First-Principles Interpretation of Ligand Electrochemical (E_L(L)) Parameters. Factorization of the σ and π Donor and π Acceptor Capabilities of Ligands

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Abstract: The ligand electrochemical series, E_L(L), has been developed for many hundreds of ligands, and provides an accurate prediction of metal-centered redox potentials for coordination complexes. Semiempirical methods are used in conjunction with second-order perturbation theory to provide a new method to factorize the E_L(L) parameter and extract a new and general measure of the σ- and π-donating and π-accepting properties of a ligand.

Introduction

Recently, a ligand electrochemical series has been introduced and developed.[1] This set of ligand parameters E_L(L), initially based on the Ru(III)/Ru(II) redox couple, is used to predict an $M(n)/M(n-1)$ redox potential by assuming that all ligand contributions are additive, $\sum E_L$(L), taking the form

$$E_{\text{redox}} = S_{\text{m}}(\sum E_L(\text{L})) + I_{\text{m}} \tag{1}$$

The values of S_m and I_m are specific for the spin state and redox couple of the metal, and the summation is carried out over all ligands in the complex. Moreover, a ligand's E_L(L) parameter is independent of the metal to which it is bound. This conclusion leads us to question the nature of the E_L(L) parameter and to propose an explanation of the apparent uncoupling of metal and ligand terms in eq 1.

A transition metal complex can be modeled as a central metal ion surrounded by a set of ligands held in close proximity by electrostatic forces. In an octahedral arrangement, the electrostatic field removes the degeneracy of the five d orbitals, leaving behind the familiar set of t_{2g} and e_g orbitals. While this model is clearly oversimplifed, it has long served as a starting point for metal–ligand interactions. Our current view replaces the electrostatic field with a molecular orbital mixing framework. The degenerate d orbitals are thought of as being split by the ligand's σ-donating and π-donating or -accepting abilities. The E_L(L) value will consequently be a function of both ligand σ and π factors.[1] In this paper we investigate the relationships between semiempirical charge distributions and experimental ligand electrochemical parameters for various ligands along the electrochemical series. One method of theoretically representing charge distributions in a molecule is through the evaluation of its molecular electrostatic potential function, V_{MEP}.[2] V_{MEP} is a continuous function which describes the electric field emanating from a molecule generated by virtue of its charge distributions. It has been demonstrated that V_{MEP} can act as a measure of molecular properties which are due primarily to electron availability. V_{MEP}, evaluated at the site of a lone pair for example, has recently been shown to correlate with a nucleophile's basicity; when evaluated at the site of an acidic proton, V_{MEP} correlates well with an acid's gas phase or aqueous acidity.[3] In this study, we begin by assuming that a ligand's E_L(L) value is determined solely by σ bonding (and π-donating ability) as measured by V_{MEP}, and subsequently add π back-donation to factorize E_L(L) in terms of all three bonding properties. This first-principles analysis not only allows for facile calculation of unknown E_L(L) parameters, but affords a new procedure for factoring out the σ and π properties of a ligand.

Methods

All ligand structures were fully geometry optimized using a Cartesian gradient optimizer at the semiempirical AM1 level.[4] The geometry optimizations were performed with a chlorine cation, Cl^+, attached to the ligand at the site of metal coordination to mimic the elecron-withdrawing effects of a metal ion. Cl^+ was chosen since transition metals are not available at the AM1 level, and chlorine provides a monatomic ion with a well-defined semiempirical parameter set. Ligand molecular electrostatic potentials (V_{MEP}) were then determined from RHF AM1 molecular wave functions as the interaction energy of a point positive charge with the electron distribution of the free (uncoordinated) ligand, as previously described.[2] V_{MEP} is a continuous function describing the electric field surrounding a molecule, and is calculated by determining the electrostatic interaction between a point probe of unit positive charge and the total electron density at a set of grid loci, r_i, in the vicinity of the molecule according to eq 2, where

$$V_{\text{MEP}}(r_i) = \sum_A \frac{Z_A}{|r_i - R_A|} - \int \frac{\varrho(r)}{|r_i - r|}\,\text{d}r \tag{2}$$

