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σ-Donor and π-Acceptor Properties of Ten Valence Electron Isoelectronic Diatomic Molecules being Potential Ligands in Transition Metal Complexes

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σ-donor and π-acceptor properties of 14-electron (10 valence electron) isoelectronic diatomic ligands with empty π-orbitals (CO, N_2, CN^-, NO^+, C_2^{2-}, O_2^{2+}) were investigated by the CNDO/2 method. The LUMO energies, the total energies of the free ligands and of the ligands bonded in Fe^{2+} complexes, the changes in local anisotropies, reactivities and bond lengths of the ligands, calculated from electronic data, are correlated with the π-acceptor abilities of the ligands. The σ-donor properties are interpreted by 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 the polarization ellipsoid weighted with σ charge densities. Other factors influencing the electron rearranging effects on coordination are also discussed. To simulate the back donation effect the number of electrons of the ligands were increased by the charge −e and the electronic structures of 11 valence electron species so obtained (CO^-, N_2^-, CN^{2-}, NO, C_2^{3-} and O_2^+) were also calculated. The differences in electronic data, as compared to those of the 10 valence electron species, were used to explain the π-acceptor properties of the ligands.

Introduction

Back-coordination occurring in transition metal complexes containing molecule ligands with π-orbitals is thought to be achieved by the d-electrons of the central metal establishing bonds with the empty π* orbitals of the electron accepting ligands [1–11]. It is expected that in the case of the same metal centre, ligands having the lower-lying orbitals suitable for such bonding will be the better π-acceptors and thus more susceptible to back-coordination. Reinhold and coworkers [12] have actually found that for some α-diimine ligands of similar structure the energies of the lowest unoccupied MOs (LUMOs) are proper measures of the π-acceptor ability of ligands.

Since both the σ-donor and π-acceptor properties of ligands can be more easily and unambiguously studied in small molecules and assigned to changes in the electronic structure of such compounds, 14-electron (10 valence electron) isoelectronic diatomic ligands having empty π-orbitals (CO, N_2, CN^-, NO^+, C_2^{2-}, O_2^{2+}) have been chosen as model substances to investigate the electron-rearranging effects mentioned. The energies of LUMOs have also been found to be closely associated with the empirical measure of the π-acceptor ability of the ligands: the energies of LUMOs of the 10 valence electron ligands studied follow the same relative order as the corresponding back-donation tendencies.

The relationship between the π-acceptor abilities and the mean values of the local anisotropies [13] has been verified. The assumptions made allowed us to draw comparisons between some calculated physico-chemical quantities and the changes in the π-acceptor property, and also to interpret such correlations on electronic grounds.

The theoretical results on σ-donor and π-acceptor features of ligands have been found to be in agreement with experimental results and the calculations of other authors [2, 5–7, 9, 11, 15, 20–28].

Method of Calculations and Results

The calculations were carried out using the restricted and unrestricted forms of the CNDO/2 method [18] and optimizing the geometries[a]. Since systematic extensions of the investigations of parent

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[a] Our CNDO/2 results for diatomic molecules, especially those regarding trends in changes of electronic data, are in good agreement with results of *ab initio* calculations on the same species [29, 30].

TABLE I. Electronic Data of Ten and Eleven Valence Electron Species of Isoelectronic Diatomic Molecules.

Species	$r_{eq.}$ in pm	$E_{tot.}$ in hartrees	Electron density	$\frac{1}{2}B_{XX}^{tot.}$	B_{AA}^{σ}	B_{AB}	L_A L_B	$\bar{L}_{AB} = \frac{(L_A + L_B)}{2}$	R_A R_B
Eleven valence electron species									
N_2^-	119.4	−22.92	N: 5.50	4.25	5.00	2.50	0.52	0.52	0.50
CO^-	124.8	−24.91	C: 4.59 O: 6.41	3.53 5.35	4.65	2.12	0.78 0.33	0.55	0.74 0.26
CN^{2-}	127.8	−17.48	C: 5.16 N: 5.84	3.93 4.62	4.83	2.45	0.64 0.45	0.55	0.58 0.42
NO	115.2	−29.89	N: 4.95 O: 6.05	3.78 4.87	4.83	2.35	0.63 0.39	0.51	0.65 0.35
C_2^{3-}	136.2	−11.70	C: 5.50	4.25	5.00	2.50	0.57	0.57	0.50
O_2^+	109.4	−36.27	O: 5.50	4.25	5.00	2.50	0.46	0.46	0.50
Ten valence electron species									
N_2	114.0	−23.09	N: 5.00	3.50	5.00	3.00	0.47	0.47	0
CO	119.1	−25.06	C: 3.92 O: 6.08	2.63 4.79	4.65	2.58	0.70 0.29	0.49	0
CN^-	120.1	−18.18	C: 4.57 N: 5.43	3.10 3.96	4.83	2.94	0.61 0.42	0.52	0
NO^+	111.3	−29.44	N: 4.37 O: 5.63	2.94 4.21	4.83	2.85	0.55 0.33	0.44	0
C_2^{2-}	125.0	−12.87	C: 5.00	3.50	5.00	3.00	0.57	0.57	0
O_2^{2+}	107.1	−35.10	O: 5.00	3.50	5.00	3.00	0.38	0.38	0

