) and 2-phenylazopyridine (papy) of type (**1**) and (**2**) where we have the possibility of varying two ligands L and L′, we find that the potentials of the Ru^{II}/Ru^{III} couple[4–6] correlate quite satisfactorily [Figure 1(*a*)

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* 'Net electron donation' refers to (σ donation from L) − (π acceptance by L).

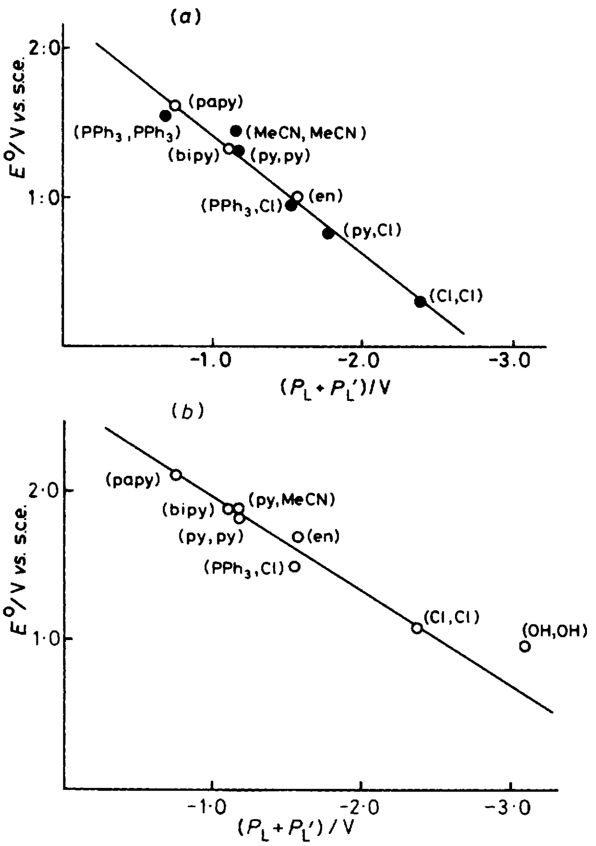
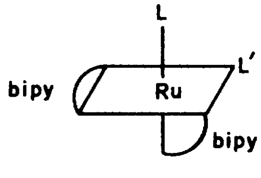
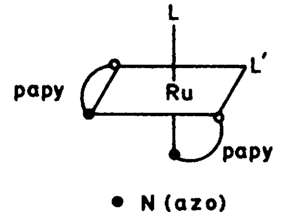


Figure 1. (*a*) Variation of the potential of the Ru^{II}/Ru^{III} couple in $[Ru(bipy)_2LL']$ (**1**) with ($P_L + P_{L'}$). L, L′ are given in parentheses; open circles are used to designate the P_L values for en, bipy, and papy. (*b*) Variation of the potential of the Ru^{II}/Ru^{III} couple in $[Ru(papy)_2LL']$ (**2**) with ($P_L + P_{L'}$). L, L′ are given in parentheses



(1)



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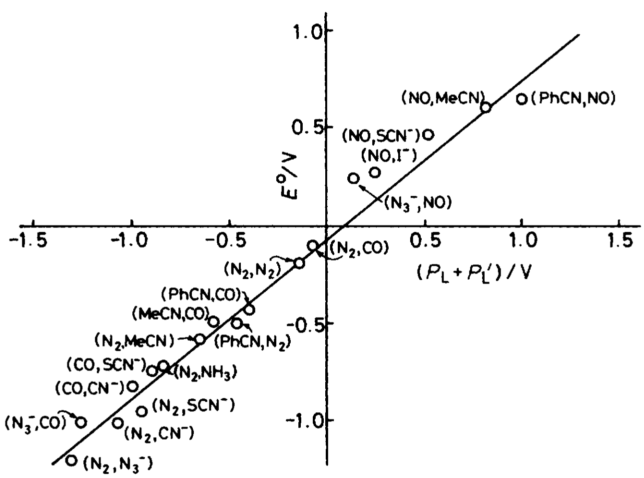

Figure 2. Variation of the potential in *trans*-$[Mo(PPh_2CH_2CH_2Ph_2P)_2LL']$ with ($P_L + P_{L'}$). The points corresponding to (NO, I^-) and (N_3^-, NO) are not included in the least-squares fit

and (*b*)] with ($P_L + P_{L'}$). This shows that these constants are more or less additive, *i.e.* the combined electronic effects of L and L′ can be described well enough by simple algebraic sum of P_L and $P_{L'}$. For comparison, data used by Chatt[1] for *trans*-$[Mo(PPh_2CH_2CH_2Ph_2P)_2LL']$ are plotted in Figure 2.

