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Correlation of the Ligand Constants P_L and Ground-state Electronic Properties in a Series of Diatomic Ligands

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Abstract

A series of quantum-chemical MO indices were evaluated at the CNDO/2 level of approximation to determine their effectiveness in parameterizing ligand bonding effects of simple diatomic species being potential ligands in organometallic and coordination compounds. Accordingly, linear correlations between these quantum-chemical indices and the experimentally determined ligand constants, P_L, have been established. It is also significant that these correlations could be possibly extended to any other homologous series of more complicated ligands, thus providing means for the theoretical calculation of the P_L constants of their donor atoms. Along these lines models accounting well for many properties of coordination compounds, depending mainly on electron drift between ligand and metal, could be designed.

Introduction

The ligand bonding effects described by the σ-donor and π-acceptor capacities of the ligands in relation to the π-donor and σ-acceptor capacities of the molecular fragments containing the central transition metal atoms or ions are the key to the understanding of the physical and chemical properties of coordination compounds. Therefore, many attempts have been made to quantify these effects in terms of both theoretical and experimental parameters. Obviously, such parameters would be very useful as predictive tools of the quantitative influence of the ligands on complex properties which depend mainly on electron drift between ligand and metal, such as electrochemical and spectroscopic properties, equilibria and reaction rates [1]. Recently Reinhold *et al.* [2], studying the bonding properties of α-diimine complexes, suggested the use of the LUMO energies of the ligands as a measure of their π-acceptor ability. The LUMO energies, as well as some other parameters calculated from the first-order density matrix, such as the local anisotropies, and Wiberg indices have also been used by Bàn *et al.* [3] to quantify the π-acceptor ability in a series of ten-valence electron isoelectronic diatomic ligands. These authors have also attempted to interpret the σ-donor abilities of the diatomic ligands on the basis of the sum of atomic orbital populations 2s and 2pσ, the σ-proportion of electrons on the bonding atom, the degree of bonding between the atoms of the ligands and the eccentricity of polarization ellipsoid weighted with σ charge densities. On the other hand, Chatt *et al.* [1, 4, 5] introduced an experimental parameter of ligand constant, P_L, closely analogous to the Hammett substituent constant, σ, as a measure of the ligand bonding effects. This ligand constant, in spite of the complexity of the ligand–metal interactions, allowed the prediction of a number of physicochemical properties of the coordination compounds. However, as far as we know, no attempt has yet been made to establish any relation between the ligand constant P_L and quantum chemical indices, analogous to that found quite recently for the Hammett σ-parameters [6]. Such a relation could help the understanding of the nature and meaning of the ligand constant P_L, as well as the parameterization of the ligand bonding effects in coordination compounds on the basis of quantum chemical indices. Consequently, the present study attempts to give an answer to this question. For this purpose a series of simple diatomic species, being potential ligands, were selected as model substances and the CNDO/2 formalism for the calculation of the MO indices was employed.

Computational Details

MO Indices Calculations

The calculations were carried out using the restricted and unrestricted forms of the CNDO/2 method and optimizing the geometries. The GEOMO system of programs (QCPE 290), including the corrections proposed by Mayer and Rèvèsz [7], has been used.

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Of the various MO indices, the following have been used as basis variables.

(i) The frontier MOs eigenvalues, ϵ_{FMO} (ϵ_{HOMO} and ϵ_{LUMO}).

(ii) The frontier MOs electrophilic and nucleophilic superdelocalizabilities, $\bar{S}_{\mathrm{E},\mu\nu}$(HOMO) and $\bar{S}_{\mathrm{N},\mu\nu}$(LUMO), as well as their components $S_{\mathrm{E},\mu}$(HOMO) and $S_{\mathrm{N},\mu}$(LUMO), respectively.

(iii) The local anisotropy, $\bar{L}_{\mu\nu}$, along with its components L_μ and L_ν.

(iv) The σ-proportion of electrons on the bonding atom μ, $\frac{1}{2}B_{\mu\mu}{}^{\sigma}$.

(v) The total energies, E_{tot}, of the free diatomic species.

The superdelocalizabilities, the local anisotropies, and the σ-proportion of the electrons on the bonding atom were calculated from the first-order density matrix of the systems according to the following equations [3, 6, 8]:

$$S_{\mathrm{E},\mu}(\mathrm{HOMO}), S_{\mathrm{N},\mu}(\mathrm{LUMO}) = 2\sum_{j}\sum_{m=1}^{N_\mu} \frac{(C_{jm}{}^{\mu})^2}{\epsilon_j} \tag{1}$$

$$\bar{S}_{\mathrm{E},\mu\nu}(\mathrm{HOMO}) = \tfrac{1}{2}(S_{\mathrm{E},\mu} + S_{\mathrm{E},\nu});$$

$$\bar{S}_{\mathrm{N},\mu\nu}(\mathrm{LUMO}) = \tfrac{1}{2}(S_{\mathrm{N},\mu} + S_{\mathrm{N},\nu}) \tag{2}$$

$$L_\mu = \sum_{m\in\mu}\sum_{n\in\mu} P_{mn}{}^2 - \sum_{l=0}^{k}\left(\sum_{m=l^2+1}^{m=(l+1)^2} P_{mm}\right)^2 \times \frac{1}{2l+1} \tag{3}$$

$$\bar{L}_{\mu\nu} = \tfrac{1}{2}(L_\mu + L_\nu) \tag{4}$$

$$B_{\mu\mu}{}^{\sigma} = \sum_{m\in\mu}\sum_{n\in\mu} P_{mn}{}^2 \tag{5}$$

In the above relationships μ denotes the atom in the molecule, m and n the AOs $x_m{}^{\mu}$ and $x_n{}^{\mu}$ belonging to atom μ, j the particular MO, l the angular momentum quantum numbers, N_μ the number of valence AO in the μth atom, $C_{jm}{}^{\mu}$ the eigenvector of the mth valence AO belonging to atom μ in the j MO, and ϵ_j is the energy of the j MO.