Z_A and R_A are the atomic number and location of atom A, respectively, and $\varrho(r)$ is the total electron density function of the molecule. The

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Table 1. Experimental Ligand Electrochemical Parameters, AM1-Calculated Molecular Electrostatic Potentials, Back-Bonding Propensities, and Calculated Electrochemical Parameters for Non-Back-Bonding and Back-Bonding Ligands

ligand	E_L (V exptl)[a]	V_{MEP} (eV)	V_b (eV)	E_L(eq 3)	E_L(eq 6)	error (E_L(exptl) − E_L(eq 6))
			Non-Back-Bonding Ligands			
F^-	−0.42	−11.1	0	−0.38	−0.38	−0.04
H^-	−0.30	−9.97	0	−0.31	−0.33	0.03
$HCOO^-$	−0.30	−9.28	0.035	−0.27	−0.25	−0.05
NCO^-	−0.25	−8.85	0.034	−0.25	−0.23	−0.02
Cl^-	−0.24	−8.20	0	−0.21	−0.24	0.00
Br^-	−0.22	−7.03	0	−0.15	−0.18	−0.04
ox^{2-}	−0.17	−8.41	0.042	−0.22	−0.19	0.02
CF_3COO^-	−0.15	−8.33	0.042	−0.22	−0.19	0.04
NCS^-	−0.06	−6.38	0.085	−0.11	−0.04	−0.02
H_2O	0.04	−2.45	0.001	0.10	0.05	−0.01
i-prNH_2	0.05	−3.28	0.056	0.06	0.08	−0.03
NH_3	0.07	−3.09	0.034	0.07	0.06	0.01
$PhCH_2NH_2$	0.14	−3.01	0.047	0.08	0.08	0.06
			Back-Bonding Ligands			
CN^-	0.02	−8.59	0.165	−0.23	−0.04	0.06
py	0.25	−2.86	0.134	0.07	0.21	0.04
pyz	0.33	−2.57	0.308	0.10	0.44	−0.11
3,5-Cl_2-py	0.33	−2.37	0.164	0.11	0.27	0.06
CH_3CN	0.34	−2.41	0.228	0.11	0.35	−0.01
PhCN	0.37	−2.30	0.238	0.12	0.37	0.00
P(Ph-*p*-Me)$_3$	0.37	−1.57	0.192	0.16	0.34	0.03
PPh_3	0.39	−1.50	0.195	0.16	0.35	0.04
$P(OMe)_3$	0.42	−0.59	0.358	0.21	0.61	−0.19
p-dicyanobenzene	0.49	−2.09	0.262	0.13	0.41	0.08
CO	0.99	−1.51	0.633	0.16	0.92	0.07

[a] Experimental E_L(L) values reported in volts with respect to NHE.

grid loci at which the V_{MEP} were evaluated were defined by the surface of constant total electron density (isodensity surface) of 0.002 esu Å^{-3}. This value was chosen because it has been previously shown to generate an isodensity surface which closely mimics the superposition of atomic van der Waals radii for most molecules.[5]

All AM1 and V_{MEP} calculations were performed using the Spartan system of programs on a Silicon Graphics 4D/35, an Indigo R3000, an Indigo R4000, or an IBM 350 RS6000 computer. Multiparameter regressions were performed by the quadratic convergent method of Powell.[6] Second-order perturbation calculations were performed using molecular wave functions stored on the Spartan archive files with in-house code. For these calculations, a chloride probe, Cl^-, was attached to the ligand at the site of metal coordination. AM1 resonance integrals between the ligand and probe orbitals were then calculated as a measure of back-donation interactions with the ligand. σ and π effects were separated by appropriate coordinate transformations of the wave functions using in-house code. The coordinate system was then translated and rotated such that the ligand's coordinating atom was at the origin with the probe lying on the z axis. Ligand π resonance integrals were then evaluated by including only interactions involving probe p_x and p_y atomic orbitals.