Obviously such plots can be used for assigning P_L values to ligands not included in Chatt's list. Attempts can be made with the additivity in mind to find out the values of P_L for chelating ligand systems. Values obtained for ethylenediamine (en), bipy, and papy from Figure 1(*a*) with the knowledge of the corresponding redox potentials are as follows: −1.57, −1.14, and −0.76 V. In the same order, the π acidity of these ligands is expected to increase. Interestingly enough, $P_{en} \approx 2P_{NH_3}$ and $P_{bipy} \approx 2P_{py}$. Strictly speaking, P_{en} is a little more (by 0.04 V) negative than $2P_{NH_3}$ and P_{bipy} is a little more (by 0.04 V) positive than $2P_{py}$. This is in order since the alkyl groups in en are expected to donate a little more electron density and the conjugation in bipy is expected to enhance its π-accepting ability. These observations tempt us to distinguish between the two binding sites of the unsymmetrical ligand papy. Approximating $P_{N(azo)}$ as ($P_{papy} - \frac{1}{2}P_{bipy}$) we have a value of −0.19 V for the azo binding site. This shows that the azo end is much more electron withdrawing than the pyridine end. This may be one of the important factors responsible for the observed shortness[6,7] of Ru–N(azo) bond length compared to that of Ru–N(py) in two isomers of $[Ru(papy)_2Cl_2]$. As shown by the P_L value, the π-accepting ability of the azo group in papy is more than for even PPh_3 ($P_{PPh_3} = -0.35$ V). The higher π acidity of papy compared to bipy is reflected in the fact that *cis*-$[Ru(bipy)_2(H_2O)_2]^{2+}$ is less acidic[7] than $[Ru(papy)_2(H_2O)_2]^{2+}$ of structural type (**2**). The P_L values obtained for en, bipy, and papy from Figure 1(*a*) are used for the plot in Figure 1(*b*) and found to fit into the pattern, showing their transferability.

The values of E_s for $[Ru(bipy)_2]^{2+}$ and $[Ru(papy)_2]^{2+}$ fragments in (**1**) and (**2**) are respectively 2.20 and 2.58 V *vs.* a saturated calomel electrode (s.c.e.) indicating that the latter is less rich in electrons. This is in accord with the π-acidity order of bipy and papy. The β values for $[Ru(bipy)_2]^{2+}$ and $[Ru(papy)_2]^{2+}$ are 0.86 and 0.64; hence the former is more polarisable by ligands.

Validity of the Concept of Additivity.—Now we examine the possible cases where the additivity of the effects of the ligands may not hold. Additivity of P_L necessarily means that the electronic effects exerted by a particular ligand are not affected by the presence of other ligands. It is observed that this additivity does not apply well if NO^+ is one of the ligands. In Figure 1(*a*) potentials of the Ru^{II}/Ru^{III} couple in *cis*-$[Ru(bipy)_2(NO)L]^{2+}$ complexes[8] do not fit at all with the line drawn. In the presence of the strongly electron-withdrawing ligand NO^+, the other ligand becomes more polarised which causes its P_L value to deviate from the calculated value and consequently the non-interacting nature of L and L′ is lost to a considerable extent. Similar loss in non-interaction is expected for ligands which are strong electron donors [see, for example, L = L′ = OH^- in (**2**) is a deviation in Figure 1(*b*)]. Thus it appears additivity may work within a narrower range of Chatt's list (*i.e.* for ligands of medium strength). That steric effects can also cause deviation has been noted in a later section.

Applicability to d^8 *Systems*.—While these constants are applicable to low-spin d^6 complexes as shown by Chatt, it

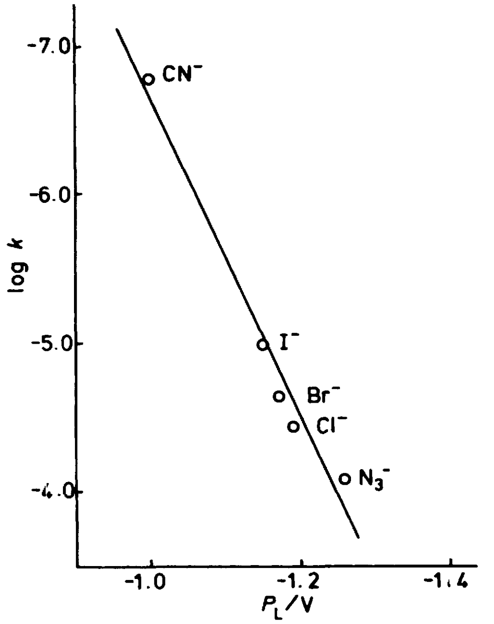

Figure 3. Variation of the rate constant k for reaction (4) with P_L

seems these can also be used for d^8 systems to correlate at least certain properties. The possibility is exemplified in Figure 3 which shows a systematic variation in the rate constant (k) of the substitution reaction (4) of the square-planar platinum(II)