Results and Discussion

Since the ligand bonding effects can be more easily and unambiguously studied in simple systems, ten-valence electron diatomic species have been chosen as model substances to investigate these effects. Furthermore, by studying the bonding effects in the simple diatomic ligands, it is hoped that sufficient experience for the application of the better indices to more complicated polyatomic ligands will be obtained. Moreover, these systems are quite simple and therefore we can avoid the problems of steric hindrance, a quantity not effectively monitored in the MO indices used. The selected diatomic species can be divided into three classes according to the size of their all valence minimal basis set: (i) Diatomic species containing two atoms of the second row elements (class 2-2), such as $C_2{}^{2-}$, CN^-, CO, N_2, NO^+ and $O_2{}^{2+}$, which are characterized by an all valence minimal basis set of eight AOs, {2s, 6p}. (ii) Diatomic species containing one atom of the second row and one atom of the third row elements (class 2-3), namely SiC^{2-}, SiN^-, CP^-, SiO, PN, CS, PO^+, NS^+ and SO^{2+}, with an all valence minimal basis set of thirteen AOs, {2s, 6p, 5d}. (iii) Diatomic species containing two atoms of the third row elements (class 3-3), such as $Si_2{}^{2-}$, SiP^-, SiS, P_2, PS^+ and $S_2{}^{2+}$, with an all valence minimal basis set of eighteen AOs, {2s, 6p, 10d}.

Most of the studied diatomic species are hypothetical ligands, since no complexes have been isolated yet. However, all these species exist taking place as intermediates in chemical reactions. Some of them have also been observed in the interstellar medium of our galaxy, either in the dense gas and/or the diffuse gas clouds [9]. Complexes of the diatomic ligands CN^-, CO, N_2 and NO^+ have been extensively studied, while there are only a few studies of complexes of the CS, NS^+ and P_2 ligands.

MO Indices and Bonding Capacities of Ligands

In a series of ligands forming coordination compounds with the same molecular fragment containing the central atom, one would expect their bonding effects to be reflected in the energies and regiospecificities of their frontier MOs. Strictly speaking by the term frontier MOs we mean the more appropriate and chemically relevant donor and acceptor MOs of the ligands which are involved in the formation of the synergic bonding (σ-dative and π-back bonding) in their coordination and organometallic compounds. Generally, in most cases these donor and acceptor frontier MOs correspond to the HOMO and LUMO, respectively. However, there are cases where these MOs do not correspond to the HOMO and LUMO, but to other close-in-energy MOs, such as the next-HOMO (NHOMO) and next-LUMO (NLUMO), etc. Therefore, attention must be paid to the choice of the appropriate frontier MOs responsible for the ligand bonding effects. For the diatomic ligands under investigation these frontier MOs are the HOMO and LUMO.

It is obvious that a ligand molecule would be a better σ-donor the lower its ionization potential is and a better π-acceptor the larger its electron affinity. In Koopmans' approximation this is tantamount to adopting the HOMO and LUMO eigenvalues of the ligand molecule as the quantum-mechanical basis parameters for the σ-donor and π-acceptor capacities, respectively. The CNDO/2 LUMO and HOMO eigenvalues as well as the resulting series of π-acceptor and σ-donor capacities of the diatomic ligands under investigation are given in Fig. 1.

It follows that the ligand bonding effects are strongly dependent upon the value and sign of the charge on the ligand. Generally, as the positive charge on the ligand increases (or the negative charge decreases) the π-acceptor capacity increases. On the other hand, the σ-donor capacity increases as the negative charge on the ligand increases (or the positive charge decreases). Although the charge on the ligand is not the sole factor determining the ligand bonding effects in the above series of isoelectronic (ten-valence electron) ligands, its influence is strong enough to overcome the role of other factors. The role of the ligand's charge on its bonding effects is more clear in the case of the same diatomic species in different oxidation states for the other factors may be assumed to be identical. Thus, for example, in the case of the disulfur species in different oxidation states, the following series of π-acceptor and σ-donor capacities have been observed:

π-acceptor capacity:

$$S_2^{2+} > S_2^{+} > S_2^{0} > S_2^{-} > S_2^{2-} > S_2^{3-}$$

σ-donor capacity:

$$S_2^{3-} > S_2^{2-} > S_2^{-} > S_2^{0} > S_2^{+} > S_2^{2+}$$

Analogous series have also been obtained for other diatomic species in different oxidation states, but we have chosen the example of the disulfur species as most of these species form stable coordination compounds. As would be expected, the positive charge on the ligand represents high electron affinity and consequently high π-acceptor capacity, while the negative charge represents low ionization potential and therefore high σ-donor capacity.