Results

A set of ligands spanning a wide range of E_L(L) values was chosen, and their molecular electrostatic potential (V_{MEP}) functions were calculated. Table 1 compares the E_L(L) parameters with the V_{MEP} evaluated at the intersection point of the isodensity surface and the interatomic axis connecting the ligating atom with a metal to which it would coordinate. For the moment excluding ligands which exhibit moderate to strong back-bonding effects, a linear correlation between E_L(L) and coordination site V_{MEP} exists with a correlation coefficient of 0.961, as represented by eq 3, where a_0 and a_1 are optimized

$$E_L(\text{calcd}) = a_0 + a_1 V_{MEP} \qquad (3)$$

regression coefficients having values of 0.246 V and 0.056 V eV^{-1}, respectively, with an RMS error of 0.046 V for 13 points. These data are tabulated in Table 1, and plotted in Figure 1; the line in Figure 1 is the zero-intercept, unity-slope line, representing the hypothetical perfect correlation. Also plotted in Figure 1 are the calculated E_L(L) (eq 3) values for moderately and strongly back-bonding ligands. For these ligands the correlation is, as expected, seriously diminished, with all points falling significantly *below* the unity-slope line (E_L(calcd) < E_L(exptl)), indicating that, where applicable, back-bonding effects are important contributors and tend to *raise* the E_L(L) value.

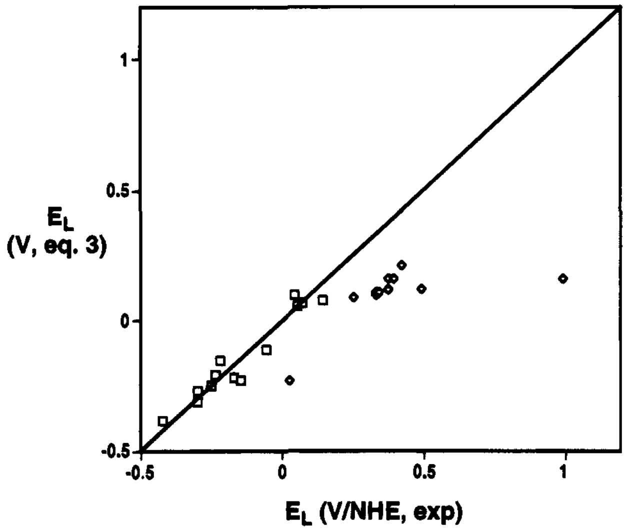

Figure 1. Correlation of experimental ligand electrochemical parameters with AM1-calculated molecular electrostatic potentials: (□) non-back-bonding ligands; (◇) moderately and strongly back-bonding ligands.

The acceptor orbitals of a ligand in an octahedral field will possess the correct symmetry to mix with the metal t_{2g} orbitals. This mixing will further lower the t_{2g} energy levels, and it becomes clear why a simple V_{MEP} model is not sufficient for

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back-bonding ligands. Developing an expression to account for π back-donation without the direct use of the specific metal is difficult. Electronic structure methods do not yield themselves to the separation of terms like "σ donation" and "π back-donation". In fact, it can be argued that V_{MEP} must couple both the σ and π donor terms. However, by using second-order perturbation theory, it is possible to construct an approximation which will yield a useful measure of a ligand's back-bonding ability. Hence, we treat the metal−ligand bond as two interacting molecular fragments, and relate the relative back-bonding ability of a ligand to the interaction energy, ΔE, including only the unoccupied molecular orbitals of the ligand.

