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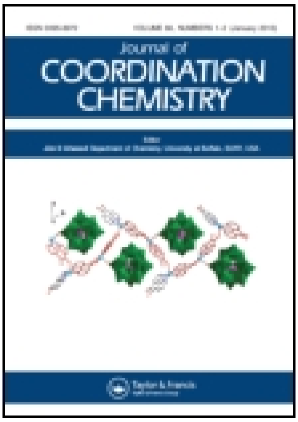

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Derivation of ligand σ- and π-bonding parameters from density functional theoretical calculations and Bursten ligand additivity relationships

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Derivation of ligand σ- and π-bonding parameters from density functional theoretical calculations and Bursten ligand additivity relationships

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New ligand additivity equations, based on the Bursten model, describing dπ orbital energies in square-planar and square–pyramidal complexes are proposed and tested for hypothetical binary Cr(0) and Mn(I) complexes of CO and CNMe. Density functional theory calculations are used to calculate the energies of dπ orbitals of binary octahedral, square–planar, and square–pyramidal d^6 complexes of Mn(I) and Cr(0). Combination of the modified equations for unsaturated species with Bursten's original equations for octahedral species allows for calculation of individual ligand bonding parameters and the separation of σ- and π-bonding effects. The calculated parameters provide interesting insight into the nature of metal–ligand bonding in the species studied. The method of separating σ- and π-bonding effects, applied here to CO and CNMe, is proposed as general method for solution of the Bursten equations for low-spin d^6 octahedral systems.

Keywords: Ligand additivity; Density functional theory; Octahedral complexes

1. Introduction

The concept of additive effects in chemical bonding is a fundamental principle underlying much of our modern understanding of chemistry. Additive effects are prevalent in all areas of chemistry, including substituent effects in organic chemistry and ligand effects in inorganic chemistry. The observation of additive effects arising from the types and numbers of functional groups or ligands in a given molecule not only allows for explanation of observed properties of molecules, but also allows for prediction of properties and the design of new systems with desired properties. In inorganic chemistry, several models have been proposed to measure and apply additive effects arising from ligand substitution. These include the models of Chatt, Leigh, and Pickett [1], Lever [2], Graham [3], and Bursten [4]. Additive behavior is observed for many properties of molecules including vibrational spectra, electrochemical potentials, electronic spectra, NMR spectra, and photoelectron spectra. Most models of ligand additivity are based on the fitting of experimental data to compositional and structural properties. One notable exception is the Bursten model, which relates calculated orbital energies to composition and structure, and in turn this information is related to photoelectron spectroscopy and electrochemical data.

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The Bursten model states that the dπ orbital energies in a series of octahedral complexes $[\mathrm{M(L)}_n(\mathrm{L}')_{n-6})]^{x+}$ can be expressed as a function of the number of each ligand present (n), the number of ligands L with which each dπ orbital can interact (x_i), and a constant that is a function of the identity of the metal and ligands (a). The relationship is given by equation (1):

$$\varepsilon_i = a + bn + cx_i \tag{1}$$

The coefficient b is isomer independent and can be considered an electrostatic term that measures the difference in the ability of the two ligands to stabilize the dπ orbitals. The coefficient c is isomer dependent and is related to the difference in the ability of the two ligands to stabilize orbitals on the metal center through π-acceptance (stabilizing) and π-donation (destabilizing) interactions. Equation (1) can also be expressed in terms of the properties of the individual ligands L and L′:

$$\varepsilon_i = a_\mathrm{M}^0 + nb_\mathrm{M}^\mathrm{L} + (6-n)b_\mathrm{M}^{\mathrm{L}'} + x_\mathrm{i}c_\mathrm{M}^\mathrm{L} + (4-x_\mathrm{i})c_\mathrm{M}^{\mathrm{L}'} \tag{2}$$

where a_M^0 is a characteristic constant of the metal in its particular oxidation state, b_M^L and $b_\mathrm{M}^{\mathrm{L}'}$ are constants describing the overall energetic effect on the metal of ligands L and L′, c_M^L and $c_\mathrm{M}^{\mathrm{L}'}$ are constants related to the π-interaction of ligands L and L′ with M and x_i is the number of ligands with which the dπ orbital can interact.

