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Electronic Structure of Tetrahedral Carbonyls and Dinitrogen Complexes of Nickel, Cobalt, and Iron as Calculated by the Multiple-Scattering Method

Manuel Braga,*[1a] Sven Larsson,[1b] and José R. Leite[1a]

Contribution from the Instituto de Física, Universidade de São Paulo,
Caixa Postal 20516, São Paulo, Brazil, and the Department of Quantum Chemistry,
Uppsala University, Box 518, S-751 20 Uppsala, Sweden.
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Abstract: A comparative study of the isoelectronic complexes $Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$, $Ni(N_2)_4$, $Co(N_2)_4^-$, and $Fe(N_2)_4^{2-}$ is made by the multiple scattering Xα method. The results show clearly a back-donation which increases in the series Ni, Co, Fe in good correlation with the decrease of the N_2 and CO stretching frequencies. The back-donation is of about the same magnitude for the carbonyl and dinitrogen complexes for a given metal. The larger stability of the carbonyls is ascribed to a stronger bonding via 4s and 4p orbitals.

I. Introduction

The nature of the chemical bond in metal carbonyls is subject to much interest in inorganic and theoretical chemistry.[2-3] Quite recently there has been a great interest also in N_2-transition metal complexes.[2] One obvious reason in the latter case is to obtain a deeper understanding of the role of transition-metal atoms in biological and industrial nitrogen fixation processes. In general, a detailed study of the interaction between CO or N_2 and transition-metal atoms is fundamental to the understanding of the bonding not only in numerous organometallic complexes but also in absorption of N_2 and CO on metal surfaces.

There have been a number of theoretical studies on $Ni(CO)_4$ and $Ni(N_2)_4$, by semiempirical,[4-7] multiple scattering,[8] LCAO-Xα,[9] pseudopotential,[10] and ab initio methods.[11-15] The isoelectronic complexes $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ have been studied by semiempirical methods[5] and approximate ab initio methods.[11] The conclusions regarding different bonding mechanisms are at some variance. The back-bonding mechanisms seems to be favored in ab initio and LCAO-Xα calculations[9,11-15] but usually the 4s bonding is considered to be small. The opposite seems to be the case in multiple scattering calculations.[8] The differences between the two methods may well be due to different means of interpreting the calculated molecular wave functions, however. It can be shown that back-bonding and back-donation occurs also in multiple scattering wave functions for $Ni(CO)_4$[16] as well as cyanides.[17]

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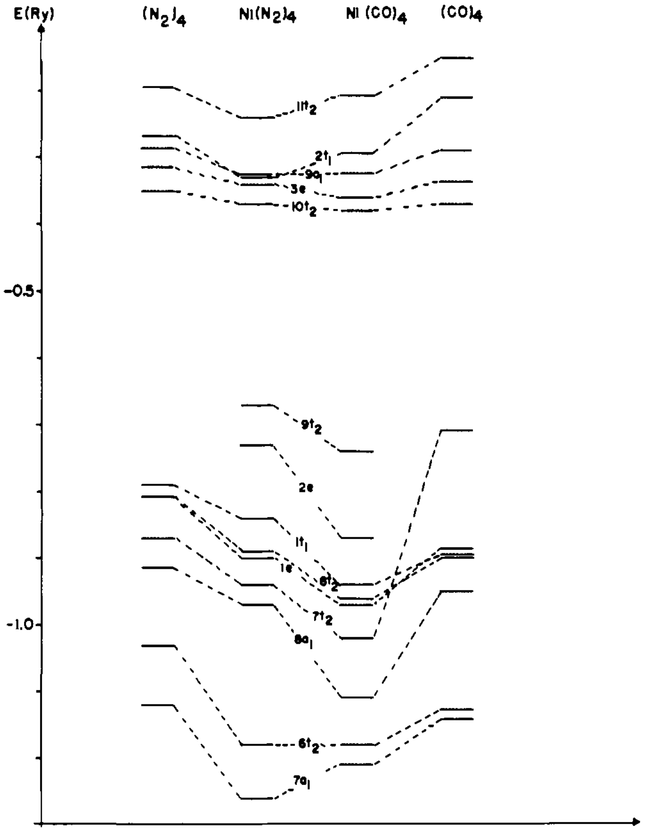

Figure 1. Orbital energy levels for the $(N_2)_4$, $Ni(N_2)_4$, $Ni(CO)_4$, and $(CO)_4$ complexes.

