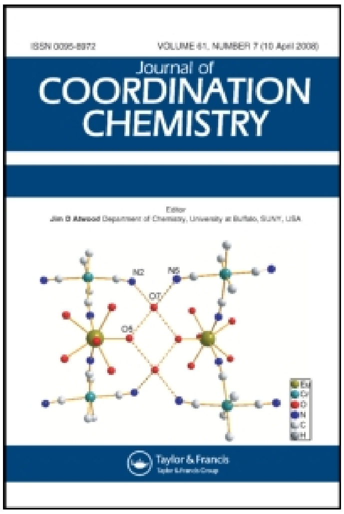

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPARATIVE STUDY OF THE π-ACCEPTOR CHARACTER OF SOME DIATOMIC LIGANDS BASED ON QUANTUM CHEMISTRY

Arnulfo Poveda[a]; Gloria E. Moyano[a]; Mabel A. Caipa[a]
[a] Departamento de Química - Ciencias, Universidad Nacional de Colombia, Santafé de Bogotá, Colombia

To cite this Article Poveda, Arnulfo , Moyano, Gloria E. and Caipa, Mabel A.(2001) 'COMPARATIVE STUDY OF THE π-ACCEPTOR CHARACTER OF SOME DIATOMIC LIGANDS BASED ON QUANTUM CHEMISTRY', Journal of Coordination Chemistry, 54: 3, 415 — 426

To link to this Article: DOI: 10.1080/00958970108022653

URL: http://dx.doi.org/10.1080/00958970108022653

J. Coord. Chem., 2001, Vol. 54, pp. 415–426
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group.

COMPARATIVE STUDY OF THE π-ACCEPTOR CHARACTER OF SOME DIATOMIC LIGANDS BASED ON QUANTUM CHEMISTRY

ARNULFO POVEDA*, GLORIA E. MOYANO
and MABEL A. CAIPA

Departamento de Química – Ciencias, Universidad Nacional de Colombia,
Santafé de Bogotá, Colombia

(Received 28 September 2000; In final form 28 February 2001)

In this paper the π-acceptor character of an isoelectronic series of ligands is analyzed quantitatively using *ab-initio* MO calculations and some criteria of MO theory that are widely known among inorganic chemists. The study describes a numerical scale in which the species can be ordered according to their donor/acceptor character and their chemical stability, as well as the possibility of making predictions about the behavior of hypothetical ligands. The results from MO calculations for ionized ligands can easily model the dynamics of the acceptor/donor character during a chemical process. We also emphasize the quickness of the calculations and the simplicity of the theoretical basis behind the analysis.

Keywords: π acceptor ligands; Diatomic molecules; Isoelectronic series; *Ab-initio* MO calculations

Diatomic species like CN^- and CO are recognized by coordination chemists as π-acceptor ligands because of their behavior in the formation of complexes with transition metals, many other ligands also act as π-acceptors. Hence, for several problems related to the synthesis of complex compounds, it would be desirable to have a quick but quantitative and reliable way to compare the π-acceptor character of a set of ligands.

Quantum chemists have developed accurate methods to calculate electronic structures of molecules, but reaching the theoretical and

---

*Corresponding author. Fax: 571 3165220, e-mail: apovedap@ciencias.ciencias.unal.edu.co computational background necessary to apply these methods to daily problems in chemistry is an obstacle for many experimental chemists. Some of them want to use quantum chemical tools to solve their problems but feel uneasy about giving up their main work in order to have enough time to stay up to date in quantum chemistry. On the other hand, computational chemists are engaged in modeling a wide variety of chemical processes but what they do is not completely followed by experimental chemists, so that, the communication barrier remains. As an illustration of the problem in many contemporary texts of inorganic chemistry (even advanced ones) as well as in communications from coordination compound laboratories, chemists still use the Molecular Orbital (MO) model in a qualitative form [1, 2]. Although quantum chemists are now quickly developing correlation methods which go beyond the MO approximation, a lot of interesting chemical problems are well modeled at the MO level, and today MO calculations are indeed a reachable tool. In the laboratory or the classroom, we only need a personal computer because the software for quantum chemical calculations is available through free packages like GAMESS [3].