Bursten hypothesized that the constant b_M^L describes electrostatic stabilization of the metal center and can be related to σ-donor and π-acceptor/donor ability as:

$$b_\mathrm{M}^\mathrm{L} = \pi_\mathrm{a} - \pi_\mathrm{d} - \sigma_\mathrm{d} \tag{3}$$

The constant c_M^L was described by Bursten as a bonding term related to π-acceptance and π-donation as follows:

$$c_\mathrm{M}^\mathrm{L} = \pi_\mathrm{a} - \pi_\mathrm{d} \tag{4}$$

The Bursten model was originally derived using Fenske–Hall [5] approximate molecular orbital calculations and used to explain electrochemical behavior of d^6 and d^1 binary octahedral transition metal complexes [4]. The model has also been applied to explain photoelectron spectra of inorganic complexes [6–8]. The Fenske–Hall method is a nonempirical molecular orbital method that is nonvariational and, as such, cannot be used to determine structural changes resulting from ligand substitution. More recent density functional calculations on Mn(I) and Cr(0) complexes indicate that despite changes in structure resulting from ligand substitution, the calculated molecular orbital energies and compositions are in agreement with the Bursten model [9]. Furthermore, it was shown that the observed structural changes and Hirschfeld charge distributions also display additive behavior [9]. Recently, a study by Moens *et al.* used DFT methods to derive an electrochemical series for $[\mathrm{M(CO)}_n\mathrm{L}_{6-n}]$ complexes consistent with Picket and Lever parameters [10].

Knowledge of the values of b_M^L and c_M^L would allow for separation of σ- and π-effects and the construction of a computationally derived scale of ligand bonding constants. The advantage of this new set of parameters would be that they could be determined from calculations on complexes containing the relevant ligands and as such can be derived for any desired ligand. Also, these parameters would give a better understanding of the origin of ligand effects in terms of σ-donor and π-donor/acceptance effects. However, to date, no method to determine individual ligand b and c parameters ($b_{\mathrm{M}}^{\mathrm{L}}$, $c_{\mathrm{M}}^{\mathrm{L}}$) has been suggested. It is proposed in this contribution that by applying the Bursten model to both octahedral and hypothetical coordinatively unsaturated complexes, a modified set of ligand additivity equations that allow for the calculation of individual ligand b and c constants arises. Subsequently, individual ligand σ- and π-bonding parameters can be calculated. The procedure is used to determine σ- and π-bonding parameters for CO and CNMe in Mn(I) and Cr(0) complexes, and the meaning of the derived parameters is discussed.

2. Computational details

All calculations were performed using the Amsterdam Density Functional 2010.02 [11–13] program on an Advanced Micro Devices Opteron workstation. All octahedral structures were optimized to energy minima without any symmetry constraints. Energy minima were confirmed using vibrational frequency calculations. Square-planar and square-pyramidal structures were derived from octahedral complexes by removal of the relevant ligands without reoptimization. The convergence criteria for geometry optimization and Self Consistent Field convergence were the default values of the ADF 2010.02 program. An integration constant (which is effectively a measure of the accuracy of calculated integrals) of 6.0 was used in all calculations. The Becke-Perdew nonlocal exchange and correlation functional [14–16] and triple-ζ with polarization functions basis set were for all atoms.