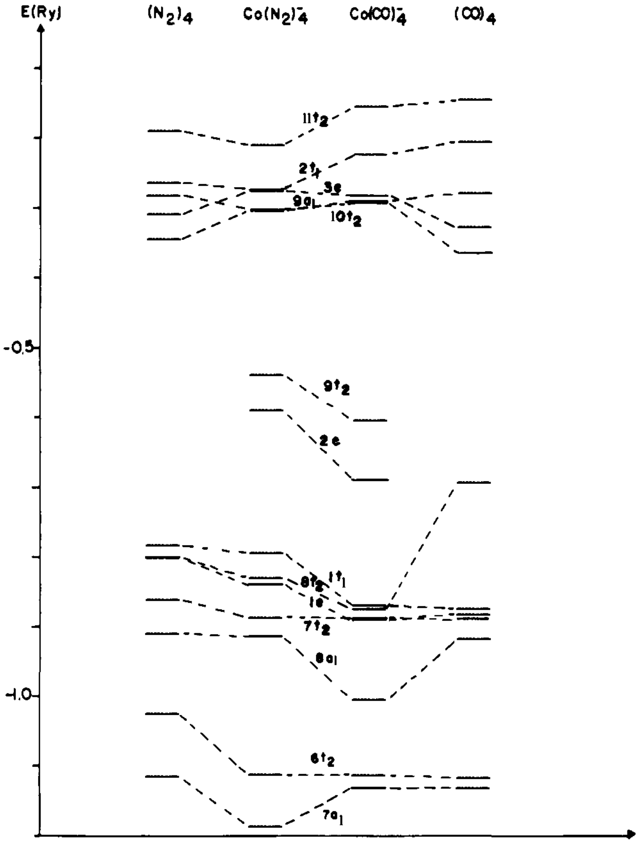

Figure 2. Orbital energy levels for the $(N_2)_4$, $Co(N_2)_4^-$, $Co(CO)_4^-$, and $(CO)_4$ complexes.

In the present work we have carried out multiple-scattering (MS) calculations on the isoelectronic tetrahedral complexes $Ni(N_2)_4$, $Ni(CO)_4$, $Co(N_2)_4^-$, $Co(CO)_4^-$, $Fe(N_2)_4^{2-}$, and $Fe(CO)_4^{2-}$. The muffin-tin approximation which often may cause large errors in the MS method may be expected to be less serious for complexes of cubic symmetry. The means of interpreting the results will be different from what has been used previously. Our main interest will be the wave function for the ground state and what it reveals in terms of bonding effects. We will also make a comparison with various experimental data.

II. Computational Method

The MS method is used in its muffin-tin form with local Slater exchange ($\alpha = 0.72$).[18] As in ref 15 we used $R_{C-O} = 2.135$ au, $R_{Ni-C} = R_{Ni-N} = 3.44$ au, $R_{N-N} = 2.074$ au. The Co-C and Fe-C distance were taken from ref 5. In the case of $Ni(N_2)_4$ and the other dinitrogen complexes the radii of the atomic spheres will be uniquely determined by requiring the spheres to be tangent. In the case of carbonyls we made one calculation with the same radii as for the dinitrogen compound and one where the oxygen radius was increased somewhat to get the proper C-O distance. All the calculations are carried to self-consistency for all orbitals, which means that we are including 84 electrons (core + valence) in each SCF cycle. The MS method has been described in detail in other papers[18] and will not be discussed here in any detail. As is very well-known, its chief advantage is that the wave functions are numerically calculated whereby the use of basis set is avoided. In each muffin-tin sphere α the orbitals are given as

$$\phi(r) = \sum_{l,m} C^{(\alpha)}{}_{lm} R_l(r) Y_{lm}(\theta,\phi) \qquad (1)$$

where the functions Y_{lm} are the usual spherical harmonic functions. In the Ni (Co or Fe) and outer region we are using $l = 2$ for orbitals of t_2 and e symmetry, $l = 0$ for a_1, and $l = 3$ for t_1. In the ligand spheres we are using $l = 0$ and 1. In the interatomic region one expands the wave function in terms of spherical Bessel and Hankel functions. The eigenvalues are determined by the condition that the orbitals and their derivatives should be continuous across the sphere boundaries.[18]

For comparison purpose calculations were carried out also for the clusters $(N_2)_4$ and $(CO)_4$ with atoms at the same coordinates as in corresponding complexes (cf. ref 19). An empty central sphere with the same angular basis functions as in the nickel (Co or Fe) sphere is used.

For the Co and Fe complexes we have stabilized the complexes by uniformly charged spheres (Watson spheres), having the charges 1+ and 2+, respectively.

III. Orbitals and Orbital Energies

The calculated molecular orbital (MO) energies are given in Figures 1-3. For $Ni(CO)_4$ they are in agreement with those of ref 13. For simplicity we use the same orbital numbering for $(N_2)_4$ and $(CO)_4$ as for the nickel (Co or Fe) complexes. The σ orbitals of N_2 and CO are distributed on the a_1 and t_2 representations, and the π orbitals on e, t_1, and t_2. σ and π may mix in t_2 but do not do so to any large extent except for the highest t_2 orbitals (see below). The orbital characters of the t_2 orbital (σ or π) are determined by inspection of the coefficients in eq 1. The orbital characters are given in Tables I-VI. In disagreement with ref 8 we find that the orbital $8t_2$ in $Ni(CO)_4$ is almost entirely a CO 1π orbital (cf. ref 13).

In the $(N_2)_4$ complex $5t_2$ and $6a_1$ (not in diagram) correspond to N_2 $2\sigma_g$ (2s + 2s), $6t_2$ and $7a_1$ to N_2 $2\sigma_u$ (2s − 2s), $8a_1$ and $7t_2$ to N_2 $3\sigma_g$, and finally 1e, $8t_2$, and $1t_1$ to π_u. In the tetrahedral array of N_2 all a_1 levels may be regarded as bonding and e, t_1, and t_2 antibonding in the central region since the latter have nodes in the central region. Hence $7a_1$ falls below $6t_2$ and $8a_1$ below $7t_2$.

