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Electronegativity: Coordination Compounds

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The utility of electronegativity and the extended electronegativity function in describing the charge distribution in simple coordination compounds of both the representative and transition metals has been explored. The extended electronegativity function has been shown to yield excellent atomic charges and charging energies. When applied to simple coordination compounds of the representative and transition elements, there is excellent qualitative agreement between the atomic charges and charging energies with the range of chemical behaviors of these compounds. In addition, the hydrolysis constants of these complexes have been used as probes to assess the success of electronegativity and the electronegativity function in describing in a quantitative manner the distribution of charge in these molecules as well as the energetics of hydrolysis of these compounds. For these simple coordination compounds the absolute electronegativities and absolute hardnesses in conjunction with the extended electronegativity function show considerable promise in their application to coordination compounds.

Introduction

Although Pauling proposed the modern definition of electronegativity over 60 years ago,[1] it is still the subject of active investigation.[2−8] This is due in large part to its role as the property of an atom that determines the distribution of charge in a molecule. In addition to the charge distribution in a molecule, electronegativity has been intimately tied to the concept of chemical hardness,[9] as well as the energetics of charge transfer in molecules.[8,10] Until relatively recently the use of electronegativity had remained for the most part qualitative and restricted to very simple molecules. This is no longer the case. There has developed considerable interest in the quantitative application of electronegativity to complex systems.

There are a number of reports on the computation of atomic charges based on a variety of electronegativity equalization procedures.[5−8] These have most frequently been formulated within the density functional model and have been successfully used to determine atomic charges for such large molecules as peptides and zeolite model compounds. The extended electronegativity function is a formulation that derives from the LCAO-MO approximation and the expression for the expectation value for the electronic energy of molecules. The extended electronegativity function has yielded, in addition to excellent atomic charges, estimates of the energies involved in charge transfer processes in molecules. Among the strengths of the extended electronegativity function is its faithfulness to Pauling's original vision. This formulation requires only the valence state electronegativities of the atoms and the bond structure of the molecule. It is very intuitive, and computations are simple, requiring only a hand calculator.

In its application to simple compounds of the representative elements the extended electronegativity function has been very successful. Despite the continued interest in electronegativity, little work has been done on its role in the chemistry of coordination compounds, a topic that also includes metal ions in solution. This is evidenced by the relatively few citations of Hinze and Jaffe's compilation of transition metal electronegativities.[11] In this report the application of the extended electronegativity function to simple coordination compounds of the representative and transition elements will be examined. Of particular interest is the appropriateness of the extended electronegtivity function in coordination compounds of the representative and transition elements. Among the questions that arise are: what are the appropriate valence states for the metal ions, what happens at discontinuities in the electronegativity, can the extended electronegativity function handle metals exhibiting a variety of stable oxidation states, and what is the appropriate ligand to metal bond order in the localized bonding model utilized by the extended electronegativity function?

Theory

Background. Pauling's definition of electronegativity as the ability of an atom to attract electrons to itself in a bond suggests that the atom must in effect persist in some form in the molecule and that a charge is associated with that atom.[12−14] Furthermore, the formulation of electronegativity by Mulliken[15] and its refinement by Ickowski and Margrave[16] described electronegativity as relating an atom's energy to its charge, eq 1.

$$\chi_i(q_i) = \frac{\partial E_i}{\partial q_i} = a_i + b_i q_i \tag{1}$$

This in a sense defines and describes both the atom in a molecule and its charge. In addition the work of Klopman[17] has provided an interpretation of the empirical constants *a* and *b* (the absolute electronegativity and absolute hardness, respectively) in terms of the Coulombic interactions present in these atoms. Because eq 1 derives from the empirical expression for the energy of an atom, which is quadratic in the atom's charge, eq 2,

$$E_i(q_i) = a_i q_i + \frac{1}{2} b_i q_i^{\,2} \tag{2}$$

the Ickowski−Margrave formulation not only identifies the atom in a molecule and its charge but also describes the relationship between that atomic charge and the atom's electronic energy.

It has been pointed out that the Ickowski−Margrave electronegativities are those of isolated atoms and are thus not

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entirely satisfactory for atoms in molecules.[5,10] However, examination of the common expression for the electronic energy of molecules (eq 3) has revealed that the Ickowski−Margrave electronegativity function (eq 1) can be derived from the molecule's electronic energy expression.[13]

$$E = \sum_{k}^{N}\sum_{a}^{A} c_{ka}{}^{2} I_a + 1/2\sum_{k}^{N}\sum_{a}^{A}\sum_{\neq b}^{A} c_{ka}{}^{2} c_{kb}{}^{2} (J_{ab} - K_{ab})\delta_{ab} + 1/2\sum_{k}^{N}\sum_{a}^{A}\sum_{\neq b}^{A} c_{ka}c_{kb}H_{ab}(1 - \delta_{ab}) + H^{\mathrm{ES}} \quad (3)$$

Here I_a and $(J_{ab} - K_{ab})$ are the electron−core and electron−electron interaction energies, respectively, and δ_{ab} equals zero unless a and b are on the same atom. H^{ES} are the through-space electrostatic interaction energies, and c_{ka} are molecular orbital coefficients. The k summation is over the occupied molecular orbitals, and a and b are the orbitals of the basis set. Klopman[17] and Reed[10] have shown that the absolute electronegativity and absolute hardness are related to these terms by

$$\begin{aligned} -a_i &= I_i + b_i N^0{}_i \\ b_i &= (1 - 1/Q_i)(J_i - K_i) \end{aligned} \quad (4)$$

where Q_i is the number of valence orbitals on atom i. These are taken to be identical. However, the influence of H_{ab}, the resonance integrals,

$$H_{ab} = \int \varphi_a \mathscr{H} \varphi_b \,\mathrm{d}\tau \quad (5)$$

is not considered in the Ickowski−Margrave electronegativity function.[10] Here φ_a and φ_b are atomic orbitals on different atoms. In order that the influence of the resonance integrals (and hence bonding) might be considered in a more complete electronegativity function, eq 3 was examined, and the extended electronegativity function was formulated:

$$\chi_i(q_i) = a_i + r_i + \frac{1}{2} b_i q_i \quad (6)$$

This electronegativity function includes the connectivity potential, r_i, which reflects the effects of bond formation on the electronegativity of atom i. It is described in more detail in the next section. A detailed derivation of the extended electronegativity function may be found in ref 13.