3. Results

Fitting of all dπ orbital energies for a series of complexes $[\mathrm{M(L)}_n(\mathrm{L}')_{6-n}]^{x+}$ allows for determination of the parameters b and c in equation (1), but does not allow for solution for the individual ligand parameters ($b_{\mathrm{M}}^{\mathrm{L}}$, $c_{\mathrm{M}}^{\mathrm{L}}$) of equation (2). It is proposed here that by applying the Bursten model to both octahedral and hypothetical square-planar binary complexes, a set of ligand additivity equations that allow for the calculation of individual ligand b and c constants arise. By removing one ligand, without allowing for any rearrangement of the remaining bonds, we effectively introduce a new "null" or virtual ligand, which contributes zero stabilization or destabilization to the dπ orbitals of the system. Likewise, removing two ligands to produce a square-planar complex effectively introduces two "null" ligands. It is noted that convergence of geometry optimization calculations on the hypothetical unsaturated complexes can prove difficult. Consequently, all of the unsaturated species were not reoptimized upon ligand removal. While this may introduce some error into the orbital energies and subsequent correlation, Bursten's results [4] indicate that static bond lengths and angles can be used to give reasonable correlation with the original model.

Considering the presence of the "null ligands", the Bursten ligand additivity equations can be rewritten as follows:

For square planar complexes,

$$\varepsilon_{xz/yz} = a^0_{\mathrm{M}} + nb^{\mathrm{L}}_{\mathrm{M}} + (4-n)b^{\mathrm{L}'}_{\mathrm{M}} + x_{\mathrm{i}}c^{\mathrm{L}}_{\mathrm{M}} + (2-x_{\mathrm{i}})c^{\mathrm{L}'}_{\mathrm{M}} \tag{5}$$

$$\varepsilon_{\mathrm{xy}} = a^0_{\mathrm{M}} + nb^{\mathrm{L}}_{\mathrm{M}} + (4-n)b^{\mathrm{L}'}_{\mathrm{M}} + x_{\mathrm{i}}c^{\mathrm{L}}_{\mathrm{M}} + (4-x_{\mathrm{i}})c^{\mathrm{L}'}_{\mathrm{M}} \tag{6}$$

For square pyramidal complexes,

$$\varepsilon_{\mathrm{xz/yz}} = a^0_{\mathrm{M}} + nb^{\mathrm{L}}_{\mathrm{M}} + (5-n)b^{\mathrm{L}'}_{\mathrm{M}} + x_{\mathrm{i}}c^{\mathrm{L}}_{\mathrm{M}} + (3-x_{\mathrm{i}})c^{\mathrm{L}'}_{\mathrm{M}} \tag{7}$$

$$\varepsilon_{\mathrm{xy}} = a^0_{\mathrm{M}} + nb^{\mathrm{L}}_{\mathrm{M}} + (5-n)b^{\mathrm{L}'}_{\mathrm{M}} + x_{\mathrm{i}}c^{\mathrm{L}}_{\mathrm{M}} + (4-x_{\mathrm{i}})c^{\mathrm{L}'}_{\mathrm{M}} \tag{8}$$

Multivariate regression can be applied to calculated orbital energies of a series of binary octahedral, square-planar, and square-pyramidal complexes to solve simultaneously equations (2) and (5–8), resulting in determination of individual ligand parameters $a^0_{\mathrm{M}}, b^{\mathrm{L}}_{\mathrm{M}}, c^{\mathrm{L}}_{\mathrm{M}}$ and subsequently σ and π parameters. The octahedral series $[\mathrm{M(L)}_n(\mathrm{L}')_{6-n}]^{x+}$ gives ten distinct species and hence 30 dπ orbital energies. The series of square-planar complexes $[\mathrm{M(L)}_n(\mathrm{L}')_{4-n}]^{x+}$ gives six distinct species, while the square-pyramidal series $[\mathrm{M(L)}_n(\mathrm{L}')_{5-n}]^{x+}$ gives 12 species. Solutions for the individual ligand constants can be derived using only a subset of all of the possible complexes (for example, selected octahedral and square-planar complexes only using equations (2), (5), and (6)), but all octahedral, square-planar, and square-pyramidal species are included in this study to test fit of the model over a maximum number of data points.