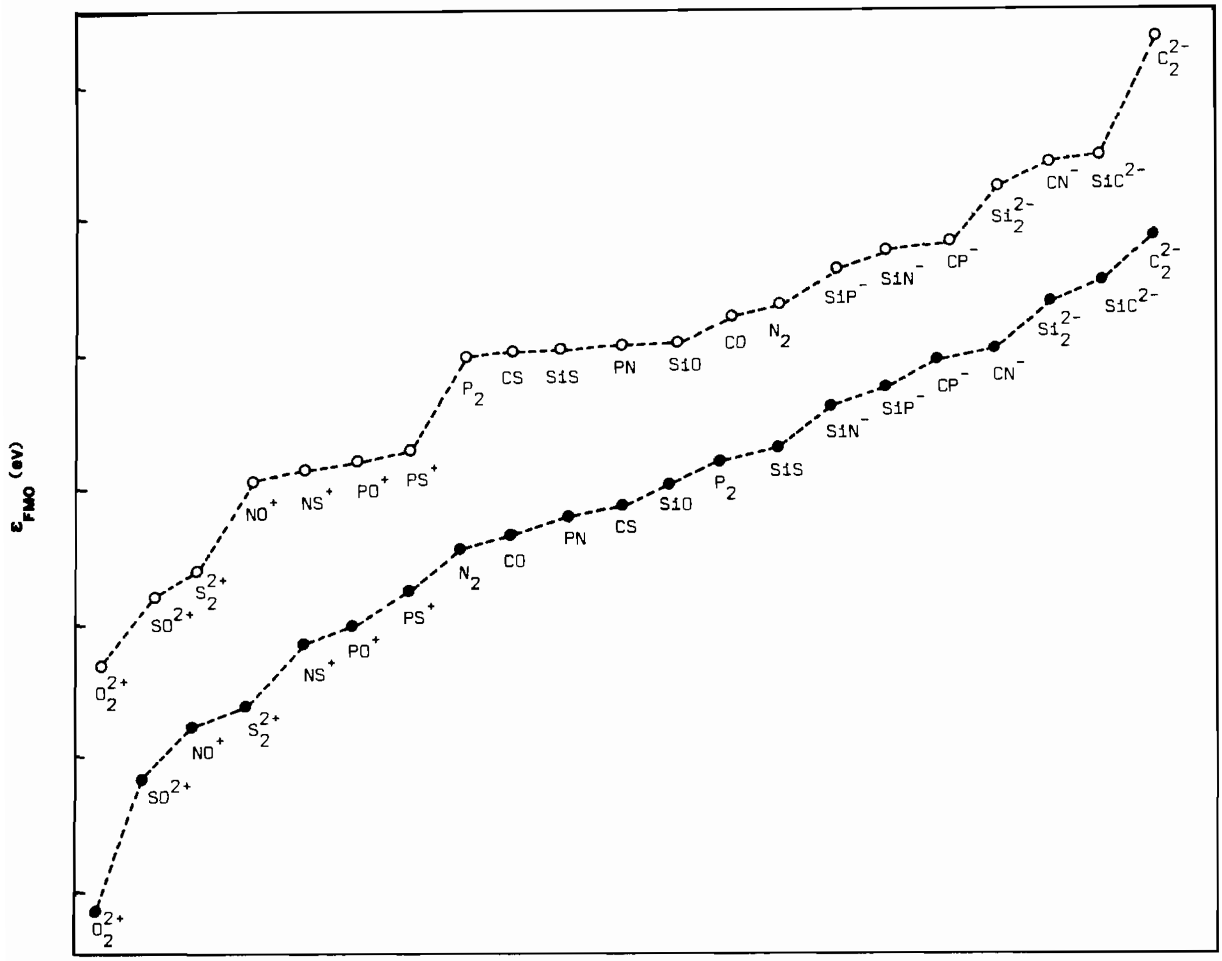

Fig. 1. CNDO/2-FMO energies of different isoelectronic diatomic ligands (filled points: HOMO; open points: LUMO).

From the series representing the π-acceptor and σ-donor capacities of the diatomic species it also follows that these properties are dependent upon the nature of the atoms of the diatomic ligands as well. Thus, in the case of the negatively charged diatomic ligands the π-acceptor capacity increases and the σ-donor capacity decreases as the total number of electrons increases. On the other hand, the opposite is true for the positively charged diatomic species. It is readily seen why this should be so. For the negatively charged diatomic species as the total number of the inner-shell electrons increases, the effective negative charge decreases and therefore the π-acceptor capacity increases and the σ-donor capacity decreases. On the contrary, for the positively charged diatomic species as the total number of the inner-shell electrons increases, the effective positive charge decreases and therefore the π-acceptor capacity decreases and the σ-donor capacity increases. In the case of the neutral diatomic ligands the changes of their bonding effects are very small and with a few exceptions as the total number of electrons increases both the π-acceptor and σ-donor capacities increase. These observations clearly indicate that the charge on the ligand has a greater influence on the bonding effects than that of the total number of the inner-shell electrons.

The present results concerning the σ-donor and π-acceptor capacity of the diatomic ligands are in accordance with experimental data based on the spectroscopic properties of their complexes [1, 3, 10, 11]. Furthermore, they confirm the evidence that the CS ligand is a better σ-donor and π-acceptor than the CO ligand [10]. However, it should be stressed that the parameterization of the ligand bonding effects by the LUMO and HOMO eigenvalues is of a qualitative nature and that only their relative magnitudes have a physical meaning. Nevertheless, in spite of the qualitative nature of the parameterization it is remarkable, considering the complexity of ligand–metal interactions, that so much information can be contained in only the HOMO and LUMO eigenvalues which account only for the energetic effects of the interactions. Therefore, in order to establish the quality of the parameterization we attempted next to apply some other MO indices which apparently include also electrostatic and/or perturbational effects of the interactions. Such MO indices are the electrophilic and nucleophilic superdelocalizabilities of the frontier donor and acceptor MOs respectively, the local anisotropy and the σ-proportion of electrons on the bonded atoms. All these parameters calculated from the first-order CNDO/2 density matrix for the diatomic ligands under investigation are collected in Table 1.