Fractional Bond Order. In the process of incorporating the bonding interactions into the extended electronegativity function, the integral

$$P_{kab} = \int [c_{\mathrm{ka}}\varphi_a + c_{kb}\varphi_b]^2 \,\mathrm{d}\mathbf{r} \quad (7)$$

was introduced. This integral may be approximately interpreted as the occupancy of a localized bonding molecular orbital. Multiplying through by H_{ab} and rearranging yields

$$c_{ka}c_{kb}H_{ab} = \frac{1}{2}[P_{kab}H_{ab}/S_{ab} - c_{ka}{}^{2}H_{ab}/S_{ab} - c_{ka}{}^{2}H_{ab}/S_{ab}] \quad (8)$$

The H_{ab}/S_{ab} (r_{ab}) term is the connectivity potential between orbitals a and b,[8] and

$$r_i = \frac{1}{Q_i}\sum_{j}^{Q_i} r_{ij} = \frac{1}{Q_i}\sum_{j}^{Q_i}\frac{H_{ij}}{S_{ij}} \quad (9)$$

where Q_i is the number of orbitals being utilized by atom i, and the summations are over the valence orbitals. The valence orbitals on each atom are chosen to be identical.[13] The connectivity potentials may be interpreted as the potentials for the attraction of electron density into the bonding regions of the molecule.

In the application of the extended electronegativity function there is one connectivity potential for each two-centered bond.[13] In this very simple description a bond requires two electrons and two orbitals, one from each atom. For many coordination compounds, however, there are too few accessible metal and ligand orbitals for this to be possible. It is most often the case that it is the acceptor atom that contributes too few atomic orbitals. As a result P_{kab} cannot approximate the occupancy of a two-centered two-electron bond, but rather some fraction, f_{ab}, thereof. Equation 8 should thus be recast as

$$c_{ka}c_{kb}H_{ab} = \frac{1}{2} f_{ab}[P_{kab}H_{ab}/S_{ab} - c_{ka}{}^{2}H_{ab}/S_{ab} - c_{kb}{}^{2}H_{ab}/S_{ab}] \quad (10)$$

If N_{o} is the number of valence orbitals being utilized and N_{e} the number of electrons available to form N_{b} pairwise bonding interactions, then f_{ab} is

$$f_{ab} = \frac{N_{\mathrm{o}} - \frac{1}{2}}{N_{\mathrm{b}}} \quad (11)$$

For example in the case of an aqueous sodium ion there are six ligand−metal interactions, 12 electrons (two from each ligand), and 10 orbitals (four from the metal and six from the ligands). Thus f equals two-thirds. The expression for the connectivity potential now becomes

$$r_i = \frac{1}{Q_i}\sum_{j}^{Q_i} f_{ij} r_{ij} = \frac{1}{Q_i}\sum_{j}^{Q_i}\frac{f_{ij}H_{ij}}{S_{ij}} \quad (12)$$

which now allows for fractional bond orders.

Valence and Core Electronegtivities. The absolute electronegativity and absolute hardness of orbitals are independent of the atom's charge. They are, however, dependent on the nature of the atomic orbitals.[15] When the increment of charge transferred is sufficiently large, a discontinuity in the electronegativity function is encountered as charge is transferred. This occurs at the point where all of the valence electrons are removed, and any additional charge must be removed from core orbitals. At this point the valence orbital electronegativities (χ^{valence}) must be replaced with core orbital electronegativities (χ^{core}). This situation arises when the ligand and metal valence orbital electronegativities have not yet equalized, even when all of the valence electrons have been transferred from the metal's valence shell.

According to the Sanderson principle,[18] if the electronegativity of the ligand (χ_{L}) is greater than the electronegativity of the metal (χ_{M}), electron density transfers to the ligand, and when $\chi_{\mathrm{M}} > \chi_{\mathrm{L}}$, electron density transfers to the metal. In addition, whereas $\chi_{\mathrm{M}}{}^{\mathrm{core}}$ is virtually always greater than χ_{L}, $\chi_{\mathrm{M}}{}^{\mathrm{valence}}$ is less than χ_{L} and increases as the charge on the metal increases. Let $q_{\mathrm{M}}{}^{\mathrm{o}}$ be an atomic charge for which an atomic charge $q_{\mathrm{M}}{}^{\mathrm{o}} + \mathrm{d}q$ involves core orbitals and $q_{\mathrm{M}}{}^{\mathrm{o}} - \mathrm{d}q$ involves valence orbitals. Consider the case where $\chi_{\mathrm{M}}{}^{\mathrm{core}}$ is greater than χ_{L} and $\chi_{\mathrm{M}}{}^{\mathrm{valence}}$ is less than χ_{L} for the charge $q_{\mathrm{M}}{}^{\mathrm{o}}$. Thus when the metal's atomic charge is $q_{\mathrm{M}}{}^{\mathrm{o}} + \mathrm{d}q$, electron density transfers to the metal, but when it is $q_{\mathrm{M}}{}^{\mathrm{o}} - \mathrm{d}q$, electron density transfers to the ligand. In either instance as charge is transferred, dq approachs zero and

TABLE 1: Absolute Elelctronegativities and Absolute Hardnesses of Selected Elements and in Selected Valence States

element[a]	absolute electronegativity[b]	absolute hardness	element[a]	absolute electronegativity[b]	absolute hardness
Li (sp^3)	2.31	3.38	In (sp^3)	5.09	6.02
Na (sp^3)	1.87	3.38	Cr (sp^3)	21.25	−29.32
K (sp^3)	2.04	2.21	Mn (sp^3)	30.17	−36.11
Rb (sp^3)	2.19	1.61	Fe (sp^3)	26.55	10.53
Be (sp^3)	3.84	6.67	Co (sp^3)	9.54	2.89
Mg (sp^3)	3.30	5.96	Zn (sp^3)	3.77	5.32
Ca (sp^3)	2.56	4.36	Cr (d^2sp^3)	22.30	−26.46
Sr (sp^3)	4.38	4.13	Mn (d^2sp^3)	30.57	−28.47
B (sp^3)	5.99	8.90	Fe (d^2sp^3)	29.43	19.30
Al (sp^3)	5.37	5.59	Co (d^2sp^3)	12.27	3.82
Ga (sp^3)	6.62	5.20			

[a] The values in parentheses are the hybridizations of the acceptor atom. [b] Data taken from refs 21−23.

the charge appoaches q_M^o. The net result is that in such cases electron transfer ceases only when the metal atomic charge becomes equal to q_M^o, which is the charge at the discontinuity in the electronegativity function.