$$[Pt(dien)L]^{2+} + py \longrightarrow [Pt(dien)(py)]^{2+} + L \quad (4)$$

complex $[Pt(dien)L]^{2+}$ (dien = diethylenetriamine) with P_L. The qualitative trend described earlier[9] is quantified only to the extent that it can be used in 'predictive' manner. It is interesting to note that the slope is negative, implying that the substitution is an electrophilic one.

Correspondence with Bursten's Model of Ligand Additivity.— Here we try to understand the meaning of Chatt's correlation in the framework of Bursten's model which appears to be theoretically more sound.

Meanings of P_L *parameters.* Consideration of Bursten's model in the case of $[Cr(CO)_5L]$ readily reveals that P_L values obtained by Chatt [through equation (1)] for ligands other than N^+ and NO^+ are actually ($B^L_{Cr} - B^{CO}_{Cr} + C^L_{Cr} - C^{CO}_{Cr}$) or ($B^L_{Cr} - B^{CO}_{Cr} - C^{CO}_{Cr}$) depending on the availability of proper π-accepting orbitals on L whereas for N^+ and NO^+, though two π-accepting orbitals (orthogonal to each other) are available in both the cases, their P_L values represent their electrostatic interaction compared to CO, *i.e.*, ($B^L_{Cr} - B^{CO}_{Cr}$). Thus for N^+ and NO^+ and for ligands, *e.g.* py, which do not have two π-accepting orbitals orthogonal to each other, π-accepting abilities are only indirectly reflected by the corresponding P_L values through the parameter B^L_{Cr}.

Additivity and Transferability of P_L *Parameters.—Carbonyl complexes.* The sort of ligand additivity discussed in an earlier section is implied within Bursten's work at least for $[Cr(CO)_4LL']$ systems. When L and L′ are poorer π acceptors than CO, the potential of Cr^0/Cr^I couples of those complexes can be written [from equation (3) with a bit of manipulation] as equation (5). This shows that E^0 varies linearly with ($P_L + P_{L'}$)

$$E^0 = A^0_{Cr} + B^{CO}_{Cr} + 4C^{CO}_{Cr} + (P_L + P_{L'}) \quad (5)$$

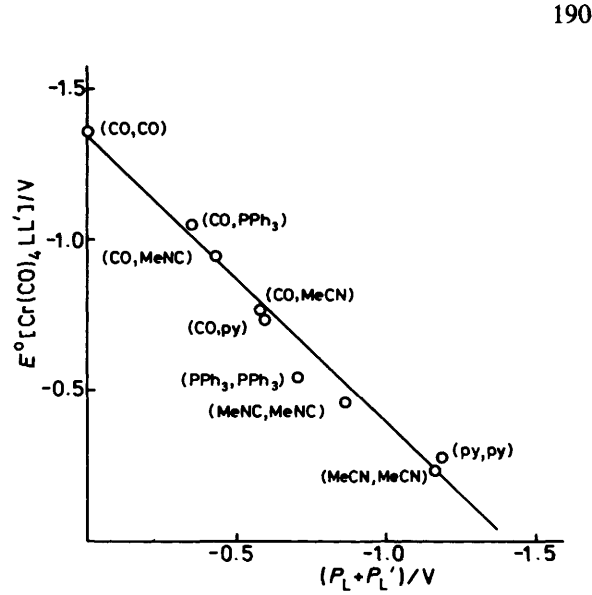

Figure 4. Variation of the potential of the Cr^0/Cr^I couple in $[Cr(CO)_4LL']$ with ($P_L + P_{L'}$). The point corresponding to (PPh_3, PPh_3) is not included in the least-squares fit

giving a slope of unity and the intercept as the oxidation potential of $[Cr(CO)_6]$. Data available for *cis*-$[Cr(CO)_4LL']$ complexes[10,11] are plotted in Figure 4 to test this.* Though the data are few, the notion of ligand additivity possibly holds as the slope is found to be 0.96 and the intercept is 1.34 V, against the experimental value 1.36 V. The deviation for L = L′ = PPh_3 might be due to the steric effects. Such effects are expected to weaken the Cr^0–P bonds resulting in a decrease of π back bonding and this is reflected in the fact that a more negative value of P_L for PPh_3 would fit into the observed variation in Figure 4.