The energy of interaction, ΔE, between filled molecular orbitals of molecular fragment A with unfilled orbitals of molecular fragment B can be expressed as[7]

$$\Delta E = \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{unocc}} \frac{2(\sum_{\mu}\sum_{\nu} c_{\mu i} c_{\nu j} \beta_{\mu\nu})^2}{|\epsilon_i - \epsilon_j|} \tag{4}$$

where ϵ_i and ϵ_j are the molecular orbital energy eigenvalues pertaining to the respective fragments, $c_{\mu i}$ and $c_{\nu j}$ are the coefficients of atomic orbitals ϕ_μ in molecular orbital i on fragment A and ϕ_ν in molecular orbital j on fragment B, respectively, and $\beta_{\mu\nu}$ is the resonance integral between ϕ_μ and ϕ_ν. In our model, eq 4 is modified such that an arbitrary probe atom is used to act as a generic metal center. Since, at present, semiempirical forms for d orbital resonance integrals are not available at the AM1 level, we chose a chloride probe (Cl^-) and queried π-symmetry interactions via the chlorine p orbitals. Although the nature of the probe atom is arbitrary, since $E_{\mathrm{L}}(\mathrm{L})$ is a property of the ligand only, chlorine was chosen due to its well-defined parameterization and demonstrated accuracy at the AM1 level in reproducing molecular properties.[4,8] With the ligand oriented in space such that the ligand−probe bond lies on the z axis, any π-symmetry metal−ligand interactions will be manifested by nonzero resonance integrals involving only probe p_x and p_y atomic orbitals; in the rotated coordinate system, probe p_x and p_y necessarily uncouple with probe−ligand σ interactions. Hence, our use of an arbitrary probe to generate a "molecular back-bonding potential" is directly analogous to the use of a point positive charge to generate a molecular electrostatic potential. The perturbation now takes the form

$$V_{\mathrm{b}} = \sum_{i}^{\mathrm{unocc}} \left[\frac{(\sum_{\mu} c_{i\mu} \beta_{\mu \mathrm{p}_x})^2 + (\sum_{\mu} c_{i\mu} \beta_{\mu \mathrm{p}_y})^2}{|\epsilon_i - \epsilon_{\mathrm{p}}|} \right] \tag{5}$$

where the coefficients of the probe atom are taken to be unity. The resonance integrals, $\beta_{\mu\nu}$, were calculated in accordance with the AM1 formalism as previously described.[9] The outer summation loops over all unoccupied molecular orbitals of the ligand. In the selected coordinate system ligand molecular orbitals which do not possess a component of probe p_x or p_y symmetry will vanish. ϵ_i are the energies of the unoccupied ligand molecular orbitals, and ϵ_{p} is the energy of the probe atomic p orbitals. Appending expression 5 onto eq 3 gives

$$E_{\mathrm{L}}(\mathrm{calcd}) = a_0 + a_1 V_{\mathrm{MEP}} + a_2 \sum_{i}^{\mathrm{unocc}} \left[\frac{(\sum_{\mu} c_{i\mu} \beta_{\mu \mathrm{p}_x})^2 + (\sum_{\mu} c_{i\mu} \beta_{\mu \mathrm{p}_y})^2}{|\epsilon_i - \epsilon_{\mathrm{p}}|} \right] \tag{6}$$

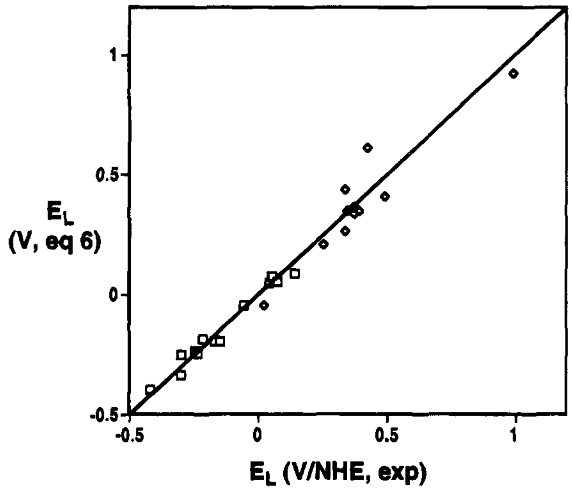

Figure 2. Correlation of experimental ligand electrochemical parameters with AM1-calculated molecular electrostatic potentials and back-bonding correction: (□) non-back-bonding ligands; (◇) moderately and strongly back-bonding ligands.