Table I. Orbital Energies and Orbital Characters for $Ni(N_2)_4$[a]

orbital	orbital energy, −Ry	charges in muffin-tin spheres: Ni	N1	N2	inter-atomic	outer sphere	orbital character
$5a_1$	7.89	1.0	0.0	0.0	0.0	0.0	Ni 3s
$6a_1$	1.88	0.0	0.30	0.28	0.41	0.0	N_2 $2\sigma_g$
$7a_1$	1.26	0.23	0.30	0.08	0.40	0.0	Ni 4s, N_2 $2\sigma_u$
$8a_1$	0.97	0.03	0.08	0.43	0.44	0.02	N_2 $3\sigma_g$
$4t_2$	5.19	1.0	0.0	0.0	0.0	0.0	Ni 3p
$5t_2$	1.87	0.0	0.30	0.29	0.41	0.0	N_2 $2\sigma_g$
$6t_2$	1.18	0.22	0.34	0.09	0.34	0.01	Ni 3d, 4p, N_2 $2\sigma_u$
$7t_2$	0.94	0.06	0.09	0.43	0.37	0.05	N_2 $3\sigma_g$
$8t_2$	0.89	0.08	0.24	0.18	0.48	0.01	N_2 $1\pi_u$
$9t_2$	0.67	0.67	0.05	0.10	0.18	0.0	Ni 3d, 4p N_2 $1\pi_u$, $1\pi_g$
$10t_2$	0.37	0.11	0.17	0.24	0.46	0.01	Ni 3d, N_2 $1\pi_g$
1e	0.90	0.23	0.22	0.14	0.41	0.01	Ni 3d, N_2 $1\pi_u$
2e	0.73	0.68	0.03	0.12	0.16	0.0	Ni 3d, N_2 $1\pi_u$, $1\pi_g$
3e	0.34	0.08	0.24	0.27	0.42	0.0	Ni 3d, N_2 $1\pi_g$
$1t_1$	0.84	0.0	0.26	0.25	0.47	0.01	N_2 $1\pi_u$

[a] N1 is the nitrogen sphere closest to Ni.

In $Ni(N_2)_4$ all levels are lowered compared to $(N_2)_4$. The new levels 2e and $9t_2$ have mainly Ni 3d character. The largest lowering occurs for the orbitals which have $2\sigma_u$ character ($7a_1$ and $6t_2$). All e and t_2 levels have some Ni 3d character. The admixture with the N_2 $3\sigma_g$ level will be discussed below.

The level structure in $(CO)_4$ is somewhat different from that of $(N_2)_4$. $7a_1$ and $6t_2$ are mainly localized on oxygen. The π orbital is less split than for N_2 since it is also mainly localized on oxygen. The highest σ orbital is mainly localized on carbon and split by 3 eV in $8a_1$ and $7t_2$.

In $Ni(CO)_4$ $8a_1$ and $7t_2$ are both considerably lowered in energy owing to interaction with 4s and 3d, respectively. Large 3d components appear in both $7t_2$ and $9t_2$. The orbital energy of $9t_2$ is lower than that of $7t_2$ in $(CO)_4$, although it is expected to have some antibonding character. One reason for this is the additional interaction with the unoccupied π^* level on CO.

In the Co and Fe complexes the orbital structure is roughly similar (Tables III–VI). One may notice that the HOMO-LUMO gap is decreasing in the series Ni > Co > Fe. The first absorption band should be in the visible spectrum, at least for $Fe(N_2)_4^{2-}$

IV. Bonding

In order to interpret our results we have to reexamine existing theories for bonding in carbonyls. In general, three bonding mechanisms are considered: σ bonding between 3d and ligand σ orbitals, π back-bonding between the 3d and the empty π^* orbital on N_2 or CO,[2,20] and bonding via 4s or 4p orbitals on metal. The analyses of ab initio wave functions[11-15] have been based on the Mulliken population analysis, which is based on the weights of the different nonorthogonal basis functions.[21] The Mulliken populations for this reason behave somewhat erratically. Almost identical wave functions obtained with different basis sets may yield widely different populations. Particularly for transition-metal compounds with a localized 3d but extended 4s and 4p orbitals the Mulliken method may be expected to be particularly unreliable. When a high-energy, diffuse orbital (like the metal 4s, 4p) is interacting with a low-energy, contracted orbital (like the ligand 2s levels) we may have a "counterintuitive orbital mixing" effect[22] which operates to reduce the Mulliken overlap populations, even making them negative; it also may result in negative gross atomic populations. From the most accurate ab initio wave function for $Ni(CO)_4$ obtained by Demyunck and Veillard[13] the 4s population is very small or even negative, which is at variance with the MS result of Johnson and Wahlgren.[8] Our calculations confirm the latter results as regards 4s bonding (see below) but not regarding 3d bonding. Johnson and Wahlgren also stated that the stability of $Ni(CO)_4$ is partly due to $7t_2$, which is a bonding orbital,[8] but apparently disregarded the fact that corresponding antibonding orbitals are also occupied. The back-donation is indeed evident in the MS-Xα wave function as will be further discussed below (see also ref 16).