What we want to propose in this paper does not represent an advance in quantum chemistry nor in modeling, but a contribution to the integration between theory and experiment in coordination compounds. In this paper we analyze quantitatively the π-acceptor character in a isoelectronic series of ligands, using *ab-initio* MO calculations and applying some criteria of MO theory which are widely known among inorganic chemists. However, we realize that using more recent quantum chemical methodologies like the analysis of the total electron density and its Laplacian [4] provides better and more general results in comparison of donor/acceptor ligands. Such an analysis will be the subject of future work.

ISOELECTRONIC SERIES OF LIGANDS

Several problems related to coordination compounds have been studied by applying methods of computational quantum chemistry. The nature of the bonding to a transition metal is one of the main subjects of those studies [5], but there are other interesting problems like the search for criteria to compare different compounds as ligands. This matter is relevant to syntheses of new stable coordination compounds of mixed ligands, *e.g.*, dinitrogen-metal-ligand complexes, which is the purpose of our study. In a review of about 200 coordination compounds with dinitrogen end-on bonded, we found that nearly 75% were hexacoordinated, with a central metal in low spin d^6 electronic configuration [6]. The characteristics of the nitrogen molecule which lead to such binding are unknown.

Therefore, in this paper we will try first to establish the criteria for the comparison of acceptor/donor character in a set of ligands, by means of the analysis of the electronic structure of such ligands. We chose an isoelectronic series of diatomic ligands, including the dinitrogen species. A large amount of work has been done in quantum chemistry on such diatomic molecules as well as on isoelectronic series [7], but very little analysis of the results has been related to coordination chemistry. Through simple chemical tools such as the orbital energy diagrams, the Koopman's theorem [8] and the HOMO/LUMO densities the following series is examined.

$$C_2^{2-}, CN^-, CO, N_2, NO^+, O_2^{2+}$$

The energy level diagrams for the closed shell states were obtained from a HFSCF calculation, using a 6-31 G (1p, 1d) basis set, made with the PCGAMESS package running under Windows/95.

The results of the calculations follows (Fig. 1):[1] The total nuclear charge of the species increases from 12^+ at the C_2^{2-} to 16^+ at the O_2^{2+}, following the order shown. At the same time, the total number of electrons in each case is constant and equals 14. Based on this information we hypothesize that C_2^{2-} ($14e^-/12^+$) is a bulky, unstable and highly donor ion, while O_2^{2+} ($14e^-/16^+$) is a small and good acceptor ion. This means that the acceptor capability of C_2^{2-} and the donor capability of O_2^{2+} should be almost null. CN^- is more donor than acceptor, or initially donor and then acceptor, so that, at the end it behaves as donor and we refer to it as σ **-donor**-π-acceptor. CO and N_2 are more acceptors than donors, finally acting as acceptors, so we refer to them as π**-acceptors**-σ-donors.

According to the orbital energy diagrams CO and N_2 are similar species, so that, we would expect similar chemical behavior. However N_2 is homonuclear, $D_{\infty h}$, and CO is heteronuclear, $C_{\infty v}$; this means that the electron density is asymmetrical, being more displaced towards the oxygen atom and the carbon atom of CO has an electrophilic (acceptor) character.

---

[1] We will use the SCF-LCAO-MO symbols for the molecular energy levels. These are $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$, $1\pi_g$ and $3\sigma_u$ for the homogeneous dinuclear species. For the dinuclear heterogeneous species the symbols do not have g or u because these entities do not have symmetry center, correspondent symbols are 1σ, 2σ, 3σ, 4σ, 1π, 5σ, 2π and 6σ. But for these discussion we will use the g and u symbols for all species as if it were homonuclear because these symbols give at a look a good idea about how the electron densities are distributed. Another point is that the discussion will be emphasized on the frontier orbitals, that is between the HOMOs $1\pi_u$, $3\sigma_g$ and the LUMOs $1\pi_g$, $3\sigma_u$. In the graphics, the two first σs are not taken into account.

