

A molecular orbital approach towards designing ligand constants

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Abstract. It is shown that by a judicious mixing of ionisation potential and electron affinity, a constant can be devised for a monodentate ligand as a measure of the electronic effects exerted by the ligand. A qualitative MO treatment is presented to justify the approach.

Keywords. Ligand constant; frontier orbital approach; Hückel molecular orbital (HMO) theory.

1. Introduction

Parametrisation of the electronic effects of the ligands on various thermodynamic and kinetic properties of a metal complex is of considerable importance in inorganic chemistry. The purpose is to rationalise/understand the variation in the physico-chemical properties of a complex with ligand change. However it was only in the beginning of the last decade that Chatt (1982) first attempted to derive a parameter P_L for some monodentate ligands (L) from the redox potentials of the d^6/d^5 couples in octahedral Cr(0) complexes of type $[\text{Cr}(\text{CO})_5\text{L}]$ as below.

$$P_L = E^\circ[\text{Cr}(\text{CO})_5\text{L}] - E^\circ[\text{Cr}(\text{CO})_6]. \quad (1)$$

These P_L 's were successfully used by Chatt to correlate linearly the oxidation potentials of the complexes of some d^6 metal ions where L can be varied systematically. Later we have shown that such parameters are additive in nature and thus can be defined for a chelating ligand also (Datta 1986). But, because of the lack of appropriate electrochemical data, not many ligands could be included in Chatt's approach. In our earlier work (Datta 1986), with the help of some exemplary calculations we indicated that such ligand constants can be obtained from the redox potential data of the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ couple in octahedral complexes of type $\text{Ru}^{\text{II}}(\text{bpy})_2\text{LL}'$ where bpy is bipyridine. This was done subsequently by Lever (1990, 1991) for a wide variety of mono- and bidentate ligands. He called the derived parameter E_L (Lever 1990, 1991), and extended (Dodsworth *et al* 1994) the concept to the ligand-based redox series (Datta 1987) also. In this article we try to devise a ligand constant from qualitative MO theory maintaining a correspondence with Chatt's P_L .

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2. An approach

A complex of type ML'_5L (M : a metal ion; L, L' : monodentate ligands) can be treated as arising out of the donor–acceptor interactions between the acceptor ML'_5 fragment and the donor monodentate ligand L . We assume that only the bonding MO resulting from the interaction of ML'_5 with L is involved in an oxidative process and the antibonding MO in a reductive one. Let ψ_M be the interacting frontier orbital on the fragment ML'_5 which will be largely localised on the metal and ψ_L the frontier orbital on the ligand L with energies ε_M and ε_L respectively. We assume ψ_M to be formally empty and both electrons responsible for bonding to reside on ψ_L . With an appropriate hamiltonian H it can be written that

$$\langle \psi_{ML} | H | \psi_{ML} \rangle = \varepsilon \langle \psi_{ML} | \psi_{ML} \rangle, \quad (2)$$

where $\psi_{ML} = c_1\psi_M + c_2\psi_L$ (c_1 and c_2 : two constants). If we want to solve (2) for ε , we obtain the following secular equation,

$$(\langle \psi_M | H | \psi_M \rangle - \varepsilon)(\langle \psi_L | H | \psi_L \rangle - \varepsilon) - (\langle \psi_M | H | \psi_L \rangle - \varepsilon \langle \psi_M | \psi_L \rangle)^2 = 0. \quad (3)$$

Now, $\langle \psi_M | H | \psi_M \rangle = \varepsilon_M$ and $\langle \psi_L | H | \psi_L \rangle = \varepsilon_L$. Using a Hückel type approach (Hati and Datta 1994a) that assumes $\langle \psi_M | \psi_L \rangle = 0$ and $\langle \psi_M | H | \psi_L \rangle = (\varepsilon_M + \varepsilon_L)/2$, we have from (3)

$$(\varepsilon_M - \varepsilon)(\varepsilon_L - \varepsilon) - (\varepsilon_M + \varepsilon_L)^2/4 = 0. \quad (4)$$

The solutions of (4) are

$$\begin{aligned} \varepsilon &= (\varepsilon_M + \varepsilon_L)/2 \pm (\varepsilon_M^2 + \varepsilon_L^2)^{1/2}/2^{1/2} \\ &= (\varepsilon_M + \varepsilon_L)/2 \pm \varepsilon_M(1 + \varepsilon_L^2/\varepsilon_M^2)^{1/2}/2^{1/2}. \end{aligned} \quad (5)$$