and mixed ligand complexes of the studied diatomic ligands coordinated to various transition metals are planned, we chose a quantum chemical method the versions of which [5, 10, 14] are suitable for the calculation of complexes as well. For the diatomic molecules studied here the LUMOs in all cases are π-type (virtual) antibonding (π^*) orbitals. Among the quantities obtained in the course of calculations, the electron density matrix, the total energies, the LUMO energies and the equilibrium bond distances have all been used directly or to derive additional quantities in order to explain the σ-donor and π-acceptor properties of the potential ligands. The σ-proportion of the density resulting from the separation of the atomic orbital populations has been employed to describe the σ-donor ability.

As a consequence of back-coordination, electrons from occupied d-orbitals of the central metal donated into the empty antibonding π^*-orbitals (LUMOs) of the ligands change the electron distribution in space around the atoms of the ligands. For the interpretation of this effect (and thus indirectly of the back-coordination), the so called local anisotropy [13] seems to be one of the most appropriate quantity. Therefore it has been supposed that the tendency to back-coordination (*i.e.* the π-acceptor ability) varies proportionately with the differences in the averages of the local anisotropies of the atoms of the ligands. To derive the necessary quantities, the back-donation effect was simulated in such a way that the number of electrons of the ligands were increased by $-e$ to give the corresponding 11 valence electron species CO^-, N_2^-, CN^{2-}, NO, C_2^{3-}, O_2^+. The differences in the calculated mean local anisotropies of these doublet species and the 10 valence electron singlet species are assumed to correlate with the tendency to back-coordination or the π-acceptor ability of the ligands.

The data obtained directly from the calculations and the basic quantities [13] derived from these results by eqns. (1)–(6) are listed in Table I.

$$L_A = \sum_{\substack{\mu \\ \text{on A}}} \sum_{\substack{\nu \\ \text{on A}}} P_{\mu\nu}^2 - \sum_{1=0}^{k} \left(\sum_{\mu = 1^2 + 1}^{\mu = (1+1)^2} P_{\mu\mu} \right)^2 \times \frac{1}{21 + 1}, \qquad (1)$$

$$B_{AA}^{\text{total}} = \sum_{\substack{\mu \text{ on A} \\ \nu \text{ on A}}} P_{\mu\nu}^2, \qquad (2)^{a}$$

$$B_{AB}(\equiv W_{AB}) = \sum_{\substack{\mu \text{ on A} \\ \nu \text{ on B}}} P_{\mu\nu}^2, \qquad (3)^{b}$$

$$R_A = V_A - \sum_{B \neq A} B_{AB}, \qquad (4)$$

where

$$V_A = \sum_{\substack{\text{all } \mu \\ \text{on A}}} 2P_{\mu\mu} - \sum_{\substack{\text{all } \mu \\ \text{on A}}} \sum_{\substack{\text{all } \nu \\ \text{on A}}} P_{\mu\nu}^2 \qquad (5)$$

$$P_{\mu\nu} = 2 \sum_{i}^{\text{occ.}} C_{i\mu} C_{i\nu} \qquad (6)^{c}$$

are the elements of the density matrix **P**, where C_{ik} are the components of the orthonormal matrix of eigenvectors **C** and the sum is over all occupied orbitals.

The first and fourth rows of Table II show the LUMO energies of the diatomic molecules and the average anisotropy changes. Both the order of the LUMOs and the differences[a] in local anisotropies are changing as (7):

$$O_2^{2+} > NO^+ > CO \gtrless N_2 > CN^- > C_2^{2-}, \qquad (7)$$

i.e. the π-acceptor ability is the largest for O_2^{2+} and the smallest for C_2^{2-}. Since no complexes of the ligand O_2^{2+} and few[b] of C_2^{2-} are known, the theoretical results can only be compared with experiences on the tendency to back-coordination of the other four ligands. Experimental observations and *ab initio* calculations [7, 11, 15, 20–24, 26–28] support the order (7) according to which the π-acceptor ability decreases from NO^+ to CN^-.