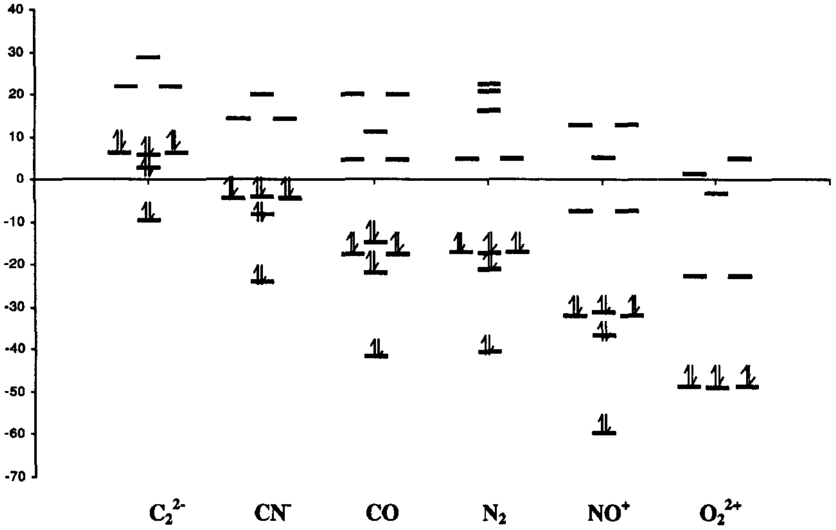

FIGURE 1 Orbital energy diagram in eV.

Compounds of these two acceptor molecules with transition metals would be obtained when the central ion has the proper symmetry to be a π donor and is in a low oxidation state, with high electron density values. Coordination compounds with CN^-, $C_{\infty v}$, which is a donor, would be easily obtained with σ-acceptor ions, which are in intermediate oxidation states. According to the comparative orbital energy diagram, NO^+ would be unstable, although inorganic chemists consider it as a ligand in that form; its behavior will be analyzed later. C_2^{2-} and O_2^{2+} are the extreme cases, they were considered mainly for theoretical interest because they are not known as ligands in the laboratory.

CN^- AS A DONOR, CO AND N_2 AS ACCEPTORS

If CN^- is mainly a σ-donor and CO and N_2 are π-acceptors then, the next question to consider is what happens when either CN^- donates $1e^-$, or CO and N_2 accept $1e^-$? We will try to answer this question with the help of Figure 2.

(a) When CN^- donates $1e^-$, the energy of all levels decreases, $3\sigma_g$ becoming less donor (*i.e.*, lower from the 0.00 level), while the $1\pi_g$ levels become more acceptors (*i.e.*, nearer from the 0.00 level). This should be understood as a dynamic process because as CN^- σ-donates electronic charge ($1e^-$ from $3\sigma_g$ orbital) to the transition ion, this ligand becomes π-acceptor so that, an equilibrium donor-acceptor is reached. However, since CN^- is more donor than acceptor, the electronic charge given to the central ion will be greater than the electronic charge received from the central ion, and CN^- will remain as a donor, depending on the particular central ion as well as the coordination rest [6].

(b) When CO and N_2 accept $1e^-$, (*i.e.*, changing from CO and N_2 to CO^- and N_2^-, respectively) the following is observed

- All the energy levels increase.
- Energy of $3\sigma_g$ HOMO levels rise to almost 0.00 eV.
- The $1\pi_g$ levels become non-degenerate and the energy of the half-occupied one changes from 4.569 in CO to 8.346 eV in CO^-, and from 4.917 in N_2 to 8.572 eV in N_2^-. Hence, these levels became more donor, and the new $1\pi_g$ is better as donor than the $3\sigma_g$ level.