To test the applicability of equations (5–8), calculations were performed on all species in the series of complexes $[\mathrm{M(CO)}_n(\mathrm{CNMe})_{6-n}]^{x+}$, $[\mathrm{M(CO)}_n(\mathrm{CNMe})_{4-n}]^{x+}$, and $[\mathrm{M(CO)}_n(\mathrm{CNMe})_{5-n}]^{x+}$, M = Mn(I), Cr(0). It has been previously shown that calculated orbital energies of octahedral species above fit the Bursten model well [9]. The additional orbital energies calculated from the series of square-planar complexes $[\mathrm{M(L)}_n(\mathrm{L}')_{4\text{-}n}]^{x+}$ (18 orbital energies) and square-pyramidal series $[\mathrm{M(L)}_n(\mathrm{L}')_{5-n}]^{x+}$ (36 orbital energies) were introduced to the multivariate regression analysis. Rehybridization of the metal dπ orbitals is not observed in any of the new unsaturated species except where energetic degeneracy occurs, and hence the descriptions given by the Bursten model for σ- and π-interactions remain valid. As an example, isosurfaces of the dπ orbitals of square-planar $[\mathrm{Mn(CO)}_3(\mathrm{CNMe})]^+$ and square-pyramidal mer-$[\mathrm{Mn(CO)}_3(\mathrm{CNMe})_2]^+$ are given in figure 1. In all cases, it is observed that the dπ orbitals retain their characteristic alignment within the *xz*, *yz*, and *xy* planes and the number of π-type interactions with each ligand is that predicted by modified Bursten equations.

All 84 orbital energies of each series of complexes were fit to equations (2) and (5–8). The plots in figures 2 and 3 show the correlation between DFT calculated orbital energies and those predicted using regression analysis with equations (2) and (5–8) for the Mn(I) and Cr(0) complexes, respectively. The correlation between predicted and DFT calculated orbital energies is excellent with R^2 values of 0.988 and 0.991, respectively, indicating that the ligand additivity equations hold in the case of unsaturated species.

From the regression analysis, the ligand parameters a^0_{M}, $b^{\mathrm{L}}_{\mathrm{M}}$, and $c^{\mathrm{L}}_{\mathrm{M}}$ given in table 1 were derived.

From the above parameters and equations (3) and (4), we can derive the σ and π parameters for individual metal–ligand interactions. The values of $\sigma^{\mathrm{L}}_{\mathrm{M}}$ and $\pi^{\mathrm{L}}_{\mathrm{M}}$ for CO and CNMe complexes of Mn(I) and Cr(0) are given in table 2.