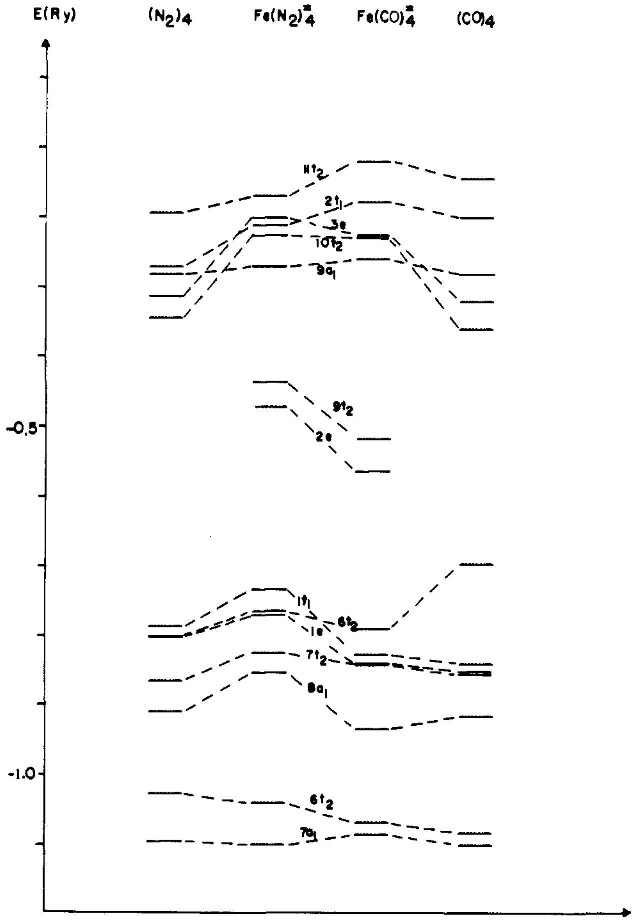

Figure 3. Orbital energy levels for the $(N_2)_4$, $Fe(N_2)_4^{2-}$, $Fe(CO)_4^{2-}$, and $(CO)_4$ complexes.

In tetrahedral complexes we have the additional complication that σ and π orbitals are mixing in the irreducible repre-

Table II. Orbital Energies and Orbital Characters for $Ni(CO)_4$

orbital	orbital energy, −Ry	charges in muffin-tin spheres: Ni	C	O	inter-atomic	outer sphere	orbital character
$5a_1$	8.01	1.0	0.0	0.0	0.0	0.0	Ni 3s
$6a_1$	2.11	0.0	0.09	0.56	0.35	0.0	CO 3σ
$7a_1$	1.21	0.07	0.13	0.39	0.41	0.01	CO 4σ
$8a_1$	1.11	0.31	0.18	0.14	0.38	0.0	Ni 4s, CO 5σ
$4t_2$	5.31	1.0	0.0	0.0	0.0	0.0	Ni 3p
$5t_2$	2.11	0.0	0.09	0.56	0.34	0.0	CO 3σ
$6t_2$	1.18	0.01	0.12	0.51	0.34	0.02	CO 4σ
$7t_2$	1.02	0.61	0.16	0.02	0.21	0.0	Ni 3d, CO 5σ
$8t_2$	0.96	0.02	0.08	0.44	0.45	0.0	CO 1π
$9t_2$	0.74	0.45	0.11	0.08	0.35	0.0	Ni 3d, CO 5σ, CO 1π, 2π
$10t_2$	0.38	0.13	0.17	0.08	0.57	0.04	Ni 3d, CO 2π
1e	0.97	0.24	0.08	0.31	0.37	0.0	Ni 3d, CO 1π
2e	0.87	0.67	0.0	0.19	0.14	0.0	Ni 3d, CO 1π, 2π
3e	0.36	0.08	0.20	0.12	0.57	0.02	Ni 3d, CO 2π
$1t_1$	0.94	0.0	0.07	0.51	0.42	0.01	CO 1π

Table III. Orbital Energies and Orbital Characters for $Co(N_2)_4^-$

orbital	orbital energy, −Ry	charges in muffin-tin spheres: Co	N1	N2	inter-atomic	outer sphere	orbital character
$5a_1$	7.27	1.0	0.0	0.0	0.0	0.0	Co 3s
$6a_1$	1.82	0.01	0.30	0.28	0.41	0.0	N_2 $2\sigma_g$
$7a_1$	1.19	0.21	0.30	0.08	0.40	0.0	Co 4s, N_2 $2\sigma_u$
$8a_1$	0.91	0.03	0.09	0.43	0.44	0.02	N_2 $3\sigma_g$
$4t_2$	4.71	1.0	0.0	0.0	0.0	0.0	Co 3p
$5t_2$	1.82	0.0	0.30	0.29	0.41	0.0	N_2 $2\sigma_g$
$6t_2$	1.11	0.19	0.34	0.10	0.36	0.01	Co 3d, 4p, N_2 $2\sigma_u$
$7t_2$	0.89	0.05	0.11	0.42	0.38	0.05	N_2 $3\sigma_g$
$8t_2$	0.83	0.05	0.25	0.19	0.50	0.01	N_2 $1\pi_u$
$9t_2$	0.54	0.64	0.02	0.11	0.23	0.0	Co 3d, 4p N_2 $1\pi_u$, $1\pi_g$
$10t_2$	0.30	0.21	0.15	0.19	0.42	0.02	Co 3d, N_2 $1\pi_g$
1e	0.84	0.11	0.25	0.18	0.46	0.01	Co 3d, N_2 $1\pi_u$
2e	0.59	0.75	0.0	0.11	0.14	0.0	Co 3d, N_2 $1\pi_u$, $1\pi_g$
3e	0.26	0.13	0.23	0.25	0.40	0.0	Co 3d, N_2 $1\pi_g$
$1t_1$	0.79	0.0	0.26	0.25	0.47	0.01	N_2 $1\pi_u$