At this point it is important to stress that the system as a whole is dynamic and synergistic, as the ligand is π-accepting, at the same time it is σ-donating to the central ion of a complex compound. In case of CN^-, it will donate more electronic charge than received. The opposite occurs in cases like CO and N_2. In this paper the main discussion is only on the basis of orbital

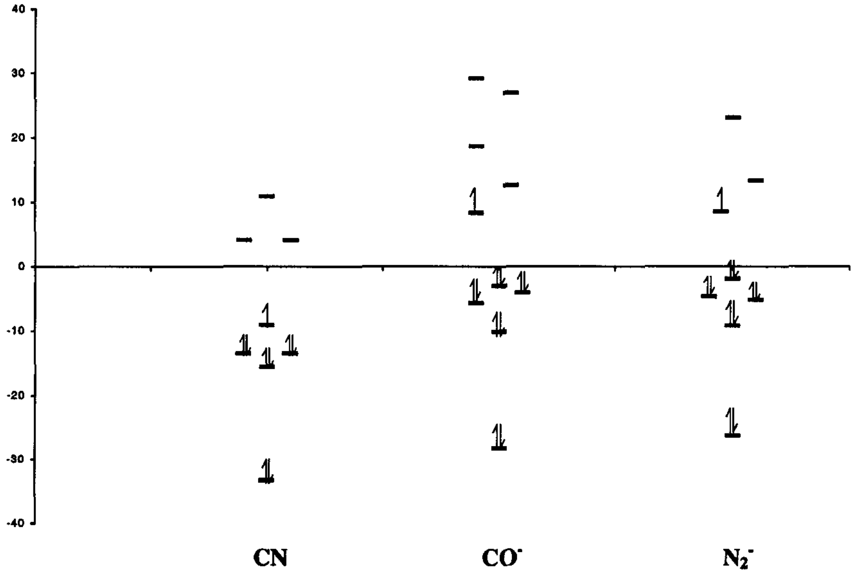

FIGURE 2 CN^- as a donor, CO and N_2 as acceptors.

energy diagrams, but it is necessary to take into account symmetry arguments too. There is evidence, for example, that the main σ-donor orbital from the CN^- is the $2\sigma_u$, which is favored by symmetry and not the $3\sigma_g$ which is favored by energy. This is why the free CN^- vibration is at $2080\,cm^{-1}$ and when it is coordinated the vibration is normally found at higher energy between $2200-2100\,cm^{-1}$.

CN^-, CO AND N_2 SYSTEMS IN THE TRIPLET STATE

It is interesting to consider what happens when these three systems donate a $3\sigma_g$-electron and accept a $1\pi_g$, π^*-electron so the net charge does not change, but multiplicity changes from singlet to triplet. This situation may be similar to the formation of a complex compound (Fig. 3). The $3\sigma_g$ level of CN^- rises to 0.503 eV. The $1\pi_g$ levels become non-degenerate and the energy of the half-occupied orbital decreases to 8.800 eV. The system becomes unstable and will tend to donate electronic charge. In the cases of CO and N_2, the energy of the $3\sigma_g$ level increases, and the $1\pi_g$ becomes non-degenerate and the energy of the half-occupied of $1\pi_g$ decreases. In both

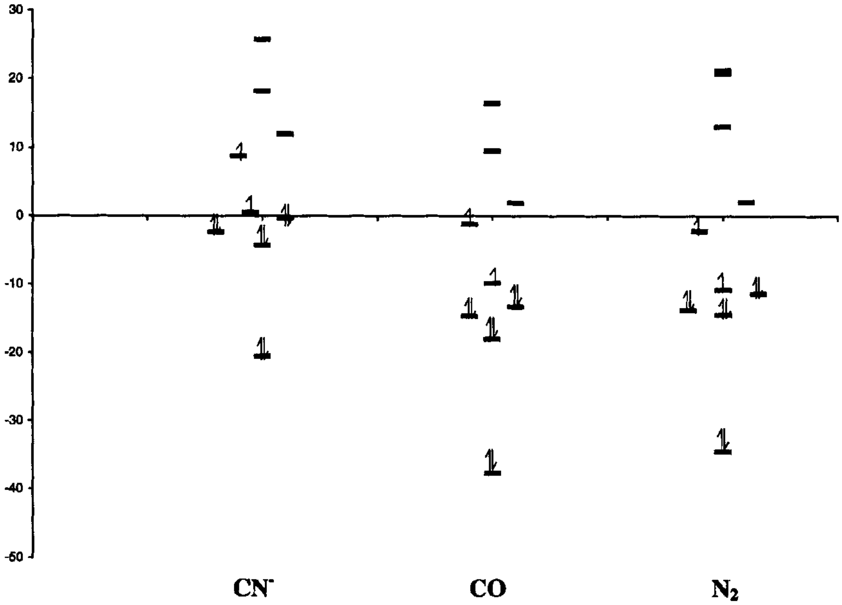

FIGURE 3 CN^-, CO and N_2 systems in the triplet state.

cases the half-occupied $1\pi_g$ levels remain under 0.00 eV. This means that the system obtained is stable.