It is to be mentioned that the total energies (Table I) and the differences in total energies of the 11 and 10 valence electron species change also as to (7) (see row 5 of Table II). The largest decrease on the effect of the charge increase (*i.e.* on coordination) is occurring at O_2^{2+} where the tendency to back-coordination is the strongest, and the smaller decrease (or larger increase) where the π-acceptor ability is the weaker. The change in total energy, of course, can be explained only to a certain extent by the variation in the π-acceptor properties, nevertheless, on the base of former considerations this relation is to be assumed. This seems also to be confirmed by the results [16] obtained by the CNDO/2 [14] calculations on complexes of the type $[Fe(CN)_5L^s]^{-3+s}$(where L = N_2, CO, CN^-, NO^+, O_2^{2+} and s is the charge of the ligand L). The decrease—according to (7)—in the total energies of these complexes (Table III, row 2) is here obviously only partly due to the relative stabilization effect resulting through back-coordination, changing

TABLE II. Calculated Quantities Reflecting the π-Acceptor Ability of Isoelectronic Diatomic Molecules.

Molecule: Quantity	CC^{2-}	CN^-	CO	NN	NO^+	OO^{2+}
LUMO	1.2074	0.7247	0.1640	0.1877	−0.4451	−1.1633
ΔL_A	0.0038	0.0328	0.0798	0.0460	0.0780	0.0792
ΔL_B	0.0038	0.0270	0.0472	0.0460	0.0607	0.0792
$\Delta \bar{L}_{AB}$	0.0038	0.0299	0.0635	0.0460	0.0693	0.0792
$\Delta E_{tot.}$	1.1710	0.7010	0.1502	0.1717	−0.4549	−1.1679
$\Delta r_{eq.}$	11.2	7.7	5.7	5.4	3.9	2.3

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[a] l = the angular momentum quantum numbers.

[b] W_{AB} is the Wiberg index between atoms A and B [19].

[c] This is strictly valid for closed shells only. In open shell cases the sum of the products of coefficients must be taken separately for α and β spins and into the eqns. (1)–(5) these values of $P_{\mu\nu}$ are to be substituted. For such cases, *e.g.* instead of (5) the equation

$$V_A = \sum_{\lambda = \alpha, \beta} \left\{ \sum_{\substack{\text{all } \mu \\ \text{on A}}} P_{\mu\mu}^{\lambda} - \sum_{\substack{\text{all } \mu \\ \text{on A}}} \sum_{\substack{\text{all } \nu \\ \text{on A}}} (P_{\mu\nu}^{\lambda})^2 \right\} \qquad (5a)$$

will hold.

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[a] The explanation is that instead of the spherical symmetry in electron distribution of the free atom, the greater the anisotropy change the larger the spatial separation of the electrons in the atoms bonded in the ligand molecule. Consequently the electrons exert smaller torque upon each other, thus resulting in weaker repulsions which is favourable for the ligand to accept electrons from the central metal.

[b] Acetylene (C_2H_2) appears as ligand more frequently than acetilide ion (C_2^{2-}).

TABLE III. LUMO Energies and Total Energies of $[Fe(CN)_5L^s]^{-3+s}$ Complexes.

Complex: Quantity	$Fe(CN)_5O_2^-$	$Fe(CN)_5NO^{2-}$	$Fe(CN)_5CO^{3-}$	$Fe(CN)_5N_2^{3-}$	$Fe(CN)_6^{4-}$
LUMO	0.1324	0.2019	0.6094	0.6071	0.9862
$E_{tot.}$	−151.25	−144.17	−139.39	−137.32	−132.17

TABLE IV. Stretching Frequencies of the Bond A–B in the Free Ligands and in Ligands of Metal Complexes.

L(igand) = AB	AB stretching frequency (cm^{-1}) in			
	Free L	$Fe(CN)_5L$	NiL_4	CrL_6
NN	2331	2135	–	–
CN^-	2080	2094 - 2006	2135	2135
NO^+	2220	1938	1872 - 1840	1645
CO	2143	–	2131 - 2057	2118 - 2000

the latter as the π-acceptor ability [25]. The LUMOs of the corresponding metal complexes (Table III, row 1) follow also the same order, apart from LUMO(N_2) $\overset{\sim}{<}$ LUMO(CO) which means that the π-acceptor ability for CO is nearly the same (or somewhat higher) as that for N_2 [22, 23].