Table IV. Orbital Energies and Orbital Characters for $Co(CO)_4^-$

orbital	orbital energy, −Ry	charges in muffin-tin spheres: Co	C	O	inter-atomic	outer sphere	orbital character
$5a_1$	7.28	1.0	0.0	0.0	0.0	0.0	Co 3s
$6a_1$	2.04	0.0	0.09	0.56	0.35	0.0	CO 3σ
$7a_1$	1.13	0.03	0.12	0.45	0.39	0.01	CO 4σ
$8a_1$	1.01	0.32	0.18	0.08	0.42	0.0	Co 4s, CO 5σ
$4t_2$	4.75	1.0	0.0	0.0	0.0	0.0	Co 3p
$5t_2$	2.04	0.0	0.09	0.56	0.34	0.01	CO 3σ
$6t_2$	1.11	0.0	0.12	0.51	0.34	0.02	CO 4σ
$7t_2$	0.89	0.01	0.08	0.45	0.45	0.01	CO 1π
$8t_2$	0.88	0.48	0.21	0.02	0.29	0.0	Co 3d, CO 5σ
$9t_2$	0.61	0.49	0.06	0.08	0.37	0.0	Co 3d, CO 5σ CO 1π, 2π
$10t_2$	0.29	0.21	0.13	0.06	0.54	0.07	Co 3d, CO 2π
1e	0.89	0.05	0.08	0.44	0.43	0.01	Co 3d, CO 1π
2e	0.69	0.81	0.01	0.07	0.12	0.0	Co 3d, CO 1π, 2π
3e	0.28	0.13	0.16	0.10	0.57	0.04	Co 3d, CO 2π
$1t_1$	0.87	0.0	0.07	0.51	0.42	0.01	CO 1π

sentation t_2. This means that there may be interaction between the σ lone pair of each CO or N_2 and the empty π^* orbitals. It has been suggested[23] that the role of the metal ion is partly to "short-circuit" carbonyl (or dinitrogen) orbitals from different CO (or N_2) groups. The importance of this bonding mechanism is under discussion[3] and several arguments are against this mechanism. As we will see below some short-circuiting does occur but not to any large extent.

σ Donation to the 3d Subshell. σ donation takes place when the σ-antibonding MO on the transition metal ion is unoccu-

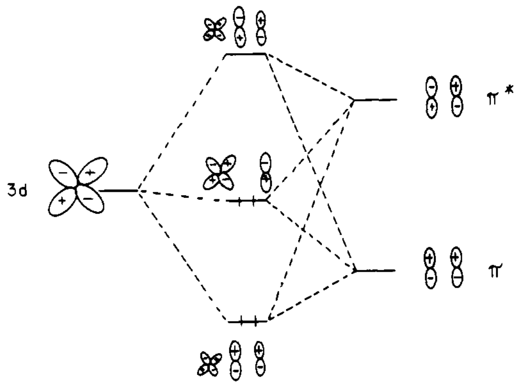

Figure 4. Interaction between N_2 π and π^* orbitals and 3d orbital for illustration of the principles of back-bonding.

pied. The amount of donated charge is equivalent to the amount of 3d charge in the corresponding bonding orbitals. It is intuitively clear that the total amount of 3d character in one bonding-antibonding pair of orbitals is equivalent to one 3d electron and this has also been found in a number of MS calculations on simple complexes.[24] In our case, corresponding to d^{10}, all antibonding levels on metal are occupied, and there is no σ donation to the 3d orbitals relative to the $3d^{10}$ atomic metal. The tetrahedral d^{10} complexes are hence different in this respect from the $Cr(CO)_6$ complex (cf. ref 19), which has empty σ 3d orbitals.

σ donation to the 4s and 4p orbitals will be discussed below.

Back-Donation and the Structure of t_2 and e Orbitals. Although no σ donation occurs, we may refer to the donation of charge from metal to the ligand π^* orbital as back-donation. Such a back-donation is necessary for the stability of the complex and is schematically shown in Figure 4 for a linear case. By mixing the occupied orbitals with the π^* level we are decreasing the Me-N antibonding character of the highest occupied MO of the complex. At the same time we are occupying part of the N-N antibonding π^*. The Me-N bond is thus strengthened and the N-N π bond weakened. The 3d charge component in the unoccupied orbitals should be roughly equal to the π^* charge components in the occupied orbitals, and thus defines the back-donated charge.