NO^+, NO AND NO^-; $14e^-$, $15e^-$ AND $16e^-/15^+$

NO^+, which is isoelectronic with the $14e^-$ groups, has the $3\sigma_g$ HOMO at -31.130 eV and the $1\pi_g$ LUMOs at -7.321 eV (Fig. 4). This means that it is a strong acceptor, though it would be unstable in such form, just like O_2^{2+}. After accepting $1e^-$, NO^+ converts into NO which is a stable molecule. NO tends equally to donate and accept electronic charge remaining as a neutral ligand. Then NO^+ would form coordination compounds with transition ions in lower oxidation states. With a highly donor coordination fragment and after coordination, it goes to the neutral stable NO. The NO^- ion would behave as a $1\pi_g$, π^* donor instead of as π^* acceptor, because the energy of the HOMO, $1\pi_g$, is 6.867 eV. However, from a different view, NO^- would be as unstable as NO^+ ion, because the acceptor potential of the last is -7.354 eV (LUMO) while the donor potential of the former is $+6.867$ eV (HOMO). In summary, NO as a ligand is better regarded as NO^0 than NO^+ or NO^- ions.

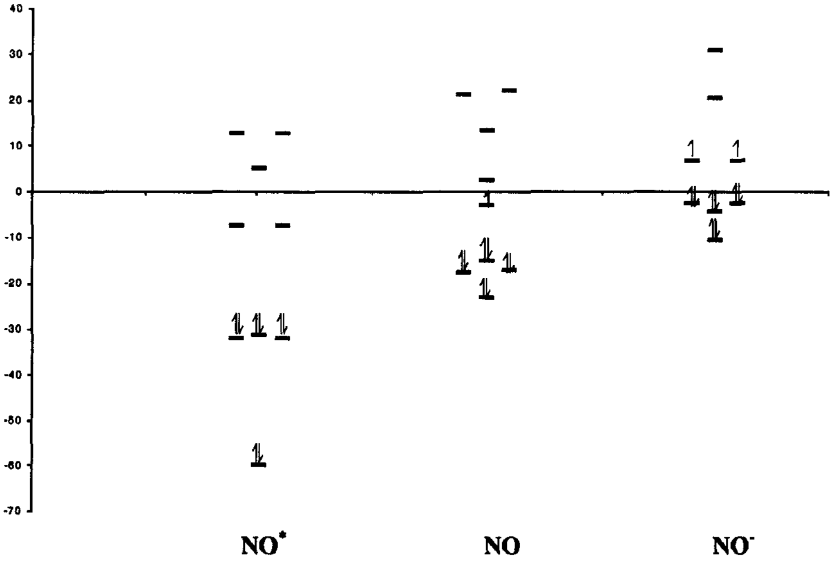

FIGURE 4 Series of NO.

O_2^{2+}, O_2^{+}, O_2, O_2^{-}, O_2^{2-}, $14e^-$, $15e^-$, $16e^-$, $17e^-$ AND $18e^-/16^+$