Charging Energy. The change in charging energy is yet another way of partitioning the change in energy for a physical or chemical process.[8] Its existence is implicit in the Ickowski−Margrave electronegativity formulation. In words, the charging energy of an atom, $E^c{}_i$, is the energy required to charge an atom in a molecule, and the change in charging energy, $\Delta E^c{}_i$, is the energy required to alter its charge. The change in charging energy is of interest, because it is a major component of the energetics of many processes. The charging energy for a molecule is the sum of the charging energies of its atoms. Thus the change in charging energy for the molecule is

$$\Delta E^C = \sum_i^A \Delta E^c{}_i = \sum_i^A \int_{q_i^{\mathrm{i}}}^{q_i^{\mathrm{f}}} \chi(q_i)\, \mathrm{d}q_i \tag{13}$$

where $\chi(q_i)$ are the Ickowski−Margrave electronegativities, the summations are over all of the atoms in the molecule, and the integrations are over the change in the atomic charge of each atom. Equation 2 yields very reasonable estimates of $E(q_i)$. Thus the integration yields

$$\Delta E^C{}_i = (a_i q_i + 1/2 b_i q_i{}^2)\big|_{q_i^{\mathrm{i}}}^{q_i^{\mathrm{f}}} \tag{14a}$$

$$\Delta E^C = \sum_i^A \Delta E^C{}_i = \sum_i^A (a_i q_i + (1/2) b_i q_i{}^2)\big|_{q_{\mathrm{i}}^{\mathrm{i}}}^{q_{\mathrm{f}}^{\mathrm{i}}} \tag{14b}$$

Thus the charging energies and change in charging energy can be evaluated from only a knowledge of the molecule's bonding and using the absolute electronegativities, absolute hardnesses, and atomic charges of the atoms in the molecule.

Electronegativity Equalization. The extended electronegativity function (eq 6) arises naturally from eq 3 using the Ickowski−Margrave electronegativity formulation, eq 1. However, the Sanderson electronegativity equalization principle requires that the electronegativities of the atoms, χ_i, equalize in a stable molecule.[18−20] This occurs naturally in eq 3 when the molecule's energy is minimized, and the electronegativities of the atoms become equal to the global electronegativity, χ^*.[13] This global electronegativity is itself a function of the molecule's charge, Z.

$$\chi^* = a^* + \frac{1}{2} r^* + b^* Z \tag{15}$$

where a^*, r^*, and b^* are the global absolute electronegativity, global connectivity potential, and global absolute hardnesss, respectively. These are derived from the corresponding atomic electronegativity constants using the following formulas.

$$a^* = \sum_i^A (a_i/b_i) b^* \tag{16a}$$

$$r^* = \sum_i^A (r_i/b_i) b^* \tag{16b}$$

$$b^* = [\sum_i^A (1/b_i)]^{-1} \tag{16c}$$

Upon the equalization of the electronegativities, eq 6 may be rearranged to allow for the determination of atomic charges.

$$q_i = \frac{\chi^* - a_i - \frac{1}{2} r_i}{b_i} \tag{17}$$

Computations

The absolute electronegativities and absolute hardnesses of the representative elements and some of the transition metals have been determined for most common hybridizations.[11,21−23] These may be found in Table 1 for the elements of interest in this report. Where sp^3 hybridizations are not reported, the procedure reported by Bratsch was used to estimate them.[21] In this procedure the $d^n sp^m$ absolute electronegativity and absolute hardness are weighted averages of those for the s, p, and d orbitals. The sp^3 hybrid valence state is taken to be a reasonable approximation for an atom having four equivalent acceptor orbitals but utilizing no d orbitals. For the cases in which the coordination number of the acceptor is six, and there are only four available acceptor orbitals, a value of 2/3 is assigned to f (eq 11), and for cases in which the coordination number is eight, f is set equal to 1/2. In all other cases f is set equal to 1.

The coordination numbers for the aquo ions have been taken from Martell and Hancock.[24]

Equation 12 suggests that in order to evaluate the connectivity potential both the overlap and resonance integrals must be evaluated. However, if the resonance integral is evaluated using the Wolfsberg−Helmholtz approximation[25] and the absolute electronegativities, a_i and a_j, are set equal to the H_{ii} and H_{jj} integrals,[13] respectively, the evaluation of the connectivity potential is very much simplified.

$$r_{ij} = \frac{H_{ij}}{S_{ij}} = \frac{k(H_{ii} + H_{jj}) S_{ij}}{2 S_{ij}} = \frac{k(a_i + a_j)}{2} \tag{18}$$

TABLE 2: Atomic Charges and Charging Energies for Selected Coordination Compounds, Computed Using Eqs 14 and 17[a]

	q_M	q_{H_2O}	q_X	q_H	$\Delta E^C(H_2O)^a$
$Na(H_2O)_6^+$	1.00	0.00		0.263	0.00
$Be(H_2O)_4^{2+}$	0.901	0.274		0.322	0.883
$Be(H_2O)_3OH^+$	0.812	0.151(H_2O)	−0.260(OH)	0.276	0.681
$Sr(H_2O)_8^{2+}$	1.49	0.064		0.267	0.030
$Cr(H_2O)_6^{3+}$	0.149	0.474		0.355	0.740
$Cr(H_2O)_5(OH)^{2+}$	0.166	0.382	−0.076(OH)	0.321	0.433
$Cr(NH_3)_5(H_2O)^{3+}$	0.227	0.325	0.490(NH_3)	0.300(O)	0.012
$Cr(NH_3)_5(OH)^{2+}$	0.240	−0.155 (OH)	0.382(NH_3)	0.273	

[a] Charging energies are for the dissociation of an aquo ligand. The changes in charging energies are in electronvolts.

where k is an empirical constant ($k = 1.75$).[8,13,25] As a result, the connectivity potentials may be computed from the absolute electronegativities of the atoms. The global electronegativities, the global hardnesses, and the local and global connectivity potentials were computed using the absolute electronegativities and absolute hardnesses of the constituent atoms and eq 16. The atomic charges were computed using eq 17, and the charging energy was computed using eq 14. The detailed procedures for computing the global electronegativities and hardnesses and the connectivity potentials (eqs 9) have been discussed in detail elsewhere.[13,26,27]

The ground state electronegativities for the core orbitals may be determined from the atom's ionization energies,[15,16] if the neutral atom is taken to be the state of zero energy. If a plot of energy versus charge for the np^6, np^5, and np^4 configurations is quadratic (eq 2), the absolute electronegativity and absolute hardness (eq 1) may be obtained from the least-squares fit to the points of the plot.