Our results follow rather well the simple scheme in Figure 4 regarding the e orbitals. The 1e orbital has a larger N 2p occupancy on the N next to Me (ratio 3:2 for the 2p occupancies of the two N atoms). In 2e the 2p occupancy on the nearest N is rather small in agreement with Figure 4 (about 25% of the occupancy on the outer N). In the unoccupied 3e level the occupancies are about the same on the two nitrogen centers. These results compare well with MS results on $Cr(CO)_6$.[19] In Figures 5 and 6 we have plotted the total radial charge distribution corresponding to $l = 2$ in the nickel sphere for occupied t_2 and e orbitals, respectively, in $Ni(N_2)_4$ (but not multiplying by the degeneracy). Similar plots are obtained for $Ni(CO)_4$ and the Co and Fe complexes. In Figures 5 and 6 we have also drawn the distribution curve summed for all t_2 and e orbitals, respectively (i.e., including 3e and $10t_2$). From Table I, it is observed that the 3d character is distributed on the orbitals $6t_2$–$10t_2$ and 1e–3e. One may then sum up the radial charges distributions for all the orbitals of a certain symmetry type (say $t_2\,xz$) and compare it to the radial charge distribution of a xz orbital in a free Ni^+ ($3d^9$ 4s configuration) or Ni^{+2} ($3d^8$) ion. It is then found that the sum of radial charge distributions for a given symmetry including the unoccupied orbital is in between the charge distributions for a 3d orbital in Ni^+ and Ni^{2+} in an $X\alpha$ calculation with $\alpha = 0.72$. This may be interpreted to mean that the d electrons in the molecule experience a shielding comparable with the shielding in a free ion with eight or nine 3d electrons. A measure of the back-donated charge is obtained by simply taking from the figures the ratio of 3d charge in the unoccupied level (shaded area) to the total 3d charge in all the molecular orbitals of t_2 and e symmetry. In the t_2 case part of the missing 3d charge is donated to 4p and this effect is larger for the carbonyl complex. As is seen in Tables I and II the total charge in the nickel region is larger for the carbonyl complex.

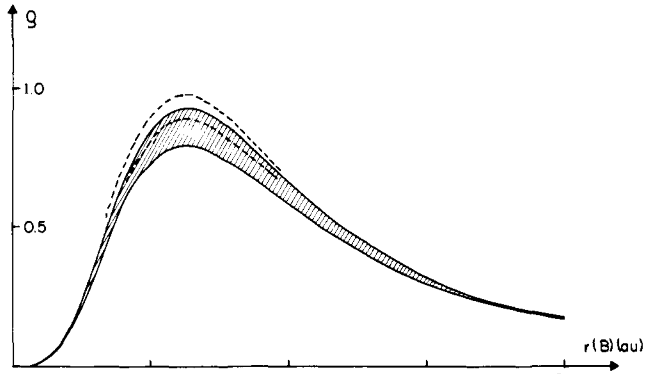

Figure 5. The upper full-drawn curve shows the sum of the radial density distributions $\chi(r) = (r\phi(r))^2$ in the Ni sphere for the orbitals $6t_2$–$10t_2$ for $Ni(N_2)_4$. The lower curve shows the same function but including only the occupied orbitals $6t_2$–$9t_2$. The dashed area represents the back-donated charge. The upper dashed curve shows the radial density distribution in an atomic Ni 3d orbital for the configuration $3d^8$ (Ni^{2+}). The lower dashed curve shows the same function but for the configuration $3d^9$ (Ni^+).

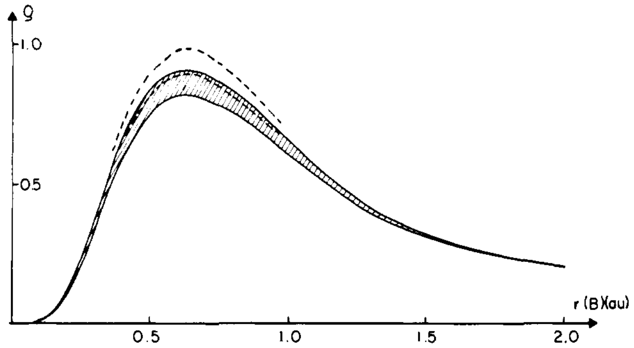

Figure 6. The same information as in Figure 5 but for the orbitals 1e–3e (the upper full-drawn curve) and 1e–2e (the lower full-drawn curve) for $Ni(N_2)_4$.

One may get a reasonable measure of the 3d population by calculating how large a proportion of charge is in the occupied orbitals (of t_2 and e symmetry) compared to the total charge including the unoccupied orbitals ($10t_2$ and 3e, respectively). Integrating the lower maxima and normalizing with respect to the higher maxima in Figures 5 and 6 and multiplying by the corresponding degeneracies we find 8.47 3d electrons in $Ni(CO)_4$ and 8.82 in $Ni(N_2)_4$. These numbers are in good agreement with the ab initio results of Jansen et al., who found 8.46 and 8.69, respectively.[14,15] In a similar way we get the corresponding 3d occupancies for the Co and Fe. The back-donation is considerably increased as we go to the Co and particularly the Fe complex (Table VII). Somewhat surprisingly we find similar amounts of back-donation for carbonyls and dinitrogen complexes.