We will also analyze the energy level diagrams for this series, in which excepting O_2^{2+}, all other species are known in compounds, (Fig. 5). O_2^{2+} has $1\pi_u$ HOMO's at -48.590 eV, hence it is an unstable strong acceptor with an acceptor potential of 22.724 eV. When it accepts an electron and converts into O_2^{+}, the new $1\pi_g$ HOMO increases its energy to -16.700 eV and the $1\pi_g$ LUMO is at -10.600 eV, still an unstable acceptor species. If one more electron is accepted, the well known O_2 in triplet state is obtained. The $1\pi_g$ levels become degenerate, and they are at -5.140 eV, while the LUMO $3\sigma_u$ is at $+12.428$ eV. At first sight, the triplet O_2 seems to be more acceptor than donor because the HOMO's under 0.00 eV are half-occupied and can accept electrons. For the sake of clarity we can examine the energy level diagrams of O_2^{+} and O_2^{-} ions and compare them with the corresponding O_2. When O_2 donates $1e^-$, its HOMO decreases in energy to a value of -16.700 eV. On the other hand, when O_2 accepts $1e^-$ the energy of the HOMO increases to $+5.279$ eV, a value that is nearer the 0.00 eV level than that of the O_2^{+}. Therefore, we conclude that O_2 is a better acceptor than donor and also that O_2^{-} is more stable than O_2^{+}. If O_2^{-} accepts one more electron converting into O_2^{2-}, then the two degenerate

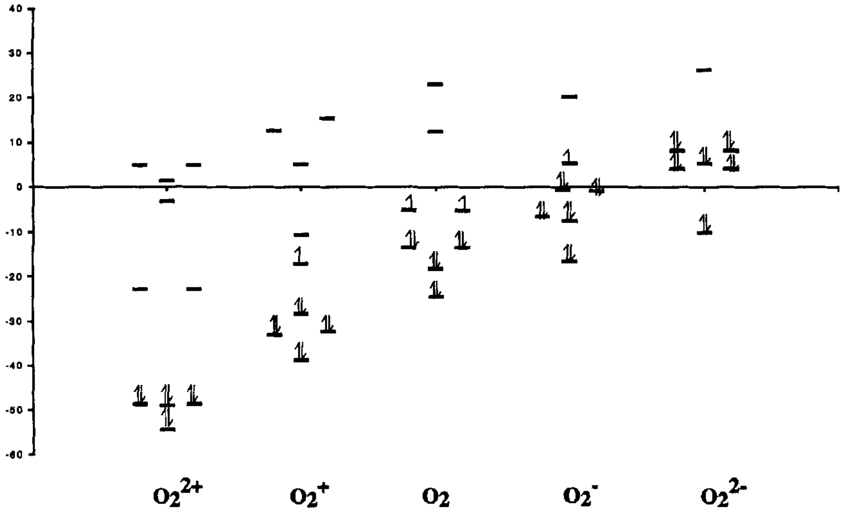

FIGURE 5 Series of oxygen.

$1\pi_g$, at +8.218 eV, become the HOMOs. Hence, O_2^{2-} is unstable and a good donor π^*; although it is more stable than O_2^+ which has its HOMO and LUMO (the possible acceptor) at −16.700 eV and −10.600 eV, respectively.

In this work we have made the simplest "assumptions" in which the ligands gain or lose an integer number of electrons. However, the formation of a coordination compound would be better modeled through the analysis of the electronic density of the reagents and their deformation during the charge transfer. This could be successfully performed with the help of Bader's theory and will be developed in future papers. Nevertheless, even at the simple level of the modeling of the charge transfer process by means of the description of the energy level diagrams of completely ionized species (gaining or losing an electron), we can observe that these are dynamic processes. This means that if the species accepts one electron, then the levels increase their energy, and the opposite occurs when the species donates electrons. Furthermore, if one electron is accepted in a virtual degenerate level, the degeneration is removed and the level splits; the same would happen whenever the degenerate level is occupied in an asymmetrical form. With the help of the energy diagrams we can see that when a ligand accepts electronic charge through $1\pi_g$ this level moves away, *i.e.*, above 0.00 eV, becoming less acceptor; while the $3\sigma_g$ approaches the 0.00 eV level, becoming more donor. So that, in a complex, the ligand should be left in an equilibrium state half-way between π^* acceptor and σ^b donor. According to the diagrams, O_2 and NO are similar, *i.e.*, the two should be π^* acceptors or π^* donors. If they accept one electron converting into O_2^- or NO^- respectively, then they become good donors, in which π^* donation prevails over σ donation. On the other hand, if the two species donate one electron, then O_2^+ and NO^+ become good π^* acceptors, O_2^+ is a better acceptor, *i.e.*, more unstable, than NO^+. This means that NO^+ may behave mainly as a π^* acceptor ligand and not as a σ donor.