The frontier MOs superdelocalizabilities apparently include both electrostatic and perturbational effects and therefore are suspected to be more effective MO indices in parameterizing the ligand bonding effects than ϵ_{HOMO} and ϵ_{LUMO} parameters. Actually, the former parameters combine the density of electrons on the frontier MO with a measure of their instability, which are the leading factors determining the ligand–metal interactions. It is obvious that the electrophilic superdelocalizability of the

TABLE 1. CNDO/2 MO Indices for a Series of Diatomic Ligands

Ligand AB	$\bar{S}_{E,AB}$(HOMO)	$\bar{S}_{N,AB}$(LUMO)	$\bar{L}_{AB}$	$\frac{1}{2}B_{AA}^{\sigma}$	$\frac{1}{2}B_{BB}^{\sigma}$
C_2^{2-}	2.20	0.83	0.57	2.50	2.50
CSi^{2-}	3.40	1.35	1.11	2.38	2.48
Si_2^{2-}	4.18	1.55	1.52	2.46	2.46
CN^-	−14.28	1.38	0.52	2.41	
CP^-	−12.97	2.38	1.00	2.35	2.57
SiP^-	−11.58	2.85	1.34	2.33	2.63
SiN^-	−10.09	2.48	0.86	2.25	2.74
SiS	−2.26	40.99	1.04	2.22	2.84
P_2	−2.20	47.85	1.32	2.48	2.48
SiO	−2.02	27.55	0.49	2.14	3.04
CS	−1.92	46.30	0.89	2.31	2.64
PN	−1.88	29.07	0.81	2.34	2.61
CO	−1.55	6.09	0.49	2.32	
N_2	−1.47	5.34	0.47	2.50	2.50
PS^+	−1.16	−2.86	1.15	2.34	2.65
PO^+	−1.00	−2.60	0.56	2.20	3.96
NS^+	−0.97	−2.35	0.82	2.49	2.44
NO^+	−0.74	−2.25	0.44	2.41	
S_2^{2+}	−0.76	−1.30	1.18	2.48	2.48
SO^{2+}	−0.64	−1.12	0.58	2.28	2.75
O_2^{2+}	−0.47	−0.86	0.38	2.50	2.50

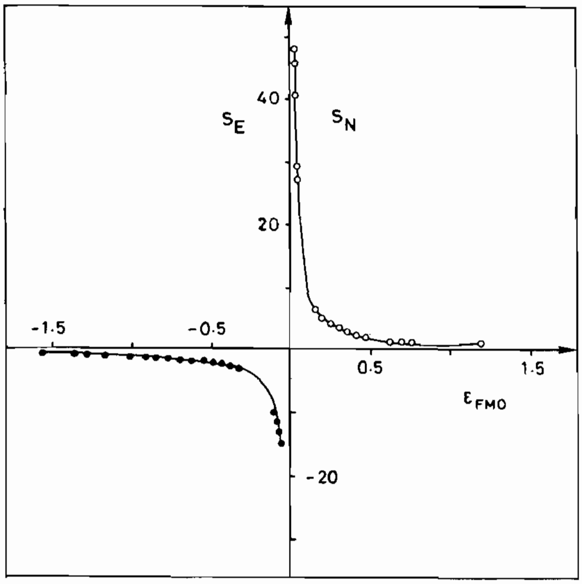

Fig. 2. Correlation of the electrophilic and nucleophilic superdelocalizabilities with ϵ_{HOMO} and ϵ_{LUMO}, respectively.

HOMO, $\bar{S}_{E,AB}$(HOMO), could be used as a measure of the σ-donor capacity of the ligand, whereas the nucleophilic superdelocalizability of the LUMO, $\bar{S}_{N,AB}$(LUMO), as a measure of its π-acceptor capacity. These two parameters are correlated with ϵ_{HOMO} and ϵ_{LUMO} parameters respectively, as is shown in Fig. 2. According to these correlations and the relations giving the S_E(HOMO) and S_N(LUMO) parameters, the following rules concerning the parameterization on the ligand bonding effects can be drawn.

(i) Ligands with positive S_E(HOMO) values are better σ-donors than those with negative ones. For the ligands exhibiting positive S_E(HOMO) values as their absolute values decrease the σ-donor capacity increases. On the other hand, for the ligands exhibiting negative S_E(HOMO) values as their absolute values increase the σ-donor capacity increases.

(ii) Ligands with negative S_N(LUMO) values are better π-acceptors than those with positive ones. For the ligands exhibiting negative S_N(LUMO) values as their absolute values decrease the π-acceptor capacity increases. On the other hand, for the ligands exhibiting positive S_N(LUMO) values as their absolute values increase the π-acceptor capacity increases.

On the basis of the above rules and the calculated values of the frontier MOs superdelocalizabilities, the series of decreasing π-acceptor and σ-donor capacities obtained were exactly the same with those derived on the basis of ϵ_{HOMO} and ϵ_{LUMO} parameters. That means that both couples of basis variables, in spite of their different nature, are effective MO indices for parameterizing the ligand bonding effects and their success lends credence to the nature of the ligand–metal interactions which are mainly frontier-controlled.

The $\frac{1}{2}B_{AA}{}^{\sigma}$ parameter representing the σ-proportion of electrons on the bonding atom A (Table 1) has been proposed by Bàn *et al.* [3] as a measure of the σ-donor capacity of diatomic ligands. However, according to our results this parameter does not seem to be an effective index for parameterizing the σ-donor capacity of ligands as it is insensitive either to the nature of the bonding atom A and/or to the charge of the ligand. For example, CN^- and NO^+ according to the $\frac{1}{2}B_{AA}{}^{\sigma}$ value have the same σ-donor capacity, although the former ligand is a well known strong σ-donor and the latter a strong π-acceptor. Furthermore, all homobinuclear diatomic ligands according to the $\frac{1}{2}B_{AA}{}^{\sigma}$ value might have the same σ-donor capacity, which is an unexpected result considering the different polarizabilities of the bonding atoms A.