The structure of the t_2 orbitals is complicated because of the σ–π mixing. In $Ni(CO)_4$ and all the dinitrogen complexes $5t_2$, $6t_2$, and $7t_2$ are σ orbitals with a very little π admixture. $8t_2$ is a π orbital with a very little σ admixture, contrary to what is stated in ref 8 (cf. ref 13). The 3d component in $8t_2$ is remarkably small. $9t_2$ should be σ antibonding to $6t_2$ for the di-

Table V. Orbital Energies and Orbital Characters for $Fe(N_2)_4^{2-}$

orbital	orbital energy, −Ry	charges in muffin-tin spheres Fe	N1	N2	inter-atomic	outer sphere	orbital character
$5a_1$	6.63	1.0	0.0	0.0	0.0	0.0	Fe 3s
$6a_1$	1.76	0.01	0.30	0.28	0.41	0.0	$N_2\ 2\sigma_g$
$7a_1$	1.10	0.20	0.30	0.09	0.41	0.0	Fe 4s, $N_2\ 2\sigma_u$
$8a_1$	0.85	0.03	0.09	0.41	0.44	0.02	$N_2\ 3\sigma_g$
$4t_2$	4.24	1.0	0.0	0.0	0.0	0.0	Fe 3p
$5t_2$	1.76	0.0	0.30	0.29	0.41	0.0	$N_2\ 2\sigma_g$
$6t_2$	1.04	0.17	0.34	0.11	0.37	0.01	Fe 3d, 4p, $N_2\ 2\sigma_u$
$7t_2$	0.82	0.05	0.12	0.41	0.38	0.05	$N_2\ 3\sigma_g$
$8t_2$	0.77	0.04	0.25	0.20	0.50	0.01	$N_2\ 1\pi_u$
$9t_2$	0.44	0.56	0.01	0.12	0.30	0.0	Fe 3d, 4p $N_2\ 1\pi_u$, $1\pi_g$
$10t_2$	0.23	0.31	0.11	0.13	0.40	0.01	Fe 3d, $N_2\ 1\pi_g$
1e	0.77	0.07	0.25	0.19	0.48	0.01	Fe 3d, $N_2\ 1\pi_u$
2e	0.47	0.72	0.0	0.11	0.17	0.0	Fe 3d, $N_2\ 1\pi_u$, $1\pi_g$
3e	0.20	0.19	0.22	0.22	0.37	0.0	Fe 3d, $N_2\ 1\pi_g$
$1t_1$	0.73	0.0	0.26	0.25	0.48	0.01	$N_2\ 1\pi_u$

Table VI. Orbital Energies and Orbital Characters for $Fe(CO)_4^{2-}$

orbital	orbital energy, −Ry	charges in muffin-tin spheres Fe	C	O	inter-atomic	outer sphere	orbital character
$5a_1$	6.71	1.0	0.0	0.0	0.0	0.0	Fe 3s
$6a_1$	2.00	0.0	0.09	0.56	0.35	0.0	CO 3σ
$7a_1$	1.08	0.02	0.12	0.47	0.39	0.01	CO 4σ
$8a_1$	0.93	0.32	0.18	0.06	0.43	0.0	Fe 4s, CO 5σ
$4t_2$	4.31	1.0	0.0	0.0	0.0	0.0	Fe 3p
$5t_2$	2.00	0.0	0.09	0.56	0.34	0.01	CO 3σ
$6t_2$	1.07	0.0	0.12	0.51	0.34	0.02	CO 4σ
$7t_2$	0.84	0.01	0.07	0.46	0.45	0.01	CO 1π
$8t_2$	0.79	0.39	0.24	0.03	0.34	0.0	Fe 3d, 4p, CO 5σ
$9t_2$	0.52	0.47	0.04	0.07	0.41	0.01	Fe 3s, CO 5σ CO 1π, 2π
$10t_2$	0.23	0.27	0.08	0.04	0.49	0.11	Fe 3d, CO 2π
1e	0.84	0.02	0.07	0.46	0.43	0.01	Fe 3d, CO 1π
2e	0.56	0.76	0.02	0.06	0.16	0.0	Fe 3d, CO 1π, 2π
3e	0.23	0.18	0.12	0.09	0.55	0.07	Fe 3d, CO 2π
$1t_1$	0.83	0.0	0.07	0.51	0.42	0.01	CO 1π

Table VII. Back-Donated Charge[a]

$Ni(CO)_4$	1.46	$Ni(N_2)_4$	1.19
$Co(CO)_4^-$	2.19	$Co(N_2)_4^-$	2.23
$Fe(CO)_4^{2-}$	3.15	$Fe(N_2)_4^{2-}$	3.30

[a] See text.

nitrogen complexes and to $7t_2$ for $Ni(CO)_4$ and at the same time mix with π. In the case of the Co and Fe carbonyls $5t_2$, $6t_2$, and $8t_2$ are σ orbitals. $7t_2$ is a π orbital with very little σ admixture. $9t_2$ should now be σ antibonding to $8t_2$. It turns out that $9t_2$ in $Ni(N_2)_4$ is mainly 3d with a large π component on the outer nitrogen and a rather small σ component on the inner nitrogen. In $Ni(CO)_4$ $9t_2$ has a smaller 3d component than for $Ni(N_2)_4$ (see Table I), a large π component on oxygen, and a rather small σ component on both carbon and oxygen. In addition, $9t_2$ has large 4p components particularly for $Ni(CO)_4$.