HETERONUCLEAR SYSTEMS CN, NO AND CO DERIVED FROM THE HOMONUCLEAR SPECIES C_2, N_2 AND O_2

Figure 6 shows the orbital energy levels for heteronuclear diatomic molecules and their homonuclear diatomic "generating" molecules with the latter species made of the elements of the former. The energy level

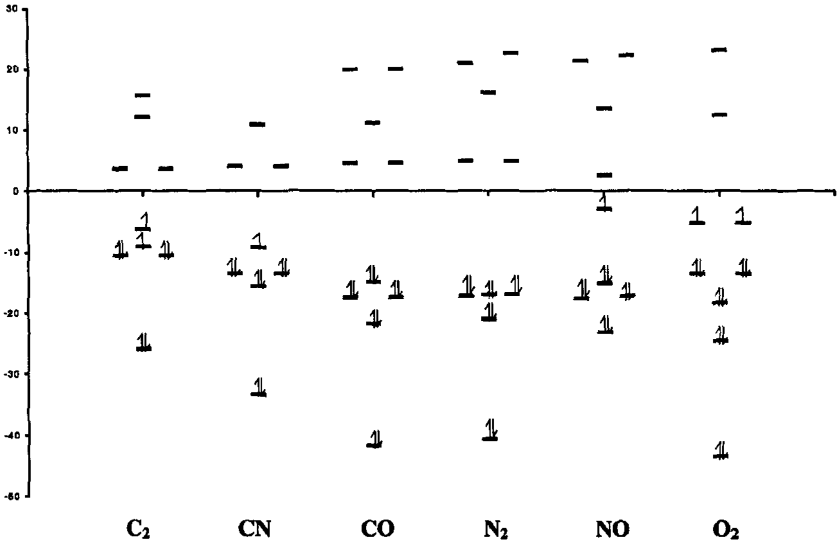

FIGURE 6 CN, NO and CO as derived from C_2, N_2 and O_2.

diagrams help us to analyze how the heteronuclear systems could be formed from the homonuclear ones. In the case of NO from N_2 and O_2, it is summarized in the scheme $N_2+O_2 \rightarrow 2$ NO. When the frontier levels of N_2 convert into the NO ones, the $1\pi_g$, π^* LUMOs of N_2, which are at +4.917 eV, decrease in energy and split into two levels; one, half-occupied, is left at −2.866 eV while the other one remains unoccupied at 2.630 eV. When the $1\pi_g$, π^* levels of NO convert into the ones of O_2, these two orbitals return to the E symmetry and become half-occupied at −5.140 eV. In the "global process" from N_2 to O_2, we observe a decrease in the energy of those $1\pi_g$ orbitals. At the same time, the $3\sigma_g$ and $1\pi_u$ levels, occupied in the three cases, do not change noticeably. Then, we can see that NO is an active species, more similar to O_2 than to N_2 (inert) and it can act either as π^* acceptor or as π^* donor. When we compare CO with O_2 and C_2. C_2 is considered as a $3\sigma_u$, acceptor and O_2 as a $1\pi_g$, π^* acceptor, but CO is much less active and does not resemble any of its generating molecules in behavior as acceptors. CN is a good $3\sigma_g$ acceptor, so it resembles more its generating C_2 molecule, which is also a good $2\sigma_u$ acceptor, although CN is better than C_2 as acceptor. This is in agreement with the fact that we find CN^-. In summary, CO is more stable than its generating molecules, while CN is a more active acceptor, and NO is a more active donor than their generating homonuclear molecules.