Results and Discussion

Although the concepts of electronegativity and chemical hardness have been much utilized by coordination chemists, the absolute electronegativities and absolute hardnesses themselves have been little utilized. The application of electronegativity to coordination compounds presents several new challenges. Among these are the presence in the valence shell of partially filled d orbitals, the assignment of unambiguous valence states, multiple oxidation states, $d\pi-p\pi$ bonding, noninteger bond order, and nonlocalized bonding. This investigation is concerned with exploring the suitability of the absolute electronegativity, absolute hardness, and the extended electronegativity function for application to coordination compounds.

Pauling's definition of electronegativity ties it intimately to the charge of the atoms in a molecule,[1] and Ickowski and Margrave's formulation ties it to the energies of these atoms.[16] Although atomic charges are obtainable via a variety of molecular orbital and density functional techniques, there is very poor agreement between charges determined by these different methods, and many times they are at odds with the known chemical and physical properties of substances. Yet in a real sense all of these atomic charges are valid. That is, all of these methodologies partition the molecular charge in accordance with specified criteria.

In that the concept of an atomic charge presupposes the persistence of atoms in molecules, the atomic charge should correspond to the charge on such atoms. This too is a criterion for an atomic charge, and it is more intuitive than others that have been proposed. For example, one should be able to treat the through-space electrostatic interaction of a molecule with an external charge as the Coulombic interaction of the atomic charge located at the nucleus of each atom with the external charge. Since such properties as the valence and the core electronic energies of atoms are functions of the charge on an isolated atom, the same should be significantly true of atoms in molecules, and the atomic charges should be suitable for use in these functions. The success of the extended electronegativity function in yielding such charges has been examined in detail and is described in a previous communiction.[8]

Although the aquo complexes of the representative elements are by far the most abundant, the coordination compounds of the first transition series are in many ways the most interesting and important of the coordination compounds. Yet comparatively little work has been done on the role of electronegativity in the chemistry of representative and transition metal coordination compounds. Hinze and Jaffe have determined the absolute electronegativities and absolute hardnesses of several metals of the first transition series,[11] but there have been comparatively few reports of their utilization. The absolute electronegativities and absolute hardnesses of several of the transition metals are tabulated in Table 1. Compared to the corresponding properties of the representative elements, the electronegativites are generally very high, exceeding even those of the reactive nonmetals. In addition, chromium and manganese exhibit negative absolute hardnesses. The significance of negative hardnesses merits further study, because the negative absolute hardnesses are difficult to reconcile with Klopman's identification of hardness with the electron−electron interaction energy.[17] The simple coordination compounds of the representative elements and first transition series have been examined in this report.

Ligand Binding and Atomic Charges. The computed atomic charges for a number of representative coordination compounds may be found in Table 2. The least electronegative elements are found in group 1 and are represented by sodium. Although a coordination compound forms as the result of the binding of the ligands to metal ions, in the utilization of the extended electronegativity function the metal atom is not assigned a charge prior to atomic charge computation. The charge carried by the metal atom arises from the equalization of the electronegativities of the atoms. Because of the very low electronegativity of some metals, they do not achieve electronegativity equalization prior to losing all of their valence electrons. In Figure 1 the electronegativity of a sodium atom is plotted against its charge. As the charge approaches unity, the electronegativity approaches 5.25, which is still less than that of the ligands ($\chi_{H_2O} = 9.271$). Hence electron density continues to be transferred to the ligands even up to unit charge. There is, however, a discontinuity in the metal electronegativity and a change in the absolute hardness at unit charge. The electronegativity of the p core orbitals is 27.32, and those of the other core states are even higher.[16] Thus at metal charges greater than unity the electronegativity of core orbitals exceeds that of the ligands, and the ligand transfers charge to the metal. The net result is that charge transfer ceases at unit charge.

Because there is a discontinuity in the group 1 electronegativity functions at unit atomic charge, the procedure for the computation of the global electronegativity must be modified.

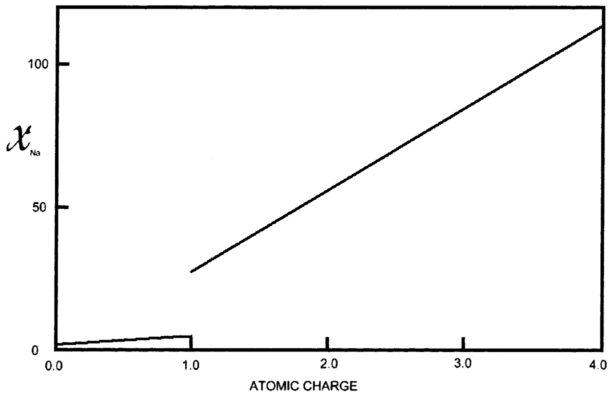


Figure 1. Plot of the of the $3sp^3$ valence orbital and 2p core orbital electronegativity of a sodium atom against its charge.

Although for computational purposes each of these coordination compounds has been treated as if it were a group of neutral atoms that form a molecule, and the charge is assigned to the whole molecule, an alternative, but mathematically equivalent, treatment is to consider the coordination compound as formed form a combination of a metal ion and associated ligands. In this case the charge is assigned to the metal. According to the Sanderson principle, the electronegativity of the metal ion (χ_{M+}) and the ligand atoms (χ_L* and χ_L) must themselves be equal and also equal to the global electronegativity. Therefore

$$\chi_{ML}^* = \chi_{M+} = \chi_{Li} = \chi_L^* = a_L^* + \frac{1}{2}r_L^* + b_L^* Z_L \quad (19)$$

where L represents the metal's ligands, and a_L*, r_L*, and b_L* are the global electronegativity constants for the ligands. The electronegativities of individual ligands are χ_L. Here Z_L is used rather than q_L, because with no charge transfer between the metal ion and the ligands, the charge is the sum of the free ligand charges rather than a partial charge. Thus the global electronegativity used in computing the atomic charges for such coordination compouns is the global electronegativity of the ligands.