As ε_M represents the energy of the acceptor orbital and ε_L that of the donor orbital, $|\varepsilon_L/\varepsilon_M| < 1$. This statement holds true unless ε_L becomes very positive, which, as we shall see later, will not occur within the framework of our approach. Accordingly (5) can be rewritten retaining only the second term of the expansion of $(1 + \varepsilon_L^2/\varepsilon_M^2)^{1/2}$ as

$$\varepsilon \approx (\varepsilon_M + \varepsilon_L)/2 \pm \varepsilon_M(1 + \varepsilon_L^2/2\varepsilon_M^2)/2^{1/2}. \quad (6)$$

Since $|\varepsilon_L/\varepsilon_M| < 1$, $\varepsilon_L^2/2\varepsilon_M^2 \ll 1$. Consequently we can neglect $\varepsilon_L^2/2\varepsilon_M^2$ in the second term of (6) in comparison with 1 to express ε as

$$\varepsilon \approx (\varepsilon_M + \varepsilon_L)/2 \pm \varepsilon_M/2^{1/2}. \quad (7)$$

The energy of the bonding MO is $\varepsilon^b = (\varepsilon_M + \varepsilon_L)/2 + \varepsilon_M/2^{1/2}$ which shows that under the assumption made above, for a given fragment ML'_5 , ε^b varies linearly with the energy of the frontier orbital on ligand L .

In the seventies, Sarapu and Fenske (1975) have demonstrated a remarkable linearity between oxidation potential and the HOMO (highest occupied molecular orbital) energy (calculated by a non-empirical method) for the $[Mn(CO)_n(CNCH_3)_{6-n}]^+$ series. Similar observations were made earlier by Peover (1967) for a series of aromatic hydrocarbons. Such linear correlations between redox potential and orbital energy has been subsequently verified or assumed (Trieichel *et al* 1976, 1977; Bursten 1982) in some families of organometallic complexes by Bursten and co-workers. Since the half-wave potential E° is known to be linearly related to the energy of the bonding MO, i.e. ε^b , it follows from (7) that for a given fragment ML'_5 , E° will vary linearly with ε_L also

(similar is the case with a reductive process which is related to the energy of the anti-bonding MO). Therefore, a ligand constant can be devised in terms of energy of the frontier orbital on the ligand L.

3. Results and discussion

The main problem now is to estimate ε_L . In a chemical reaction, as first shown by Fukui *et al* (1952), of all the orbitals on the interacting species, HOMO and LUMO (highest occupied and lowest unoccupied molecular orbitals respectively) take part most actively. This would mean that the interaction between ML'_5 and L can be very well represented by a four-level (two sets of HOMO and LUMO) interaction. Nevertheless, here we have reduced it to the interaction between two frontier orbitals – one on the ML'_5 fragment and another on the ligand L. We assume that the frontier orbital on an interacting species can be obtained by a judicious mixing of the HOMO and LUMO. This is, however, nothing new. A similar approach was adopted much earlier by Klopman (1968) to elucidate an acid-base interaction. He introduced the concept of such a frontier orbital as a reactivity index (Klopman 1968; Datta 1992; Hati and Datta 1994). By Koopman's theorem, for a closed-shell species the ionisation potential I characterises the HOMO, and the electron affinity A the LUMO. All the common inorganic ligands are closed-shell species. Consequently we use the I and A values of a ligand to estimate its ε_L (8) following Klopman's strategy. In (8) below, k is a constant which takes different values for the anionic donors and the neutral ones.

$$-\varepsilon_L = I - K(I - A). \quad (8)$$

To optimise the values of K we have chosen Chatt's P_L values as the reference data set. For most of the monodentate anionic ligands A values are not accessible experimentally (Pearson 1988; Hati and Datta 1996). However, here we have found that the knowledge of these A values is not necessary since for some 5 anionic and 7 neutral ligands where the P_L and I values for the anionic ligands, and the I and A values for the neutral ones are available (table 1; Huheey 1983; Pearson 1988, 1989), the maximum linear correlation between ε_L and P_L (figure 1, H^- excluded, correlation coefficient $r = 0.969$) is obtained with $K = 0$ for the anionic donors and $K = 0.25$ for the neutral ones. It seems reasonable that for the anions the frontier orbital is represented by the HOMO only. In a way, the very good linear correlation obtained between the ε_L values and the P_L constants justifies our simple model.

For some 14 neutral and 10 anionic ligands where the required I and A data (Huheey 1983; Pearson 1988, 1989) and Lever's E_L constants are known (table 1), a satisfactory linearity is observed (figure 2; $r = 0.941$; H^- , H_2O and C_2H_4 are excluded from the list given in table 1 for correlation) between the E_L constants and our ε_L values. Here we would like to note that Lever has discussed the practical difficulties in the accurate determinations of the electrochemical parameters for H^- and H_2O ; he feels that in these two cases the errors in the E_L values are rather large (Lever 1990). For example, Lever prefers an E_L value of -0.5 V for H^- (instead of -0.3 V, table 1) which fits our regression quite well. In the case of C_2H_4 , our MO model is too simple to describe its bonding with a metal centre.