Finally, the local anisotropy $\bar{L}_{AB}$ representing the anisotropy of the electronic environment in the molecule, which has also been proposed as a qualitative measure of the π-acceptor capacity of diatomic ligands, was not found in the present study to be a sufficiently effective parameter. Thus, although it gives the right trends for the π-acceptor capacity of the dinegative, uninegative and neutral diatomic ligands, it fails in the case of the positively charged ones. In the last cases the observed trends are reversed with regard to those established on the ϵ_{LUMO} and S_N(LUMO) parameters. Furthermore, it does not give the right trends for the ligands in each homologous series and, of course, for the complete series of the ligands under investigation. This is not surprising as the anisotropy of the electron density around the atoms of the ligands is not expected to be a leading factor in the frontier-controlled ligand–metal interactions. Therefore, its contribution is overcome by the leading electrostatic, energetic and perturbational effects. However, as will be discussed later on, this parameter, as well as the $\frac{1}{2}B_{AA}{}^{\sigma}$ parameter, could be instrumental as predictors of the bonding mode of ligands and in multidimensional analysis (multiple regressions) of the ligand bonding effects.

MO Indices and Bonding Mode of Ligands

The coordination modes of ligands in their complexes depend on several factors, the effects of which in individual compounds may have a different order of priorities. Such factors are the internal disposition of the ligands which results from their bonding possibilities, as well as the internal disposition of the central atom which depends on its characteristic as a soft or hard acid. Considering the complexity of ligand–metal interactions, we can assume that

TABLE 2. CNDO/2 MO Indices and Bonding Mode of Diatomic Ligands

Ligand AB	$S_{E,A}$(HOMO)	$S_{E,B}$(HOMO)	$S_{N,A}$(LUMO)	$S_{N,B}$(LUMO)	L_A	L_B	Bonding mode
C_2^{2-}	2.20	2.20	0.83	0.83	0.57	0.57	end-to-end; side-on; bridged side-on
CSi^{2-}	3.43	3.37	0.32	2.38	0.48	1.74	end-to-end; side-on; bridged side-on
Si_2^{2-}	4.18	4.18	1.55	1.55	1.52	1.52	end-to-end; side-on; bridged side-on
CN^-	−18.82	−9.75	1.15	1.61	0.61	0.42	C-end-on linear
CP^-	−15.29	−10.65	1.03	3.74	0.51	1.49	C-end-on bent
SiP^-	−13.68	−9.49	3.63	2.08	1.40	1.28	Si-end-on linear
SiN^-	−14.20	−5.99	4.65	0.41	1.40	0.33	Si-end-on linear
SiS	−3.09	−1.43	59.14	22.83	1.08	1.00	Si-end-on linear; Si-bridged
P_2	−2.20	−2.20	47.85	47.85	1.32	1.32	end-to-end; side-on
SiO	−3.47	−0.58	51.90	3.20	0.82	0.16	Si-end-on linear; Si-bridged
CS	−2.37	−1.46	32.82	59.78	0.57	1.21	C-end-on bent; C-bridged
PN	−1.98	−1.77	50.01	8.12	1.28	0.34	P-end-on linear; P-bridged
CO	−2.39	−0.72	8.76	3.43	0.70	0.29	C-end-on linear; C-bridged
N_2	−1.47	−1.47	5.34	5.34	0.47	0.47	end-to-end; side-on; end-on
PS^+	−1.21	−1.12	−3.56	−2.17	1.13	1.17	P-end-on bent
PO^+	−1.26	−0.74	−4.76	−0.45	0.94	0.18	P-end-on bent
NS^+	−1.02	−0.91	−1.02	−3.69	0.38	1.26	N-end-on linear
NO^+	−0.90	−0.57	−2.85	−1.65	0.55	0.33	N-end-on bent
S_2^{2+}	−0.76	−0.76	−1.30	−1.30	1.18	1.18	end-to-end; side-on; end-on
SO^{2+}	−0.67	−0.60	−1.94	−0.29	0.93	0.22	S-end-on linear
O_2^{2+}	−0.47	−0.47	−0.86	−0.86	0.38	0.38	end-to-end; side-on; end-on

the superdelocalizabilities including these effects warrant their successful use as predictors of the bonding mode of ligands. In this respect partitioning of the superdelocalizabilities of the donor and acceptor frontier MOs into their components describing the superdelocalizabilities of each nucleus in the molecular skeleton provides effective MO indices for predicting the bonding possibilities of the ligand. Actually, these MO indices represent the relative regiospecificities of the donor and acceptor frontier MOs for each atom of the ligand and consequently its relative σ-donor and π-acceptor capacity. In this respect, the components of the local anisotropy, L_A and L_B, representing the lability of an atom in a particular environment seem also to be good predictors. Actually, these MO indices are expected to copy the behavior of the superdelocalizabilities and in particular the nucleophilic ones. The calculated $S_{E,\mu}$(HOMO), $S_{N,\mu}$(LUMO) and L_μ CNDO/2 MO indices along with the bonding mode of the diatomic ligands under investigation are listed in Table 2.

As for the homobinuclear diatomic ligands both atoms have the same values for all MO indices and therefore these ligands will be coordinated to a central atom either in an end-to-end, **1**, or a side-on, **2**, fashion [12]. Furthermore the homobinuclear diatomic ligands which are strong σ-donors (e.g. C_2^{2-}, CSi^{2-} and Si_2^{2-}) could be also coordinated in a bridged side-on, **3**, fashion. Such complexes have been isolated and studied in the case of the disulfur ligand which according to our calculations was found to be a strong σ-donor in the −1 and −2 oxidation states existing in these compounds. On the other hand, the homobinuclear diatomic ligands which are poor σ-donors (e.g. N_2, O_2^{2+} and S_2^{2+}) could be also coordinated in an end-on, **4**, fashion [13].