One result is that the atoms of the aquo ligands of group 1 metals have the same computed atomic charges as those of an isolated water molecule. Thus since the metal ion accepts no electron density from the ligands, the bonding may be described by the electrostatic interaction of the ligand atoms' atomic charges and that of the metal ion. It has been shown that these simple electrostatic interactions account for 83−90% of the interaction energy for the $Li(H_2O)_6^+$, $Na(H_2O)_6^+$, and $K(H_2O)_6^+$ ions.[8]

The group 2 metals are represented in Table 2 by $Be(H_2O)_4^{2+}$ and $Sr(H_2O)_8^{2+}$. Since the metals' atom charges do not exceed 2+, the discontinuity (at $q_M = +2$) in the electronegativity function is not a problem. In $Be(H_2O)_4^{2+}$ the atomic charge on each ligand is 0.274, which is consistent with the moderate level of covalent character expected for ligand binding to this metal ion. In the $Be(H_2O)_3OH^+$ ion the hydroxo ligand donates 0.740 unit of charge, which makes its bonding very covalent, and the aquo ligand now donates only 0.151 unit, which is a significant decrease in covalence compared to $Be(H_2O)_4^{2+}$. On the other hand in $Sr(H_2O)_8^{2+}$ the aquo ligand transfers only 0.0540 unit of charge. Such a low level of covalence makes the metal−ligand interaction very similar to the group 1 metals. As would be expected, all of the transition metal complexes have considerable covalent character in their metal−ligand bonding. For example in the $Cr(H_2O)_6^{3+}$ ion the ligands each donate 0.474 unit of charge to the metal, which indicates a great deal of covalent character. In a mixed ligand complex such as $Cr(NH_3)_5(H_2O)^{3+}$ the ammines each donate 0.490 unit of charge, but the aquo ligand donates only 0.325 unit. This suggests that the ammine−metal bond is more covalent than the aquo−metal bond, which is consistent with the chemistries of these ligands.

During a heterolytic dissociation of a ligand the electron density that is donated to the metal to form the coordinate bond must be transferred back to the ligand, and the reverse of this process occurs upon ligand association. There is associated with this back transfer of charge a change in charging energy, $\Delta E^C(L)$, which constitutes part of the energetics of ligand exchange and substitution. Below, a general substitution reaction has been partitioned into steps that illustrate the role of the charging energy.

$$[M(H_2O)_5^{(n-q')} - L^{(q')}]^{n+m} \rightarrow [M(H_2O)_5^{(n)} - L^{(m)}]^{n+m} \quad \Delta E^C(\text{dissoc}) \quad (20a)$$

$$[M(H_2O)_5^{(n)} - L^{(m)}]^{n+m} \rightarrow M(H_2O)_5^{n+} + L^m \quad (20b)$$

$$M(H_2O)_5^{n+} + H_2O \rightarrow [M(H_2O)_5^{(n)} - H_2O^{(0)}]^{n+} \quad (20c)$$

$$[M(H_2O)_5^{(n)} - H_2O^{(0)}]^{n+} \rightarrow [M(H_2O)_5^{(n-q)} - H_2O^{(q)}]^{n+} \quad -\Delta E^C(\text{assoc}) \quad (20d)$$

In step 20a a ligand having a charge of q' acquires electron density from the metal until it acquires the free ligand charge, m. Step 20d depicts the reverse of step 20a for the incoming water molecule.

The change in charging energy for the step preceding ligand dissociation (2a) makes a major contribution to the activation energy for the reaction. These and selected atomic charges for a number of aquo ions may be found in Table 2. In the case of the group 1 metal ions where the ligands donate no electron density to the metal, the change in charging energy contributes nothing to the kinetic barrier, and such complexes are correspondingly labile. On the other hand, an aquo ligand on the beryllium(2+) ion must acquire 0.274 unit of charge prior to dissociation, which requires 0.883 eV in charging energy. The 0.883 eV contribution to the barrier actually derives from two sources. The process of decreasing the ligand charge from +0.274 to 0.0 actually releases 2.390 eV (ΔE^C for H_2O), but 3.273 eV is required to distribute this charge over the rest of the ion (ΔE^C for $Be(H_2O)_3^{2+}$). In $Cr(NH_3)_5(H_2O)^{3+}$ there is a considerably greater contribution to the barrier for the ammine ligands than for the aquo ligands, which is a result consistent with the ground state substitution chemistry of these ligands, where the aquo ligand is more substitution labile. On the other hand, for the $Cr(NH_3)_5(OH)^{2+}$ ion the hydroxyl ligand donates 0.845 unit of charge compared to 0.382 unit of charge for the ammines. This would result in a very large barrier to hydroxyl ligand substitution, which is also born out by experiment. In the case of the hexaaquochromium(III) ion the loss of a proton reduces the charge on the remaining aquo ligands by 0.153 unit, which is consistent with the much greater rate of substitution on the later ion.[29]

Both the change in charging energy for the step preceding dissociation (2a) and for the step following ligand association (2d) contribute to the overall energy change for the reaction. The change in charging energy for the reaction

$$M(H_2O)_5CH_3CO_2^{\,m} + H_2O \rightleftharpoons M(H_2O)_6^{\,m+1} + CH_3CO_2^- \quad (21)$$

TABLE 3: Charging Energies and Acid Dissociation Constants for Selected Coordination Compounds, Computed Using Eq 14

molecule	$E^a((H_2O)_5M-L)$	$E^a((H_2O)_6M)$	E^a(react.)	log K^b
$Li(H_2O)_5CH_3CO_2^0$ (sp^3)	−12.546	−3.70	−0.402	0.26
$Na(H_2O)_5CH_3CO_2^0$ (sp^3)	−13.299	−4.45	−0.399	−0.18
$Be(H_2O)_3CH_3CO_2^+$ (sp^3)	2.263	12.435	0.924	1.62
$Mg(H_2O)_5CH_3CO_2^+$ (sp^3)	−0.322	9.548	0.627	0.51
$Ca(H_2O)_5CH_3CO_2^+$ (sp^3)	−2.380	7.213	0.345	0.53
$Sr(H_2O)_7CH_3CO_2^+$ (sp^3)	−4.523	4.803	0.078	0.43
$Cr(H_2O)_5CH_3CO_2^+$ (d^2sp^3)	3.837	13.922	0.837	1.25
$In(H_2O)_5CH_3CO_2^{2+}$ (sp^3)	10.984	21.716	1.484	3.50
$Cr(H_2O)_5CH_3CO_2^{2+}$ (d^2sp^3)	13.756	24.833	1.829	4.63
$Mn(H_2O)_5CH_3CO_2^+$ (d^2sp^3)	7.533	17.341	0.560	0.80
$Fe(H_2O)_5CH_3CO_2^+$ (d^2sp^3)	−4.671	5.977	1.40	1.40
$Fe(H_2O)_5CH_3CO_2^{2+}$ (d^2sp^3)	6.174	17.946	2.524	3.38
$Co(H_2O)_5CH_3CO_2^+$ (d^2sp^3)	2.971	13.223	1.004	1.1