ϵ_{p} was set as the p atomic orbital eigenvalue from a closed-shell AM1 calculation of Cl^- (−2.890 eV), and eq 6 was fit to the $E_{\mathrm{L}}(\mathrm{L})$ values of the entire set of ligands in Table 1. The resulting correlation of $E_{\mathrm{L}}(\mathrm{exptl})$ with $E_{\mathrm{L}}(\mathrm{calcd})$ from eq 6 is also presented in Table 1, and graphically in Figure 2. The optimized parameters are $a_0 = 0.175$ V, $a_1 = 0.050$ V eV^{-1}, and $a_2 = 1.290$ V eV^{-1}, and the correlation coefficient is 0.984, with an RMS error of 0.060 V for 24 points. The line in Figure 2 is the zero-intercept, unity-slope line. Note the markedly improved correlation for moderately and strongly back-bonding ligands over that obtained using eq 3. Moreover, the improvement does not occur at the expense of correlation with non-back-bonding ligands; i.e., the V_{b} term is generally very small for non-π-accepting ligands as expected. As it may be argued that the unoccupied molecular orbitals are referred to an arbitrary zero in a Hartree−Fock formalism, a check was performed on our choice of ϵ_{p} by allowing ϵ_{p} to optimize along with the regression coefficients. This produced an ϵ_{p} of −2.31 eV and less than a 1% change in the values of a_0, a_1, and a_2, and decreased the rms error of the fit by less than 1 mV.

Although the purpose of this analysis is to enable a fundamental understanding of the nature of the empirically derived $E_{\mathrm{L}}(\mathrm{L})$ parameters, one cannot overlook the obvious practical utility of eq 6 in predicting the $E_{\mathrm{L}}(\mathrm{L})$ of a yet to be studied ligand, or in the molecular design of ligands with specific electrochemical influences on a metal center. Consequently, eq 6 suggests that a measurement of a ligand's $E_{\mathrm{L}}(\mathrm{L})$ is in fact a measurement of the ligand's propensity for back-bonding. Rearranging,

$$V_{\mathrm{b}} = \sum_{i}^{\mathrm{unocc}} \left[\frac{(\sum_{\mu} c_{i\mu} \beta_{\mu \mathrm{p}_x})^2 + (\sum_{\mu} c_{i\mu} \beta_{\mu \mathrm{p}_y})^2}{|\epsilon_i - \epsilon_{\mathrm{p}}|} \right] \approx \frac{E_{\mathrm{L}}(\mathrm{exptl}) - a_1 V_{\mathrm{MEP}} - a_0}{a_2} \tag{7}$$

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Although a detailed analysis employing eq 7 is, at this point, premature, the predicted general trend of relative back-bonding ability, NO > CO > CH_3NC > $P(OCH_3)_3$ ≈ PPh_3 ≈ CH_3CN > py > Me_2S > Cl^-, appears to agree well with that obtained from a Cotton–Kraihanzel (CK) analysis of IR vibrational data, although exact numerical relationships of back-bonding ability between ligands are not rigorously obtainable from a CK approach.[10] Since V_{MEP} is easily calculated (and readily available from most electronic structure programs), eq 7 may provide an electrochemical means by which relative back-bonding ability may be assessed. Further investigations into the utility of eq 7 in determining relative back-bonding capabilities from electrochemical data are presently underway in our laboratories.

Aside from providing a first-principles basis for additive ligand electrochemical parameters, it is evident at this point that the analysis summarized in eqs 6 and 7 leads to fundamental insight into the nature of metal–ligand bonding. Moreover, the analysis demonstrates that, when parameterized with readily obtained electrochemical data, a simple second-order perturbation approach using semiempirical ligand wave functions can effectively afford the relative importance of electrostatic field and ligand back-bonding effects on the electrochemical properties of a transition metal complex, and provides a unique assessment of the σ and π characteristics of any ligand.

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