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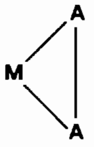

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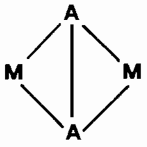

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Hori *et al.* [14], studying theoretically the stable geometry and rotation of the dinitrogen ligand in the $Ni(O_2)(N_2)$ complex, have pointed out that the N_2 end-on and O_2 side-on geometry is the most stable one. This is in accordance with our predictions as the dioxygen ligand is a stronger σ-donor than the dinitrogen ligand (ϵ_{HOMO} for O_2: −0.5461 eV, ϵ_{HOMO} for N_2: −0.6804 eV). Finally, it is worth noting that the P_2 ligand exhibiting an intermediate σ-donor capacity is mainly coordinated in an end-to-end fashion in full agreement with our predictions.

In the case of the heteronuclear diatomic ligands, the superdelocalizabilities are also good predictors of their bonding modes. Thus, CN^-, CO and CS must be coordinated through the carbon donor atom, whereas NO^+ and NS^+ are through the nitrogen donor atom, in full agreement with the experimental data concerning a variety of their complexes. The predicted linear bonding modes of the CN^-, CO and NS^+ ligands and the bending modes of the CS and NO^+ ligands are also in accordance with experimental data. In contrast to the linear bonding mode of the CN^- ligand, the analogous CP^- ligands is predicted to exhibit a bending bonding mode. Unfortunately, no complexes of the CP^- ligand have been isolated yet to verify the prediction. The same is also true for the PS^+ and PO^+ ligands which must be coordinated in a bending mode via the P donor atom. According to our calculations the bending in the PO^+ ligand is predicted to be higher than that of the PS^+ ligand. All silicon-containing diatomic ligands, e.g. CSi^{2-}, SiP^-, SiN^-, SiS and SiO are predicted to be coordinated via the silicon donor atom in a linear bonding mode. However, the values of the MO indices for the CSi^{2-} ligand provide also support for an end-to-end or a side-on coordination of the ligand in analogy with the homonuclear diatomic ligands. Finally, the PN and SO^{2+} ligands are predicted to be coordinated through the P and S donor atoms respectively, in a linear bonding mode. It is worth noting that the heteronuclear diatomic ligands exhibiting comparable σ-donor and π-acceptor capacities, such as CO, CS, SiO, SiS and PN could be also coordinated in a bridged fashion through the corresponding donor atom. Such a bonding mode has already been observed in the case of the CO and CS ligands.

MO Indices and P_L Constants

After the establishment of the qualitative parameterization of the ligand bonding effects by the MO indices described previously, we attempted next to quantify the effects on the basis of possible correlations between the MO indices and an experimental parameter, the ligand constant P_L. This parameter is defined as the change in oxidation potential measured in volts induced by the replacement of one carbonyl ligand in $Cr(CO)_6$ by the ligand L:

$$P_L = E_{1/2}{}^{ox}[Cr(CO)_5L] - E_{1/2}{}^{ox}[Cr(CO)_6] \qquad (6)$$

From this definition it follows that the CO ligand has P_L of zero. It is obvious that the ligand constant P_L accounts for the overall attracting or releasing quality of a ligand and therefore could be used to illustrate how effectively the various MO indices may reflect the ligand bonding effects. In fact, there are very good linear correlations between the FMO eigenvalues and the P_L constants (Fig. 3). These correlations are represented by the following linear equations

$$P_L^{2\text{-}2} = 0.37 - 1.97\epsilon_{LUMO}^{2\text{-}2} \qquad (R = 0.978) \qquad (7)$$

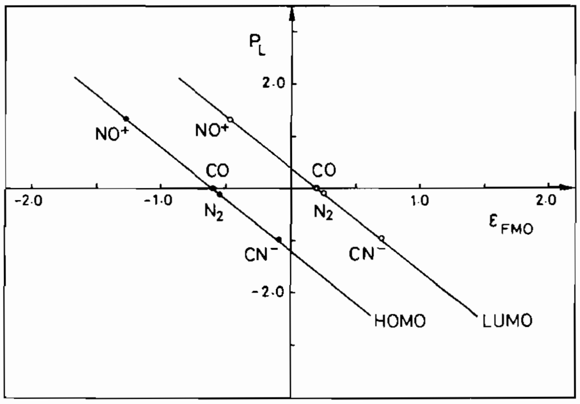

Fig. 3. Correlation diagram between the FMO eigenvalues and the experimental P_L constants of some ligands.

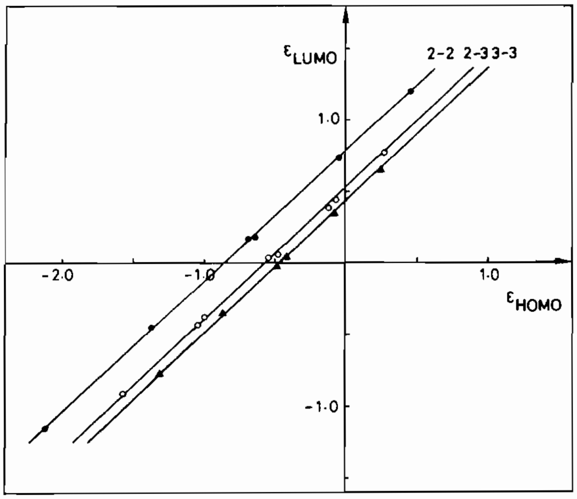

Fig. 4. $\epsilon_{LUMO}/\epsilon_{HOMO}$ correlations for each class of the diatomic ligands under study.