[a] The valence states for the electronegativities of the metals are indicated in the parentheses. The change in charging energy is for the reaction depicted in eq 21. The charging energies for $CH_3CO_2^-$ and H_2O are −10.083 and −0.835 eV, respectively. The charging energies are in electronvolts [b] The data were taken from ref 28.

has been tabulated in Table 3 along with the logarithms of the stability constants (the reverse of eq 21). The atomic charges of both lithium and sodium are unity. The result is that the change in charging energy for these metals is zero. The stability constants and changes in charging energies have been plotted in Figure 2 for a series of representative and transition metal ions. There in fact does appear to be a good correlation between the change in charging energy and the change in free energy for these reactions. This would suggest that charging energy is a major component of the free energy and that charging energies and atomic charges generated by the extended electronegativity function are consistent with the proposed intuitive atomic charges.

Bronsted Acidity. It has been demonstrated that the atomic charge of a hydrogen atom qualitatively correlates with the acidity of that hydrogen in a large variety of molecules and that it yields excellent semiquantitative correlations with the acidity of hydrogens in groups of similar molecules.[10,29,30] In aqueous solution molecules less acidic than water will not behave as Bronsted acids, and any solute having an acidity greater than hydronium ion will be "completely" dissociated. By extension a solute molecule hydrogen having an atomic charge less than 0.263, which is the hydrogen atomic charge in water, is expected to be nonacidic in water, whereas one having an atomic charge greater than 0.426 (hydrogen atomic charge in hydronium ion) is expected to be strongly acidic in water. Thus the computed hydrogen atomic charges might be expected to correlate with the Bronsted acidity of metal aquo complexes, and the extent of hydrolysis of the aqueous cations should reflect the distribution of charge in the aqueous ion.

$$H_2O + M(H_2O)_6{}^{n+} \rightleftarrows M(H_2O)_5OH^{n-1} + H_3O^+$$

$$K_a = \frac{[H_3O^+][M(H_2O)_5OH^{n-1}]}{[M(H_2O)_6{}^{n+}]} \qquad (22)$$

All of the group 1 hexaaquo metal ions have hydrogen atomic charges of 0.263, which are identical to those of the solvent molecules. Their hydrogens are thus predicted to be nonacidic, which, of course, is the case. All of the group 2 metals are more electronegative and harder than the group 1 metals. As a result, their ions exhibit a range of behaviors in aqueous solution. Whereas beryllium is extensively hydrolyzed in water, strontium has very low Bronsted acidity (Table 4). This is consistent with the 0.322 hydrogen atomic charge for the aquo complex of beryllium and the 0.267 hydrogen atomic charge in the aquo complex of strontium.

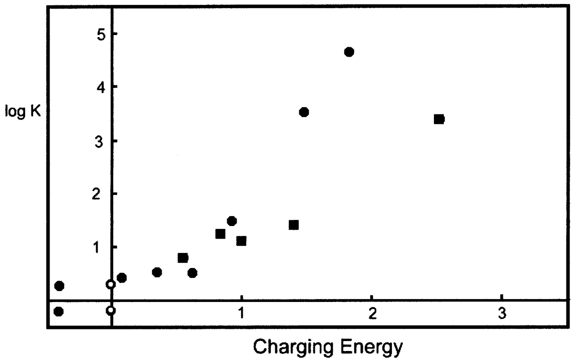
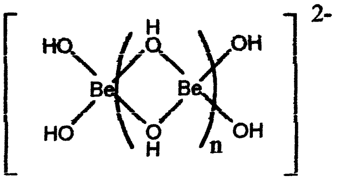


Figure 2. Plot of the charging energy versus the logarithms of the stability constants for the formation of the monoacetato complexes of a number of aqueous metal ions (representative elements ○ and ●, transition elements ■).

Beryllium ions, as do other ions of groups 2 and 13, have a complex aqueous chemistry, forming many complex species in solution. Among them are polymeric species such as



Much of the speciation in aqueous solution can be understood in part as the result of the charge redistribution resulting from the loss of a proton by the aqueous metal ion to form $Be(H_2O)_3OH^+$. In this case upon dissociation of the hydrogen, electron density is transferred onto the oxygen, making it less electronegative, which in turn causes it to transfer more electron density to the metal. Upon becoming less electronegative, the metal causes the charge carried by the remaining aquo ligands to decrease from 0.274 to 0.150, which decreases the change in charging energy required for substitution and makes them much more labile toward substitution. The hydroxo ligand charge is −0.260 and is thus very resistant to substitution. In addition, the atomic charge carried by the hydroxyl oxygen is −0.536, which is now greater than that on the oxygen in water ($q_{H_2O} = -0.526$). This would be expected to give it a base strength greater than that of water[31] and thus favor substitution to yield the bridging hydroxyl structures such as those occurring in the polymer. All of the group 13 aqueous ions exhibit some degree of Bronsted acidity. The hydrogen atomic charge in $B(H_2O)_4{}^{3+}$

TABLE 4: Atomic Charge, Charging Energy, and Acid Dissociation Constants for Selected Coordination Compounds, Computed Using Eqs 14 and 17[a]