The calculated relative tendencies of ligands to back-coordination are in good agreement with the observed decreases of stretching frequencies (Table IV) of the ligands in metal complexes compared to those of the free ligands [26, 28]. The decrease in stretching frequencies is due to the population, by back-donation, of the antibonding π^* (2π) orbital of the ligands loosening the bond between the atoms of the ligand.

Since the anisotropy term L_A is associated with the lability of the atom A in a particular environment, then larger or smaller values of local anisotropies on the atoms may explain why the one and not the other atom of the same ligand is coordinated to the central metal. Larger L_A values (high labilities) may indicate higher susceptibilities for bonding by the C atoms instead of O and N atoms in CO and CN^- or by the N atom instead of O in NO^+. The same trend is reflected also in the ΔL_A and ΔL_B values: $\Delta L_A \overset{=}{>} \Delta L_B$ where the equality holds for A = B (homonuclear diatomics) and the inequality for A ≠ B (heteronuclear diatomics) (Table II, rows 2 and 3).

For the open shell case, the quantity R_A defined by equations (4)–(6) is a measure of the reactivity of the atom A. The values of this quantity (Table I) may be interpreted in a similar manner as those of the local anisotropy, and they represent exactly the same trend: $R_A \overset{=}{>} R_B$, with the variation that for the closed shell case $R_A = 0$, $R_B = 0$ (in the 10 valence electron singlet state). The differences in the reactivities are therefore identical with the corresponding values in the doublet state (11 valence electron case). These results may be explained by (partial) electron transfer to the ligand on coordination, the reactivity of the binding atom (atom A) being increased in a larger extent with respect to the average of R_A and R_B (to 0.5).

Similar changes can also be observed in the bond distances of the molecules. Here, considering the differences Δr_{eq} appearing in the equilibrium bond distances obtained for the 11 and 10 valence electron species by optimization, the values displayed in row 6 of Table II are found. The sequence of these values is the same as in (7) but the order is reversed: the increase of the bond distances on electron acceptance is the largest in C_2^{2-} and the smallest in O_2^{2+}. A plausible explanation is that electron acceptance is accompanied by the increase of repulsion forces. Thus by the loosening of bonds this effect is expected to be stronger the larger the absolute extent of the negative charge on the molecule. Naturally this change—as that of the total energy—can only in part be assigned to the increase in π-acceptor ability. Lengthening of bonds, taking place on the effect of charge transfer to the free ligands, is occurring also for the same ligands bonded in appropriate complexes [5–7, 10, 11, 15, 26, 28].

The σ-donor properties have been concluded from the σ-electron densities (the sums of atomic orbital populations 2s and $2p\sigma$). The larger this value (row 1, Table V), the stronger the σ-donor ability expected. Similar sequence is obtained by the $B^{\sigma}_{AA}/2$ values representing the σ-proportion of electrons on the bonding atom A (row 2, Table V). Neglecting other factors, both results produce the same order (8):

TABLE V. Calculated Quantities Reflecting the σ-Donor Ability of Isoelectronic Diatomic Molecules.

Molecule: Bonding atom: Quantity	CC^{2-} C	NN N	OO^{2+} O	CN^- C	NO^+ N	CO C
$2s + 2p\sigma$	3.00	3.00	3.00	2.90	2.90	2.78
$\frac{1}{2}B^{\sigma}_{AA}$	2.50	2.50	2.50	2.41	2.41	2.32
$\sigma^{wt.}_{ecc.}$	2.56	2.31	2.18	2.13	1.96	1.63

$$C_2^{2-} = N_2 = O_2^{2+} > CN^- = NO^+ > CO, \tag{8}$$

i.e. the σ-donor effect is the greatest for the homonuclear diatomic molecules, and the smallest for the CO ligand. It is worth noting that the number of electrons in bonds between atoms A and B, the 'degree of bonding' B_{AB} (Table I) defined by (3), is changing also as (8), parallel with the total number of electrons on atom A (Table I). However, in the latter cases the values for CN^- are always greater than those for NO^+. For diatomic ligands, the 'quasi lone pair' densities [12], assuming digonal hybridization and using accordingly the formula $\frac{1}{2}$ $POP_s + \frac{1}{2}$ $POP_{p\sigma}$, would obviously give no departure from the order in (8). The σ-donor properties of ligands are determined considerably by charge densities accumulated on σ-type orbitals. To estimate the σ-charge densities of non-overlap character ideal for the donor effect, a polarization ellipsoid of σ-charges was also defined (see Appendix). Arranging in decreasing order the ligands on base of the virtual eccentricity (weighted by the σ-charges) of the polarization ellipsoid (Table V, row 3), the following sequence (9) can be obtained:

$$C_2^{2-} > N_2 > O_2^{2+} > CN^- > NO^+ > CO, \tag{9}$$

thus even the donor properties of the ligands in the group of homonuclear diatomics can be specified and the relative order of CN^- and NO^+ can be established. These results agree, in general, with the experimental observations[a] and the theoretical results obtained for ligands in complexes by *ab initio* methods [6, 7, 15, 20, 21, 23–25, 27].