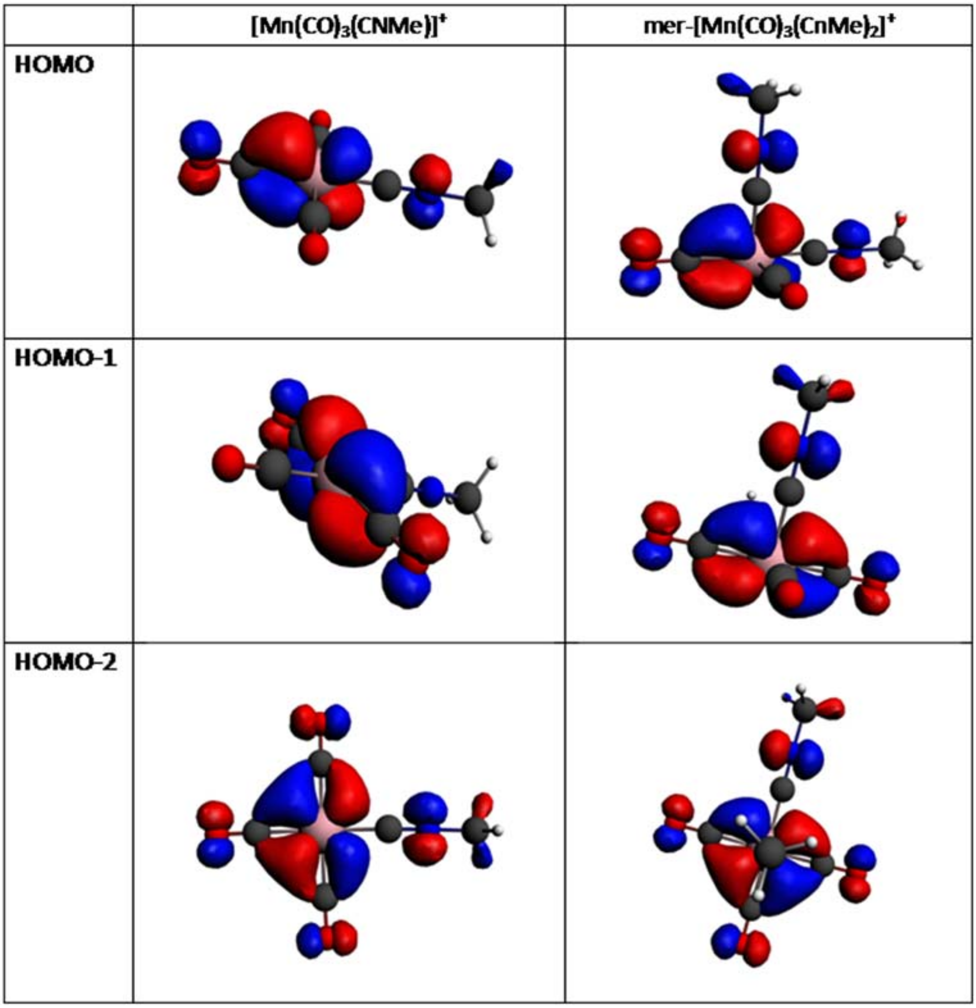

Figure 1. Isosurfaces of the dπ orbitals in square–planar $[Mn(CO)_3(CNMe)]^+$ and square–pyramidal mer-$[Mn(CO)_3(CNMe)_2]^+$.

Inspection of the σ- and π-bonding parameters provides some insight into the bonding in theses complexes: Consistent with the generally accepted view, the π-stabilizing effect of CO is greater than that of CNMe and σ-donation from CNMe is greater than that from CO. Considering the constants for Mn(I) first, the much greater value of $\sigma_{\mathrm{Mn(I)}}^{\mathrm{CNMe}}$ compared to $\sigma_{\mathrm{Mn(I)}}^{\mathrm{CO}}$ indicates that CNMe is a much stronger σ-donor than CO in these systems. The negative value of $\pi_{\mathrm{Mn(I)}}^{\mathrm{CO}}$ is consistent with stabilization of the metal dπ orbitals through net π-backbonding. The almost zero value of $\pi_{\mathrm{Mn(I)}}^{\mathrm{CNMe}}$ indicates that net π-interactions with CNMe are negligible in these Mn(I) systems.

In the Cr(0) systems, π-bonding parameters for both ligands are more negative than those calculated for Mn(I), indicating that greater backbonding is observed for Cr(0) and that π-stabilization is now significant for CNMe. These results are consistent with the more electron rich metal center. The σ-bonding parameters for both ligands are reduced in Cr(0)