An implication of our (7) is that for a given ligand, the constant, of the kind being discussed here, does not depend on the nature of the metal ion to which the ligand is bound. Experimentally this is indeed found to be true for Lever's E_L parameters (Lever

Table 1. The ε_L , P_L and E_L data for various monodentate ligands used in the present study^a

Ligand	<i>I</i>	<i>A</i>	$-\varepsilon_L^b$	P_L^c	E_L^d
N ₂	15.58	2.2	11.13	0.07	0.68
CO	12.42	-1.8	10.05	0.00	0.99
CH ₃ NO ₂	11.13	0.45	8.46	—	0.72
CH ₃ CN	12.2	-2.8	8.45	-0.58	0.34
CH ₂ CHCN	10.91	-0.21	8.13	—	0.38
H ₂ O	12.6	-6.4	7.85	—	0.04
<i>p</i> -Cl-py	10.1	-0.22	7.52	—	0.26
<i>p</i> -CH ₃ C(O)-py	9.75	0.82	7.52	—	0.30
C ₂ H ₄	10.5	-1.8	7.42	—	0.76
C ₆ H ₅ CN	9.7	0.3	7.35	-0.40	0.37
<i>p</i> -CH ₃ -py	9.50	-0.65	6.96	—	0.23
py	9.3	-0.6	6.82	-0.59	0.25
NH ₃	10.7	-5.6	6.62	-0.77	0.07
(CH ₃) ₂ S	8.7	-3.3	5.7	—	0.31
(CH ₃) ₃ P	8.6	-3.1	5.67	—	0.33
CH ₃ NH ₂	9.0	-5.3	5.42	-0.79	0.06
NO ₃ ⁻	3.93 ^e	—	3.93	—	-0.11
CN ⁻	3.82	—	3.82	-1.00	0.02
Cl ⁻	3.62	—	3.62	-1.19	-0.24
F ⁻	3.40	—	3.40	—	-0.42
Br ⁻	3.36	—	3.36	-1.17	-0.22
N ₃ ⁻	3.32	—	3.32	—	-0.30
I ⁻	3.06	—	3.06	-1.15	-0.24
C ₆ H ₅ S ⁻	2.47	—	2.47	—	-0.53
CH ₃ S ⁻	1.9	—	1.9	—	-0.56
OH ⁻	1.83	—	1.83	-1.55	-0.59
H ⁻	0.74	—	0.74	-1.22	-0.30

^apy = pyridine; relevant *I* and *A* data are taken from Pearson (1988, 1989) unless otherwise specified; ^bin eV; calculated using (8) with $K = 0$ for the anionic ligands and $K = 0.25$ for the neutral ones (see text); ^cin V; from Chatt (1982) except for CH₃NH₂ which was set equal to $\frac{1}{2}$ of the P_L value for ethylenediamine (see Datta 1986); ^din V; taken from Lever (1990, 1991) except for methylamine which was set equal to the E_L value of ethylenediamine (Lever 1990) because of substitutional similarity; ^efrom Huheey (1983).

1990, 1991; Fielder *et al* 1995). The situation seems to be similar for Chatt's P_L parameters also (Datta 1986).

We now examine the nature of ε_L . Almost at the same time as Chatt (1982), Bursten (1982) proposed a model of ligand additivity from qualitative MO theory on the redox potentials of octahedral mixed carbonyl complexes of type $M(\text{CO})_n(\text{CNR})_{6-n}$ and $M(\text{CO})_n(\text{NCR})_{6-n}$ where *M* has d^6 configuration. In Bursten's model, each ligand is assigned two parameters – *B* and *C* to indicate respectively the σ -donation and the π -back acceptance abilities of the ligand. Earlier we have shown (Datta 1986) that for ligands that are weaker π -acids than CO, Chatt's P_L constants are composed of the *B* and *C* parameters. But, there are some problems in deriving the ligand constants from the redox data of the Ru^{II}/Ru^{III} couple in Ru(bpy)₂LL' complexes. It can be shown