molecule	q_H[b]	q_M[b]	$\Delta E^C(H^+)$[c]	$\Delta G°_a$[c]	pK_a[d]
$Li(H_2O)_6^+$ (sp^3)	0.263	1.00	1.814	0.8147	13.82
$Na(H_2O)_6^+$ (sp^3)	0.263	1.00	1.814	0.8536	14.48
$K(H_2O)_6^+$ (sp^3)	0.263	1.00	1.814		
$Rb(H_2O)_8^+$ (sp^3)	0.263	1.00	1.814		
$Be(H_2O)_4^{2+}$ (sp^3)	0.322	0.901	0.598	0.3832	6.50
$Mg(H_2O)_6^{2+}$ (sp^3)	0.297	1.01	0.969	0.6732	11.42
$Ca(H_2O)_6^{2+}$ (sp^3)	0.273	1.40	1.275	0.7487	12.70
$Sr(H_2O)_8^{2+}$ (sp^3)	0.267	1.49	1.378	0.7770	13.18
$B(H_2O)_4^{3+}$ (sp^3)	0.429	0.694	−0.544		
$Al(H_2O)_6^{3+}$ (sp^3)	0.356	0.998	0.269	0.3030	5.14
$Ga(H_2O)_6^{3+}$ (sp^3)	0.357	0.943	0.189	0.2004	3.40
$In(H_2O)_6^{3+}$ (sp^3)	0.359	0.960	0.266	0.2182	3.70
$Cr(H_2O)_6^{3+}$ (d^2sp^3)	0.355	0.149	−0.293	0.2364	4.01
$Mn(H_2O)_6^{2+}$ (d^2sp^3)	0.263	0.344	0.399	0.1655	11.70
$Fe(H_2O)_6^{2+}$ (d^2sp^3)	0.314	−0.440	−0.487	0.5954	10.1
$Fe(H_2O)_6^{3+}$ (d^2sp^3)	0.374	−0.400	−0.994	0.1291	2.19
$Co(H_2O)_6^{2+}$ (d^2sp^3)	0.308	0.284	0.370	0.5660	9.6
$Cr(NH_3)_5H_2O^{3+}$ (d^2sp^3)	0.300(O) 0.174(N)	0.227	0.722	0.3124	5.3
$Co(NH_3)_5H_2O^{3+}$ (d^2sp^3)	0.330(O) 0.204(N)	0.005	0.382	0.3891	6.6
$Co(NH_3)_4(H_2O)_2^{3+}$ (d^2sp^3)[e]	0.335(O) 0.208(N)	0.091	0.248	0.3537	6.0

[a] The valence states for the electronegativities of the metals are indicated in parentheses. The change in charging energy is for the reaction depicted in eq 22. The charging energies are in electronvolts. [b] Data taken from refs 11 and 21−23. [c] The energies are in electronvolts. [d] Data taken from refs 30 and 31. [e] The aquo ligands are trans.

($q_H = +0.429$) predicts that it should be strongly acidic, which is consistent with the absence of this ion in aqueous solution. The remaining group 13 ions have intermediate hydrogen atom atomic charges, which is consistent with their rich aqueous chemistry, which includes speciation similar to that of the $Be(H_2O)_4^{2+}$ ion.

Consistent with the hydrogen atom atomic charges of the aquo ligands, all of the transition metal ions exhibit some degree of Bronsted acidity. Although all of the transition metals form aquo ions with well-defined stoichiometries and geometries, the absolute electronegativities and absolute hardnesses are available for only a limited number of them. Hinze and Jaffe have provided the valence state ionization energies and electron affinities for scandium through cobalt, but for only chromium through cobalt are they reported for the d^2sp^3 valence state.[11] It is interesting that the $Cr(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ ions, which have a rich and complex aqueous chemistry, also have large electronegativities and high hydrogen atom atomic charges. These large acidities and the concomitant changes in the remaining ligands upon proton dissociation seem to give rise to extensive speciation similar to that found for group 2 and group 13 ions. An unusual case is the Mn^{2+} ion, which is significantly acidic (pK_a = 11.70), but has a computed hydrogen atom atomic charge that is essentially the same as that of water. This may be a result of its unusual hardness. Since ammine ligand nitrogens are less electronegative than the oxygens in the aquo ligands, the aquo ligand hydrogens are more positive than those of the ammines (Table 4). They are thus expected to be more acidic than the ammine ligand hydrogens. This is the case although the O−H bond energy is larger than the N−H bond energy. In addition, because the ammine ligands in $Cr(NH_3)_5(H_2O)^{3+}$ are better donors ($q_{NH_3} = 0.490$) than the aquo ligands ($q_{H_2O} = 0.325$), the aquo ligand hydrogen is less positive than those in the hexaaquo complex ($Cr(H_2O)_6^{3+}$). They are thus expected to be less acidic (Table 3), and this is in fact the case, Table 4.

To gain a deeper insight, the computed hydrogen atom atomic charges are plotted against the experimental acid dissociation constants (as pK_a's, eq 22) for the representative elements in Figure 3. The plot shows a good linear correlation with a correlation coefficient of −0.987. That there should be a correlation between the acid dissociation constant (as pK_a) and the hydrogen atom atomic charge arises from the relationship between the pK_a and the free energy, $\Delta G_a°$ ($\Delta G_a° = -RT \ln K_a$), and the near linear relationship (for small q_H) between charging energy and atomic charge. When the free energies are plotted against the charging energies for the acid dissociation of these ions (eq 23), there is in fact a linear correlation, Figure 4.

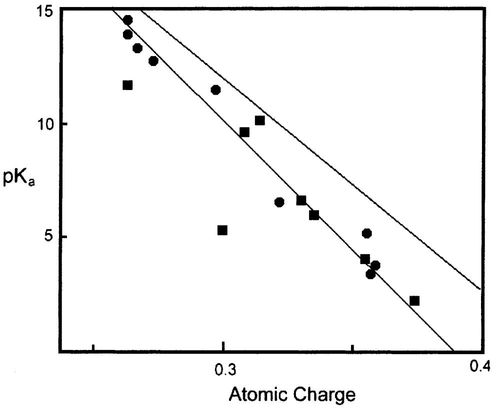


Figure 3. Plot of the pK_a's of aqueous representative (●) and transition (■) metal ions against the hydrogen atom atomic charges (q_H). The upper line is generated using water and hydronium ion as reference acids, and the lower line is the least-squares fit to all of the points except the $Cr(NH_3)_5H_2O^{3+}$ and $Mn(H_2O)_6^{2+}$ ions.

$$[M(H_2O)_5OH^{(n-q)} - H^{(q)}]^{n+} \rightarrow [M(H_2O)_5OH^{(n-1)} - H^{(+)}]^{n+} \quad \Delta E^C(H^+) \tag{23}$$

The correlation coefficient is 0.969, the slope is 0.402, and the intercept is 0.169 eV. That the slope is less than 1 suggests that in addition to the charging energy there are other processes that affect dissociation which are also dependent on or correlate with charging energy. The nonzero intercept points to the existence of contributions to the dissociation that are not dependent or correlated with charging energy.