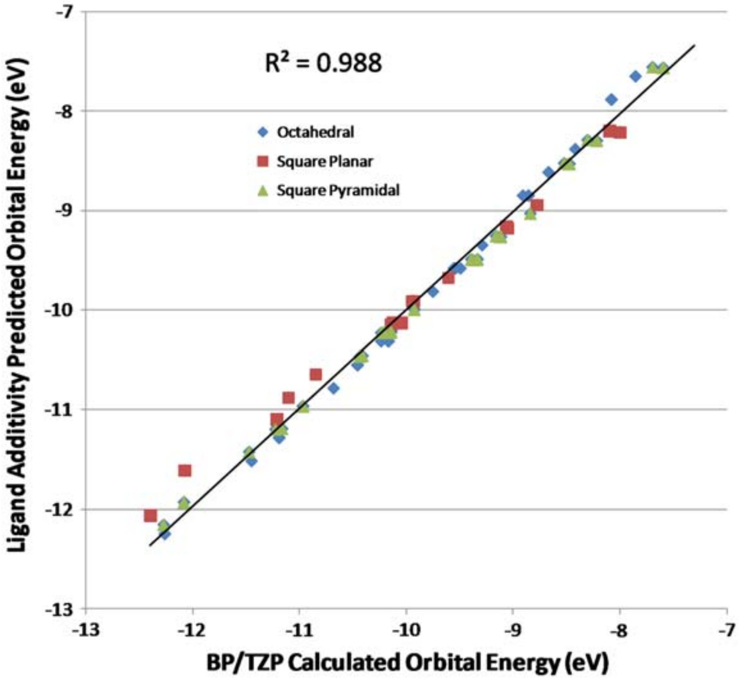

Figure 2. Plot of DFT calculated orbital energies *vs*. ligand additivity predicted energies for $[\mathrm{Mn}(\mathrm{CO})_n(\mathrm{CNMe})_{6-n}]^{x+}$, $[\mathrm{Mn}(\mathrm{CO})_n(\mathrm{CNMe})_{4-n}]^{x+}$ and $[\mathrm{Mn}(\mathrm{CO})_n(\mathrm{CNMe})_{5-n}]^{+}$.

complexes, again consistent with a more electron rich metal center. The σ-parameters indicate that in both Mn(I) and Cr(0) complexes, CNMe is approximately five-times stronger σ-donor than CO.

The question naturally arises if equations (5) and (6) and equations (7) and (8) can be applied directly to real complexes with square-planar and square-pyramidal geometries, respectively. While it is apparent that these equations could provide a starting point for the study of additive relationships in such complexes, the following issues would need to be considered:

(a) The original Bursten equations and the new equations presented in this contribution describe only the energy of the three occupied dπ orbitals in low-spin d^6 complexes. Square-planar and square-pyramidal geometries are not common for d^6 systems and generally encountered for other electron counts (for example, d^8 square-planar systems). As such, an additional occupied d orbital needs to be considered in the analysis if energies of all occupied metal-based orbitals are required (by traditional coordinate systems, this would be the d_z^2 orbital for d^8 systems). For the description of spectroscopic and electrochemical properties in some systems, such orbital energies may be essential. The symmetry of the additional orbital is such that π-bonding interactions are not present, but direct σ-interactions with the ligands are important. The original Bursten equations and the new equations presented in this contribution treat σ-interactions in an averaged way and describe directly only discrete π-interactions for individual orbitals. Hence, the model would need to employ

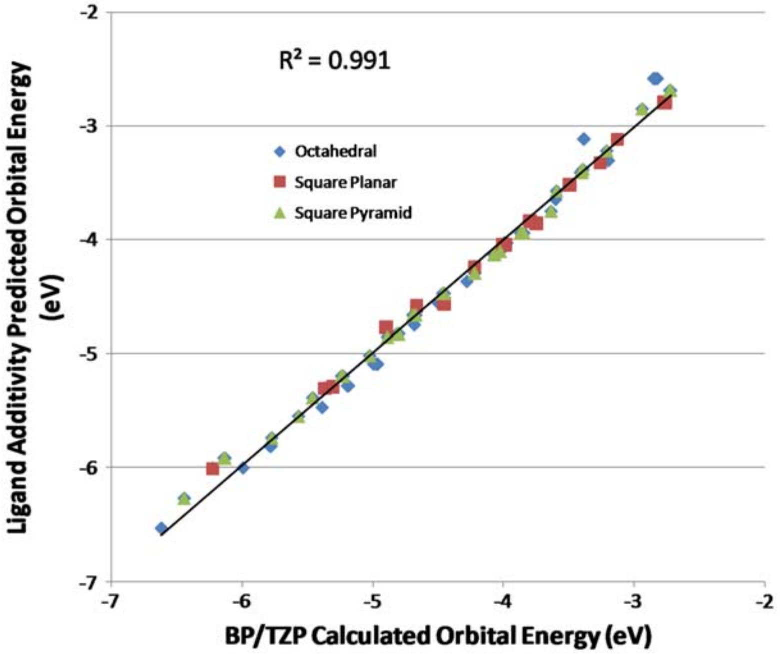

Figure 3. Plot of DFT calculated orbital energies *vs*. ligand additivity predicted energies for $\mathrm{Cr(CO)}_n\mathrm{(CNMe)}_{6-n}$, $\mathrm{Cr(CO)}_n\mathrm{(CNMe)}_{4-n}$ and $\mathrm{Cr(CO)}_n\mathrm{(CNMe)}_{5-n}$.