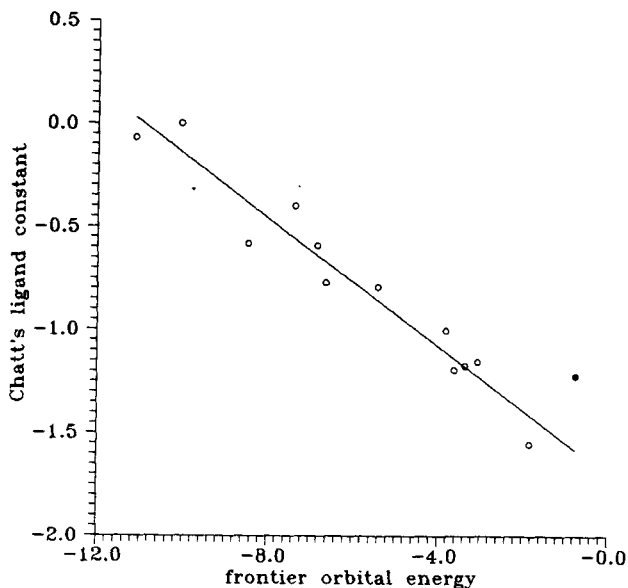


Figure 1. Final correlation between Chat's ligand constant P_L (in V) and the frontier orbital energy ϵ_L (in eV) for some monodentate ligands (see text). For data, see table 1. $r = 0.969$; H^- , marked by a dark circle, is excluded from the correlation.

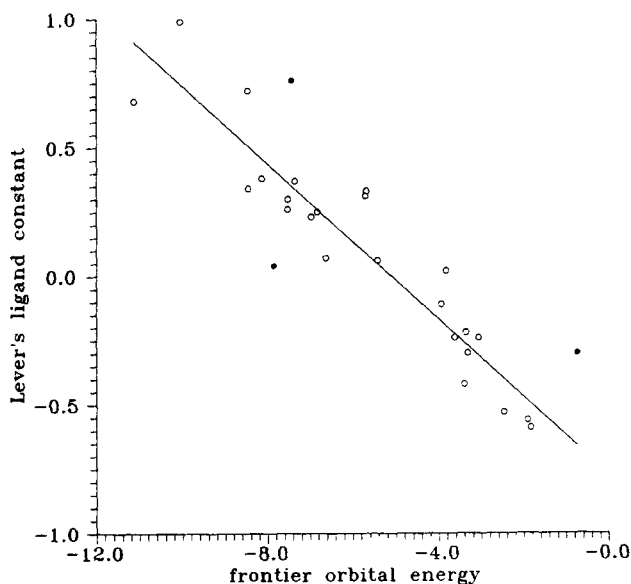


Figure 2. Correlation of Lever's ligand constants E_L (in V) with the frontier orbital energy ϵ_L (in eV) for some monodentate ligands. For data, see table 1. $r = 0.941$; H^- , H_2O and C_2H_4 , marked by dark circles, are not included in the least squares fit.

within the framework of Bursten's model, which is theoretically quite reasonable though qualitative, that for ligands that are stronger π -acceptors than bpy, the E_L constants can be expressed in terms of the B parameters only. For this reason, for

ligands like nitriles which are stronger π -acids than bpy, Lever had to introduce some "corrections" to their E_L values in certain cases (Lever 1990, 1991). However, since B parameters indicate the net donation of electrons which is related to $[(\sigma \text{ donation from L}) - (\pi\text{-back acceptance by L})]$, it is expected that E_L indirectly reflects some effects of the π -back acceptance by a ligand. This is evident from the results of the recent AM1 calculations and subsequent mapping of ligand molecular electrostatic potentials done by Lever and co-workers on $\text{Cl}^+ - \text{L}$ systems where Cl^+ is assumed to play the role of a transition metal ion (Fielder *et al* 1995). On the other hand, our ϵ_L parameters, since obtained from the energies of the HOMO and LUMO of a ligand, are expected to reflect both σ -donation and π -acceptance abilities of a ligand. It should be mentioned here that since we feel E_L does not indicate the π -accepting ability of a ligand explicitly, for optimising the values of K in (8) we have not used the E_L parameters as the reference data set. The ϵ_L parameters for π -acids are found to be more negative than those for pure σ -donors.

4. Conclusions

Here we have proposed a very simple approach to devise ligand constants from a judicious mixing of their ionisation potential and electron affinity. We have tried to justify our approach by using qualitative MO theory. The MO treatment, though discussed for $L'_s/M-L$ type of interaction, can evidently be applied to describe the change in the energy of the bonding orbital (ϵ^b) of a system of two interacting species where one of the entities forms the unchanged (core) fragment and the other one is varied systematically. A condition other than those mentioned above for the applicability of our model is that the metal ion and the ligands should be closed shell species.

Our results also help in understanding the real nature of the two electrochemical constants, P_L and E_L , at the MO level.

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