CO, CO^+ AND CO^- COMPARED WITH N_2, N_2^+ AND N_2^-

Why are carbonyl complexes more easily obtained than dinitrogen complexes? The purpose of this comparison is to try to find an answer to this question based on the study of the structure of the ligands. Analyzing Figure 7 CO and N_2 behave in a similar way, mainly as $1\pi_g$ acceptors. When they accept one electron and convert into CO^- and N_2^-, the behavior of the new species is similar. However if they donate one electron they convert into CO^+ and N_2^+, N_2^+ is a bit better as an acceptor than CO^+. From this analysis we conclude that the behavior of CO as a ligand is similar to that of N_2, hence, one might be able to synthesize dinitrogen complexes similar to the existent carbonyl ones.

From the complete analysis of the calculations, we deduce that N_2 and CO should behave similarly as ligands, and different than CN^-. In order to obtain metal complexes, central ions with high electron density are required, *i.e.*, metal ions in lower oxidation states with auxiliary ligands enriching the negative charge.

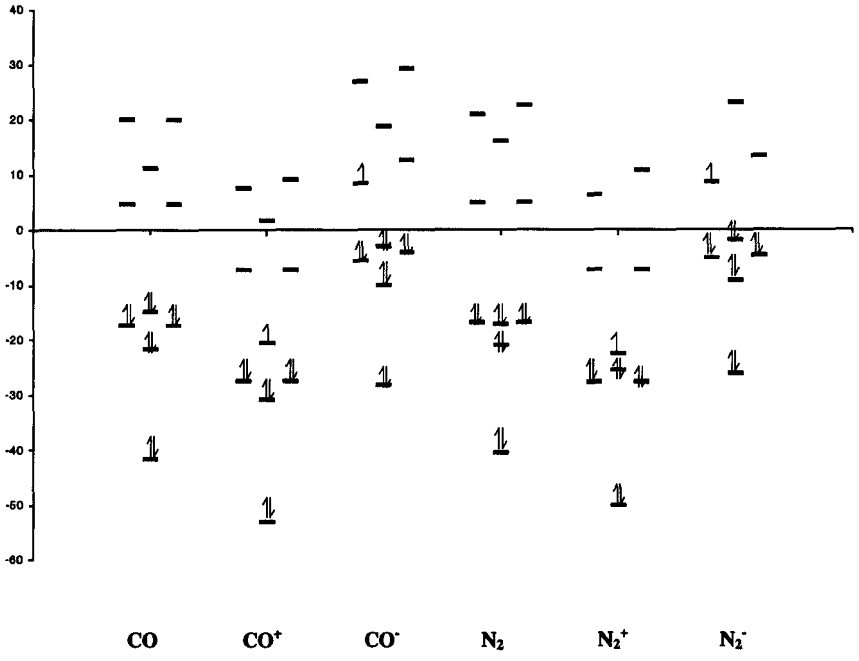

FIGURE 7 Series of CO compared with series of N_2.

Acknowledgements

This work was possible thanks to a contribution between Theoretical and Coordination Compounds groups from the Chemistry Department at the Universidad Nacional de Colombia.

References

[1] J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity* (Collins College Publishers, New York, 1993).

[2] E. Ochiai, *J. Chem Educ.* **73**, 130 (1996).

[3] M. Schmidt, K. Baldridge, J. Boatz, S. Elbert, M. Gordon, J. Jensen, S. Koseki, N. Matsunaga, K. Nguyen, S. Su, T. Windus, M. Dupuis and J. Montgomery, *J. Comp. Chem.* **14**, 1347–1363 (1993).

[4] R. Bader, *Atoms in Molecules* (Clarendon Press, Oxford, 1990).

[5] See *e.g.*, G. Frenking and U. Pidun, *J. Chem. Soc., Dalton Trans.* pp. 1653–1662 (1997) and references cited therein.

[6] A. Poveda, I. C. Perilla and C. R. Pérez, *J. Coord. Chem.*, This issue.

[7] See *e.g.*, A. Szabo and N. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (MacMillan, New York, 1964).

[8] See *e.g.*, G. Berthier, The Three Theorems of the Hartree Fock Theory and Their Extensions, In: *Quantum Chemistry – Basic Aspects, Actual Trends, Proceedings of the International Workshop on Quantum Chemistry*, Girona, Spain, 13–18 June, 1988, R. Carbó (Ed.) Elsevier series Vol. 62 (1989).