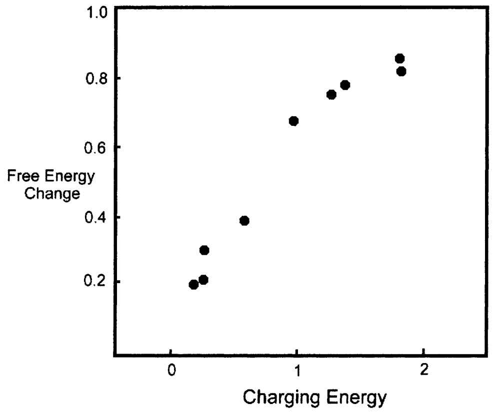


Figure 4. Plot of charging energy (E^c) of aqueous representative metal ions against the free energy of acid dissociation ($\Delta G°$).

The energetics of the acid dissociation may be partitioned as depicted in Scheme 1. In it the reactants are first desolvated, followed by a charge transfer to bring the dissociating hydrogen to unit positive charge. The O−H bond then cleaves and the products are solvated. The energy for the charge transfer step is estimated as the charging energy.

On the basis of the partitioning in Scheme 1 the energy change for the dissociation is

$$\Delta E(\text{acid dissociation}) = [-\Delta E_{\text{solv}}(H_2O) + \Delta E_{\text{solv}}(H_3O^+)] + [-\Delta E_{\text{solv}}([M(H_2O)_6]^{n+}) + \Delta E_{\text{solv}}(M(H_2O)_5OH)] + \Delta E^c + \Delta E(O{-}H) \quad (24)$$

The plot and a correlation coefficient of 0.969 would suggest that to a reasonable approximation eq 23 should be linear in ΔE^c. If all of the remaining terms were independent of and did not correlate with ΔE^c, a unit slope would be expected. This is not the case. The terms within the first square brackets are obviously independent of and do not correlate with ΔE^c. Their contribution is to the intercept. Although independent of ΔE^c, ΔE(O−H) might have a very weak correlation with ΔE^c. The terms within the second square brackets, on the other hand, are expected to have a quite significant correlation with ΔE^c. Of the many contributions to the solvation energy, the change in hydrogen bonding would be expected to contribute most significantly to the energetics of acid dissociation. One might expect in the case of the alkali metals the hydrogen bonding between the ligands and the solvent to be comparable to the solvation of water. On the other hand in the case of very acidic coordination compounds the hydrogen bonding is very much stronger due to the high hydrogen atom atomic charge. This being the case, the terms in the second set of square brackets correlate negativity to the ΔE^c and would contribute to diminish the slope. Thus the correlation of pK_a and q_H reflects the influence of not only the change in the charging energy but also the change in the extent of hydrogen bonding which is dependent on and correlates with the hydrogen atom atomic charge.

The acid dissociation constants for these transition metal aquo ions (Table 4) cover the full range spanned by the aquo ions of the representative metals. When the hydrogen atom atomic charges are plotted against the pK_a's on the same plot as the representative elements (Figure 3), the points appear to fall about the same straight line. However, in this case the correlation coefficient is only 0.955. As has been pointed out, the $Mn(H_2O)_6^{2+}$ ion appears to be an anomaly. If it is not included in the correlation, the correlation coefficient increases to 0.990, which is actually better than that for the representative elements.

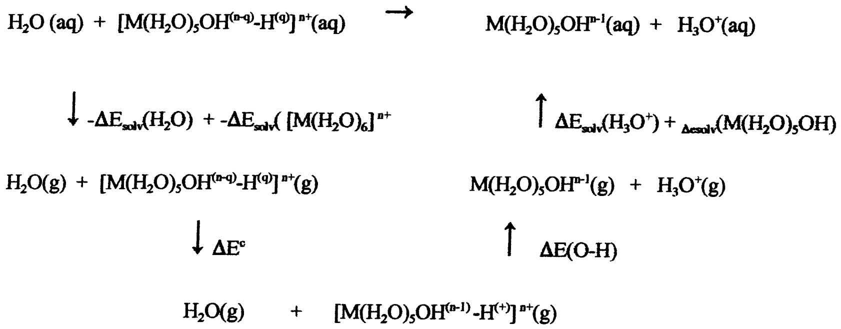
A change in ligation about a metal ion is known to have a pronounced affect on its chemistry and on the chemistry of its ligands. To examine this, a number of aquo ligands of hexaaquocobalt and hexaaquochromium ions have been replaced by ammine ligands. Whereas the cobalt(III) complexes ($Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_4(H_2O)_4^{3+}$) fall on the line generated by the remaining ions, the mixed ligand chromium(III) complex ($Cr(NH_3)_5H_2O^{3+}$) does not. It seems difficult to attribute this anomalous behavior to inaccuracies in the electronegativities, since the hexaaquochromium(III) ion correlates very well. This notwithstanding, if the two anomalous complexes are not included, the correlation coefficient for all the complex ions in Table 4 for which we have pK_a's is 0.986, which is quite good.

For comparison purposes the line generated by the reference molecules, which were water (q_H = 0.263 and pK_a = 15.75) and hydronium ion (q_H = 0.463 and pK_a = 0), is included in the plot, Figure 2. The points in the q_H−pK_a plot fall about a line that is parallel and quite close to that generated by water and hydronium ions as references. That the experimental acidities of metal complexes are systematically greater than that of the reference molecules results from a variety of factors. The fact that the lines are parallel suggests that the influence of charge and charge transfer is much the same in both the simple reference molecules and the coordination compounds.

In Closing

An active interest in electronegativity persists despite ready access to molecular orbital and density functional methologies, in part because of its simplicity and intuitive nature. Among the strengths of the extended electronegativity function are its simplicity in application, its faithfulness to the intuitive nature of Pauling's original electronegativity concept, and its ability to provide semiquantitative information related to the distribution of charge in molecules or ions. Furthermore, these charges are consistent with the intuitive concept of atomic charges discussed previously.[8] Previously, the potential utility of electronegativity in its application to coordination compounds of both representa-

SCHEME 1



tive and transition elements had been little explored. In this report the compounds that have been selected for comparison have simple ligands in which σ ligand−metal bonding dominates. The qualitative and quantitative correlations of the results generated by the extended electronegativity function and experiment are very encouraging. Furthermore, the importance of the influence of atomic charge on hydrogen bonding has been illustrated. Unfortunately the range of transition metals has been limited, because absolute electronegativities and absolute hardnesses are available for a limited number of metals in a limited number of valence states. It would thus appear that the next step in developing the potential of electronegativity in its application to coordination compounds is to develop a more precise treatment of π bonding in the electronegativity function and to determine the electronegativities and absolute hardnesses for the remainder of the transition metals.

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