Transferability of P_L values to carbonyl complexes of other d^6 metal centres does not follow immediately from Bursten's model. The oxidation potential E^0_M for the d^6/d^5 couple of $[M(CO)_4LL']$ (L and L′ are poorer π acceptors than CO) complexes can be expressed as equation (6) [from equation

$$E^0_M = A^0_M + 6B^{CO}_M + 4C^{CO}_M + (\pi_L + \pi_{L'}) \quad (6)$$

(3)], where π_L or $\pi_{L'} = E^0_M[M(CO)_5(L \text{ or } L')] - E^0_M[M(CO)_6]$. Linear variation of E^0_M with ($P_L + P_{L'}$) would then mean ($P_L + P_{L'}$) ∝ ($\pi_L + \pi_{L'}$) and the proportionality constant would be given by the slope of the plot. In the case when data are scarce, the anodic peak potentials of the irreversible cyclic voltammograms obtained at a scan rate of 0.2 V s^{-1} for $[W(CO)_4LL']$ complexes[10] are plotted *vs.* ($P_L + P_{L'}$) in Figure 5. ($\pi_L + \pi_{L'}$) is indeed found to be proportional to ($P_L + P_{L'}$) with a proportionality constant of 0.84. In this connection one of the results obtained by Bursten should be noted. He has observed[3] that, though ($B^{CNMe}_M - B^{CO}_M$) and ($C^{CNMe}_M - C^{CO}_M$) varied from metal to metal [for Re^I, Mn^I, and Cr^0], their sum total [*i.e.* π_L for Re^I and Mn^I and P_L for Cr^0] remained

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* Data for L = CNMe, L′ = CO, and L = L′ = CNMe are taken from ref. 11 and corrected by the difference in E^0 values of $[Cr(CO)_6]$ reported in refs. 10 and 11. Values of P_L for py, PPh_3, and MeCN could also be obtained from the data of ref. 11. But I chose to use those of Chatt, since the purpose, other than stated in the text, is to show the variations in the experimental measurements. It is noted that the P_L values calculated for MeCN and py from ref. 10 differ a little (10—30 mV) from those of Chatt.[1]

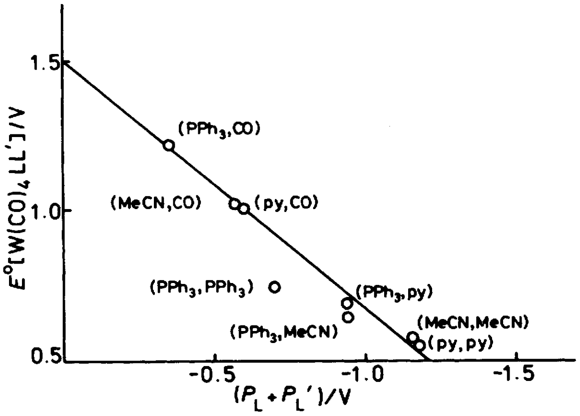

Figure 5. Variation of the potential of the W^0/W^I couple in $[W(CO)_4LL']$ with $(P_L + P_{L'})$. The point corresponding to (PPh_3, PPh_3) is not used for the least-squares fit

the same, −0.51 V [compare with Chatt's value, $P_{MeNC} = -0.43$ V]. Though this rather interesting observation is not clearly understood at the molecular orbital (m.o.) level, it appears the interactions of a particular ligand with various isoelectronic metal centres are approximately proportional to each other.

Other complexes. The situations with low-spin d^6 complexes where ligands other than CO form the majority are rather complicated. These are dealt with in the Appendices. It is observed that the applicability of the $P_{L'}$ parameters and their additivity should hold for those complexes where π-accepting abilities of the substituting ligands are less than those forming the core (unchanged) fragment.

Meanings of β *and* E_s. For completeness of the correspondence between Chatt's approach and that of Bursten, the meaning of the two site constants β and E_s of Chatt is also explored in Bursten's notion. β is the proportionality constant between π_L and P_L. The constant E_s, the potential at $P_L = 0$ or $(P_L + P_{L'}) = 0$, as the case may be, is not necessarily (see Appendices) the pure oxidation potential of the species having CO in place of the substituting ligands.

Conclusions

I have attempted to justify Chatt's correlations within the framework of Bursten's semiempirical approach. However, for understanding the real basis of the present correlations, the physical nature of P_L should be studied thoroughly at the m.o. level.

Appendix I

Complexes of Type $[ML_5L']$.—*The ligands are poorer* π *acceptors than* CO. There are two cases depending on the relative π-accepting abilities of L and L′. For simplicity it is assumed that L and L′ both have two π-accepting orbitals orthogonal to each other.