As mentioned above, the σ-donor and π-acceptor abilities are, of course, not the sole factors determining the σ-coordination and π-back-coordination of the ligands and the metal. Other properties (differences in electronegativities, net charges on the atoms, polarization effects, *etc.*) may also influence and modify the 'pure' effects considered in this paper. Consequently only concrete investigations on a given complex can provide accurate information on the actual situation. It should also be stressed that the calculated data are of qualitative nature [17], so that only their relative magnitudes and tendencies have physical reality and the absolute values are without meaning.

Obviously there are factors enhancing or reducing the σ-donor and π-acceptor abilities of the ligands in the surrounding of other ligands and the metal centre. It may be expected *e.g.* that the π-acceptor property is strongly dependent upon the value and sign of the charge on the ligand. Negative charge (on the ligand) represents smaller relative electronegativity which does not favour the π-acceptor ability. Decreasing negative (or increasing positive) charge on the ligands is increasing the tendency to back-coordination. The differences in electronegativities seem to be affecting the σ-donor properties preferably. The (relatively) more electropositive ligand (or its atom) will be coordinated to the same metal centre since this is repulsing the electrons more strongly. Accordingly, *e.g.* in the case of CN^-, CO and NO^+ the bonding atoms will be C, C and N, respectively, while the bonding (not the σ-donor) property will be changing in the order $CO > NO^+ > CN^-$.

If the role of charge is considered it is evident that the bonding ability will be larger for the ligands being stronger Lewis bases and inversely, the order $CN^- > CO > NO^+$ will be valid, which also contradicts the former outcome. The coordination will appear as a result of these and similar factors. Although the σ-donor and π-acceptor properties are playing perhaps the most important roles in determining the coordination effect, other factors may occasionally change the orders calculated on idealistic grounds.

Appendix

The elements of matrix blocks belonging to the orbitals of the bonding centers of the density matrix can be correlated with the actual values of the variables of an ellipsoid. As the sum of squares of the density matrix elements is constant ($\sum_{\mu,\nu} P^2_{\mu\nu} = 2N$, where N is the total number of electrons), this can be regarded as an admissible approximation if, assuming only slight changes in the charge distribution, the σ-proportion of the total charge density can be taken constant as well. After substituting in the

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[a] The observations found in ruthenium complexes containing molecular N_2 ligands [31], that N_2 is a weak Lewis base so that the bond between metal and nitrogen may be attributed mainly to $d-\pi^*$ interactions seems to be inconsistent with our results. Nevertheless, more recent papers [32] come to the conclusion that though both σ-donation and π-back-donation contribute to the formation of the metal–nitrogen bond in N_2-complexes, the former is more important than is the latter.

general equation of the ellipsoid the quadratic terms by the squares of the σ-type diagonal elements, and the products of the variables by those[a] of the corresponding off-diagonal elements, the equation

$$\frac{s^2}{a^2} + \frac{p_x^2}{b^2} \pm sp_x = \text{const.} \qquad (10)$$

can thus be obtained, from which the a and b intersections (virtual semi-axes) can be determined. The 'virtual eccentricities'[b] of the polarization ellipsoid arising in the form of $\frac{b}{a}$ are multiplied (weighted) by $\sum\limits_{\substack{\text{all } \mu \\ \text{on A}}} P^{\sigma}_{\mu\mu}$ to give the $\sigma^{\text{wt.}}_{\text{ecc.}}$ values displayed in Table V.

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[a] The error committed here is small since the magnitudes of these elements are in the interval of 0.4–0.6, so the differences $2P^2_{\mu\nu} - |P_{\mu\nu}|$ are also small and therefore by a suitable choice of the constant in the equation (10) the relative error can be reduced to a minimum.

[b] The 'virtual eccentricity' derived in the reference system from the intersections of the general ellipsoid with the coordinate axes is defined as a formal analogue of the eccentricity of the canonical ellipsoid.