and

$$P_L^{2\text{-}2} = -1.19 - 1.81\epsilon_{HOMO}^{2\text{-}2} \qquad (R = 0.985) \qquad (8)$$

The linear correlation of the P_L constant either to the ϵ_{LUMO} or ϵ_{HOMO} eigenvalues means that ϵ_{LUMO} and ϵ_{HOMO} must be also linearly correlated. As a matter of fact there are very good $\epsilon_{LUMO}/\epsilon_{HOMO}$ linear correlations for each class of the diatomic ligands under study. These correlations, depicted schematically in Fig. 4, are represented by the following linear relationships

$$\epsilon_{LUMO}^{2\text{-}2} = 0.79 + 0.92\epsilon_{HOMO}^{2\text{-}2} \qquad (R = 0.999) \qquad (9)$$

$$\epsilon_{LUMO}^{2\text{-}2} = 0.49 + 0.90\epsilon_{HOMO}^{2\text{-}3} \qquad (R = 1.000) \qquad (10)$$

$$\epsilon_{LUMO}^{3\text{-}3} = 0.43 + 0.91\epsilon_{HOMO}^{3\text{-}3} \qquad (R = 0.999) \qquad (11)$$

It is remarkable that the slope of all these straight lines is about the same (≈0.91) which means that the lines are almost parallel. This is very important, since the parallelicity of the $\epsilon_{LUMO}/\epsilon_{HOMO}$ straight lines means also parallelicity of the P_L/ϵ_{LUMO} and P_L/ϵ_{HOMO} straight lines, providing thus the basis for the establishment of P_L/ϵ_{LUMO} and P_L/ϵ_{HOMO} relationships for the 2-3 and 3-3 classes of the diatomic ligands under investigation. These relationships are the following

$$P_L^{2\text{-}3} = 0.23 - 1.97\epsilon_{LUMO}^{2\text{-}3} \quad (R = 0.988) \tag{12}$$

$$P_L^{3\text{-}3} = 0.23 - 1.97\epsilon_{LUMO}^{3\text{-}3} \quad (R = 0.988) \tag{13}$$

and

$$P_L^{2\text{-}3} = -0.74 - 1.81\epsilon_{HOMO}^{2\text{-}3} \quad (R = 0.993) \tag{14}$$

$$P_L^{3\text{-}3} = -0.65 - 1.81\epsilon_{HOMO}^{3\text{-}3} \quad (R = 0.993) \tag{15}$$

Furthermore, considering the validity of the relationships

$$\epsilon_{LUMO} = a + 0.91\epsilon_{HOMO} \tag{16}$$

and

$$P_L = c - 1.97\epsilon_{LUMO} \tag{17}$$

for any member of the series of the diatomic ligands under study or for any other homologous series of ligands, a more general three-dimensional relationship results, e.g.

$$P_L = -0.43\epsilon_{HOMO} - 1.50\epsilon_{LUMO} \quad (R = 0.988) \tag{18}$$

Equation (18) indicates clearly that the P_L constants are more sensitive (about 3.5 times) to the variations of the ϵ_{LUMO} than the ϵ_{HOMO} eigenvalues. This is not surprising as the ligand constants P_L, being related to the oxidation potential of the metal center, are directly determined by the π-back bonding effects and only indirectly by the σ-bonding effects. This is due to the fact that the electron transferred in the oxidation process belongs to d AOs of the central atom which are involved in the formation of the π-back bonds. In contrast, the σ-bonding effects affect the oxidation potential only through the change in part of the electron density on the central atom.

On the basis of eqn. (18) the P_L constants for all the diatomic ligands under investigation have been calculated and the results are summarized in Table 3. The same results were also obtained using the eqns. (7), (12) and (13) or (8), (14) and (15). From the values of the calculated P_L constants it follows that high positive P_L values characterize the strong π-acceptors (top of the list), while high negative P_L values are characteristic of the strong σ-donors (bottom of the list). Obviously, high positive P_L values indicate poor σ-donor capacity, whereas high negative P_L values indicate poor π-acceptor capacity. The neutral diatomic species with low positive P_L values should show comparable π-acceptor and σ-donor capacities.

TABLE 3. CNDO/2 FMO Eigenvalues and Calculated P_L Constants of a Series of Diatomic Ligands

Ligand	FMO eigenvalues (a.u.)		P_L (V)
	ϵ_{HOMO}	ϵ_{LUMO}	
O_2^{2+}	−2.1075	−1.1641	2.65
SO^{2+}	−1.5694	−0.8972	2.02
S_2^{2+}	−1.3095	−0.7691	1.72
NO^+	−1.3752	−0.4451	1.26
NS^+	−1.0342	−0.4248	1.08
PO^+	−1.0011	−0.3834	1.00
PS^+	−0.8591	−0.3497	0.89
CS	−0.5224	0.0216	0.19
PN	−0.5328	0.0344	0.18
P_2	−0.4537	0.0209	0.16
SiO	−0.4947	0.0363	0.16
SiS	−0.4425	0.0244	0.15
CO	−0.6444	0.1640	0.03
N_2	−0.6804	0.1877	0.01
SiP^-	−0.0863	0.3504	−0.49
SiN^-	−0.0990	0.4034	−0.56
CP^-	−0.0771	0.4195	−0.60
CN^-	−0.0700	0.7247	−1.06
Si_2^{2-}	0.2394	0.6432	−1.08
CSi^{2-}	0.2941	0.7403	−1.24
C_2^{2-}	0.4537	1.2074	−2.01

The present results concerning the σ-donor and π-acceptor capacity of the diatomic ligands are again in accordance with experimental data [1, 3, 10, 11] based on spectroscopic properties of their complexes. Moreover, they give an answer to the assessment of the relative π-acceptor to σ-donor ratios of the NS^+ and NO^+ ligands put forward by Greenhough *et al.* [11]. The NO^+ ligand is a slightly stronger π-acceptor than the NS^+ ligand, while the latter is a slightly stronger σ-donor. This may also explain the dichotomy concerning the ligating properties of these two ligands [11].