Case I: L′ *is a poorer* π *acceptor than* L. It then follows from equation (3) that E^0 is given by equation (7) where $\pi_{L'}$ =

$$E^0 = A_M^0 + 5B_M^L + 3C_M^L + B_M^{CO} + C_M^{CO} + \pi_{L'} \quad (7)$$

$B_M^{L'} - B_M^{CO} + C_M^{L'} - C_M^{CO}$. As $\pi_{L'} \propto P_{L'}$, E^0 is expected to vary linearly with $P_{L'}$. Since L is a poorer π acceptor than CO, from equation (3) follows equation (8). Comparison of

$$E^0[ML_5(CO)] = A_M^0 + 5B_M^L + B_M^{CO} + 4C_M^L \quad (8)$$

equations (7) and (8) shows that the potential at $P_L = 0$ in equation (7) is not really the oxidation potential of $[ML_5(CO)]$ as would have been expected from Chatt's notion, but it is a little more positive than that, the difference being $C_M^{CO} - C_M^L$.

Case II: L′ *is a better* π *acceptor than* L. This situation is given by equation (9). This shows that, unless $C_M^{L'}$ is negligible

$$E^0 = A_M^0 + 5B_M^L + B_M^{CO} + 4C_M^L + C_M^{CO} - C_M^{L'} + \pi_{L'} \quad (9)$$

compared with C_M^{CO}, E^0 is not expected to bear a linear relationship with P_L {giving rise to an intercept equal to $E^0[ML_5(CO)]$}, *i.e.* the applicability of P_L becomes questionable in such cases. However, it may be worth examining the deviations of the potentials corresponding to various P_L values of the ligands falling under case II from the line obtained in case I. As the proportionality constant between P_L and π_L is expected to be the same in both cases, comparison of equations (7) and (9) shows that the deviation of each point will be negative and of magnitude $(C_M^{L'} - C_M^L)$.

Thus if the difference $(C_M^L - C_M^{L'})$ is small, in practice a reasonable linearity between E^0 and $P_{L'}$ is expected for a number (depending on the position of L in Chatt's list) of substituting ligands in a series of complexes of type $[ML_5L']$ considering the limitations of the precision of experimental measurements.

Appendix II

Complexes of the Type $[ML_4L'L'']$.—*The ligands are poorer* π *acceptors than* CO. For simplicity it is again assumed that each of L, L′, and L″ has two π-accepting orbitals.

Case I: *both* L′ *and* L″ *are poorer* π *acceptors than* L. This situation gives equations (10) and (11). These show that E^0

$$E^0 = A_M^0 + 4B_M^L + 2B_M^{CO} + 2C_M^{CO} + 2C_M^L + (\pi_{L'} + \pi_{L''}) \quad (10)$$

$$E^0[ML_4(CO)_2] = A_M^0 + 4B_M^L + 2B_M^{CO} + 3C_M^L + C_M^{CO} \quad (11)$$

will vary with $(P_{L'} + P_{L''})$ linearly with an intercept of $\{E^0[ML_4(CO)_2] + C_M^{CO} - C_M^L\}$. This holds for *cis* and *trans* isomers.

Case II: *both* L′ *and* L″ *are better* π *acceptors than* L; L″ *is a better* π *acceptor than* L′. For *cis* isomers $P_{L'}$ is transferable, but not $P_{L''}$, equation (12). However, for *trans* isomers it can be

$$E^0 = A_M^0 + 4B_M^L + 3C_M^L + 2B_M^{CO} - C_M^{L''} + (\pi_{L'} + \pi_{L''}) \quad (12)$$

$$E^0 = A_M^0 + 4B_M^L + 2C_M^L + 2B_M^{CO} + 2C_M^{CO} - C_M^{L'} - C_M^{L''} + (\pi_{L'} + \pi_{L''}) \quad (13)$$

seen from equation (13) that P_L values for both L′ and L″ are not applicable. However, the deviation of a data point from the line obtained in case I for a *cis* isomer is $(C_M^L - C_M^{L'})$ and for a *trans* isomer $(- C_M^{L'} - C_M^{L''})$. For both the isomers the deviations are negative and the oxidation potentials of the *cis* isomers are expected to lie closer to the line considered than those of the *trans* isomers.

Similar conclusions are drawn if L′ = L″ in case II. However, the other possible case, where *one* of the ligands L′ and L″ is a better π-acceptor than L, is complicated as the knowledge of relative magnitudes of the corresponding C_M parameters becomes necessary to determine the nature of the d_π orbital forming the h.o.m.o.

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