Table 1. Derived Bursten ligand a_{M}^{0}, $b_{\mathrm{M}}^{\mathrm{L}}$ and $c_{\mathrm{M}}^{\mathrm{L}}$ parameters from regression analysis of orbital energies.

	a_{M}^{0}	$b_{\mathrm{M}}^{\mathrm{CO}}$	$b_{\mathrm{M}}^{\mathrm{CNMe}}$	$c_{\mathrm{M}}^{\mathrm{CO}}$	$c_{\mathrm{M}}^{\mathrm{CNMe}}$
Mn(I)	−10.79	−0.09	0.64	−0.23	0.01
Cr(0)	−3.53	−0.26	0.26	−0.35	−0.17

Table 2. Derived Bursten ligand σ- and π-bonding parameters.

	$\sigma_{\mathrm{M}}^{\mathrm{CO}}$	$\sigma_{\mathrm{M}}^{\mathrm{CNMe}}$	$\pi_{\mathrm{M}}^{\mathrm{CO}}$	$\pi_{\mathrm{M}}^{\mathrm{CNMe}}$
Mn(I)	0.13	0.63	−0.23	0.01
Cr(0)	0.09	0.43	−0.35	−0.17

new parameters that account for individual σ-interactions in a manner similar to that currently included for π-interactions (for example, to distinguish between the d_z^2 and $\mathrm{d}_{z^2-y^2}$ orbitals in square-planar systems). This is not a problem in the present study as the only metal d orbitals studied are the dπ orbitals which do not have the correct symmetry to engage in direct σ-bonding interactions with the ligands present. In summary, the dπ orbitals in these systems appear to be described correctly but other occupied d-orbitals will need a new description.

(b) It should also be noted that a complete set of binary square-planar complexes or square-pyramidal complexes, each comprised of all possible isomers, provides insufficient information to solve the ligand additivity equations for individual ligand parameters (analogous to a complete set of octahedral complexes). However, combining orbital energies of any two sets (or select subsets) of complexes with different numbers of ligands (for example, square–planar and square–pyramidal) allows for determination of the ligand parameters.

(c) Square–pyramidal complexes are commonly distorted from ideal geometries, with apical angles ranging from 100–106° [17]; one of the fundamental postulates of the Bursten model is the retention of angles of 90° between ligands so as to separate σ- and π-bonding effects. Other systems in which angles between ligands deviate significantly from 90° (for example, due to steric effects) would also be unsuited to the model.

(d) The model does not apply to paramagnetic systems such as Co(II) d^7 complexes or any other high-spin system.

(e) Currently, investigations are underway to derive ligand σ- and π-bonding parameters for other common ligands using the methods described in this contribution. Investigations are also underway to study the applicability of the new equations to determine $d\pi$ orbital energies in classical square-planar coordination compounds and to develop equations that account for differences in σ-bonding for individual metal d-based orbitals in such systems.

4. Conclusions

The use of hypothetical coordinatively unsaturated complexes allows for the separation of ligand σ- and π-bonding parameters within the Bursten model of ligand additivity. Orbital energies for the complexes studied fit well with the modified additivity equations presented in this work. The derived parameters provide interesting insight into the nature of metal–ligand bonding in the systems studied. The method used to derive the ligand parameters should be generally applicable for d^6 octahedral species with close to ideal 90° angles between ligands. The new equations presented herein may also provide a starting point for the development of ligand additivity models for square–planar and square–pyramidal complexes.

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