We have also calculated the P_L constants for the disulfur species in different oxidation states. An inspection of the results shown in Table 4 clearly indicates the strong dependence of the P_L constants on the charge of the diatomic species. The set of data gives a linear plot which can be represented by the following equation

$$P_L = 0.18 + 0.77q \quad (R = 0.999) \tag{19}$$

So far we have concerned ourselves with the correlation of the FMO eigenvalues with the P_L constants. We attempted next to correlate the P_L constants with the other MO indices employed in the present study. However, no one of these parameters gave respectable results. Although this result may be somewhat disappointing, it should not be surprising, considering the nature of the parameters. The superdelocalizabilities are associated with the

TABLE 4. FMO Eigenvalues and Calculated P_L Constants for Disulfur Ligands in Different Oxidation States

Ligand	q	FMO eigenvalues (a.u.)		P_L (V)
		ϵ_{HOMO}	ϵ_{LUMO}	
S_2^{2+}	+2	−1.3095	−0.7691	1.72
S_2^{+}	+1	- 0.8377	−0.3932	0.95
S_2^{0}	0	−0.4073	−0.0197	0.20
S_2^{-}	−1	−0.0383	0.4477	−0.66
S_2^{2-}	−2	0.3186	0.8012	−1.34
S_2^{3-}	−3	0.7495	1.1846	−2.10

reactivity of the individual atoms in the molecule towards electrophilic or nucleophilic attack, and therefore should be expected to perform well as reactivity indices. In fact, the superdelocalizabilities were found to be effective MO indices for parameterizing the reactivity in the electrophilic substitution reactions of aromatic compounds. On the other hand, the P_L constants, according to their definition, are associated with the oxidation potentials which are mainly determined by the frontier MOs energies. The correlation of the P_L constants with the oxidation potentials of the M_sL complexes (M_s = metal and associated non-substituted ligands) is given by the linear equation

$$E_{1/2}^{ox}[M_sL] = E_s + \beta P_L \tag{20}$$

where E_s and β are two site constants characterizing the metal site binding of the ligand L. We feel that superdelocalizabilities must be correlated with the site constants or may help to introduce a reaction constant corresponding to Hammett's ρ constant, needed for predictions outside the area of oxidation and reduction potentials. We are currently studying the possible correlations of the MO indices with the site constants in an attempt to define theoretically the nature of the site in complexes of different oxidation states, coordination numbers and geometries.

The local anisotropy and $\frac{1}{2}B_{\mu\mu}{}^{\sigma}$ parameters gave also very poor correlations since both these parameters account only for second-order effects in the metal–ligand interactions. This becomes clear also from a multidimensional analysis of the P_L constants which afforded the following linear relation

$$P_L = 0.02 - 0.43\epsilon_{HOMO} - 1.49\epsilon_{LUMO} - 0.01(\tfrac{1}{2}B_{\mu\mu}{}^{\sigma}) + 0.002L_{\mu} \tag{21}$$

In fact, the contribution of these two parameters is very small and therefore (for the sake of simplicity) could be omitted from the relation without loss in the accuracy of the results. The introduction of these two parameters, although it does not affect the correlation coefficient, increases the significance of the analysis about four times. Finally, it is worth noting that the superdelocalizabilities were also not useful in multivariable regressions of the systems under investigation.

Conclusions

The CNDO/2 eigenvalues of the frontier donor and acceptor MOs appear to give good correlations for predicting quantitatively the ligand bonding effects of diatomic ligands in their coordination compounds. It is also significant that these correlations could be easily extended to any other homologous series of more complicated ligands, thus providing means for the theoretical calculation of the P_L constants of their donor atoms. These ligand constants P_L are sufficiently fundamental to allow the prediction of many properties of coordination compounds which depend mainly on electron drift between ligand and metal. Actually, according to our calculations the ligand constants P_L account for the σ-donor and π-acceptor capacities of the ligands which are the leading factors determining the ligand bonding effects. The predictive utility of the approach used in this work derives from the introduction of theoretical parameters in the quantification of the ligand bonding effects. This could lead to an 'a priori design' of new, interesting ligands intended for a specific purpose. Moreover, considering the extended donor–acceptor approach for nearly all kinds of molecular interactions, the calculated P_L constants could prove to be generally useful. Thus, for example, they can be used to parameterize with only a single parameter the donor and acceptor properties of solvents [15]. These properties have been already parameterized by the empirical solvent parameters of the donor and acceptor number which were shown to be related to the HOMO and LUMO energies [16], respectively. In this respect, the introduction of the P_L constant will reduce also the basis variables used in the classification of solvents.

The nucleophilic and electrophilic superdelocalizabilities, although they provide a good qualitative measure of the π-acceptor and σ-donor capacities respectively, do not correlate linearly with the P_L constants. It seems that these parameters must be more effective as reactivity indices, and therefore could be proven useful for the theoretical definition of the metal site binding the ligand L, or to serve as a reaction constant needed for prediction of properties outside of the area of oxidation and reduction potentials. Studies on this field are currently in progress in our laboratory and the results will be published soon. Finally, the local anisotropy and the $\frac{1}{2}B_{\mu\mu}{}^{\sigma}$ parameters proposed as measures of the π-acceptor and σ-donor capacities of diatomic ligands respectively, were proven in the present study to be not effective MO indices. This is due to the fact that both these two MO indices account only for second-order effects of the ligand–metal interactions.

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