Comparing with the 1e–2e pair we thus get an additional π component at the expense of the σ charge in the t_2 symmetry block. This may be regarded as a short-circuiting effect.[3,23] Its magnitude is fairly small, however. If the oxygen π component is compared in e and t_2 orbitals in $Ni(CO)_4$ the excess of π charge in t_2 is only 3% of an electron per bond.

In Table I we find a larger electronic density on the outer nitrogen atom than on the inner one. The difference is 0.15 electron but this number has to be scaled up by about 50% to account for the fact that only the charge within the relatively small muffin-tin spheres is counted. We then obtain 0.23 electrons compared to 0.31 electrons in the ab initio calculation by Jansen and Ros.[15]

4s and 4p Bonding. The Mulliken population analysis of accurate ab initio wave functions shows a very small population (or even negative) in the metal 4s orbital,[13] but in this case the Mulliken populations are particularly useless as a measure for charge distributions. The reason is that the ligand orbitals overlap to the 4s region. A large part of what could be described as a 4s component is instead counted to the ligands. Moreover, the Mulliken analysis does not tell what kind of 4s orbital is involved.

Disregarding constant amplitude factors the molecular orbitals with metal 4s components as well as the atomic 4s orbitals for the metal atoms or ions behave like the metal 3s orbital in the core region. There is a nodal surface (a sphere for the atom) at about one-third of the distance to the first ligand atom. Then follows the outer lobe which smoothly joins the ligand σ orbitals (Figure 7). If the amplitudes of the molecular orbitals are divided by the amplitude of an atomic 4s orbital in the metal region, we get an almost constant value until well beyond the outermost nodal surface. We may take the square of these quotients as a measure of the 4s characters (for a more detailed discussion see ref 25). This is done in Table VIII,

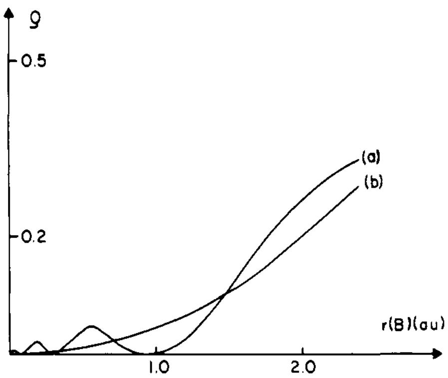

Figure 7. Radial charge distributions for a_1 orbitals in Ni region for (a) $Ni(N_2)_4$ and (b) $(N_2)_4$.

Table VIII. Squared Quotients between Orbitals with 4s and 4p Components and Atomic 4s and 4p Orbitals in the Me^{2+} Ground State Configurations, Multiplied by the Number of Electrons in Each Orbital

orbital	Ni-$(N_2)_4$	Co-$(N_2)_4^-$	Fe-$(N_2)_4^{2-}$	Ni-$(CO)_4$	Co-$(CO)_4^-$	Fe-$(CO)_4^{2-}$
$6a_1$	0.02	0.0	0.0	0.0	0.0	0.0
$7a_1$	0.71	0.69	0.62	0.22	0.10	0.06
$8a_1$	0.08	0.10	0.11	1.04	1.09	1.10
sum	0.81	0.78	0.73	1.26	1.19	1.16
$5t_2$	0.03	0.04	0.04	0.00	0.0	0.0
$6t_2$	1.13	1.22	1.17	0.03	0.03	0.02
$7t_2$	0.09	0.19	0.25	0.77	0.19	0.16
$8t_2$	0.30	0.21	0.16	0.27	1.28	1.66
$9t_2$	0.71	0.83	0.84	2.43	1.89	1.54
sum	2.26	2.48	2.46	3.50	3.38	3.38

where the Xα 4s or 4p orbitals (unoccupied) of the 2+ ions are used as reference orbitals. If a 4s orbital for the atom were used we would have obtained almost 30% larger values.

As is seen in Table VIII the 4p populations are about three times as large as the 4s populations, which suggests sp^3 hybridization.[15] The populations for the carbonyls are considerably larger than for the dinitrogen complexes, suggesting larger sp^3 bonding for the carbonyls. The populations are roughly the same for all the metals. Finally the highest MO for CO but the next to highest for N_2 is involved in the 4s, 4p bonding. Since none of these orbitals has a strong bonding character it is not likely that 4s, 4p bonding changes the strength of the CO or N_2 bonds to any large extent.

V. Comparison with Experiments

The back-bonding mechanism leads to weakened N_2 and CO π bonds. It is interesting to study the correlation between IR stretching frequencies and the back-donated charge according to our rough estimations. In Figure 8 is seen that this correlation is rather good for the carbonyls. It should be remembered that the correlation should not be expected to be perfect since a small part of the back-donated charge goes to 4p rather than to π^* on the ligand and since some π^* charge is received via short-circuiting. Disregarding the latter small charge displacements, Figure 8 shows that our method for estimating the back-donated charge is basically correct. Our results regarding the d populations are also in qualitative agreement with the results of Hillier.[5]

Our orbital energies given in the tables are from the ground-state calculations and should therefore not be considered as calculated ionization energies. According to our experience transition-state calculations do not change the ground-state orbital energies very much, however. The agreement with the experimental photoelectron spectrum[26] for $Ni(CO)_4$ is satisfactory, and also compares favorably with other methods.[27]

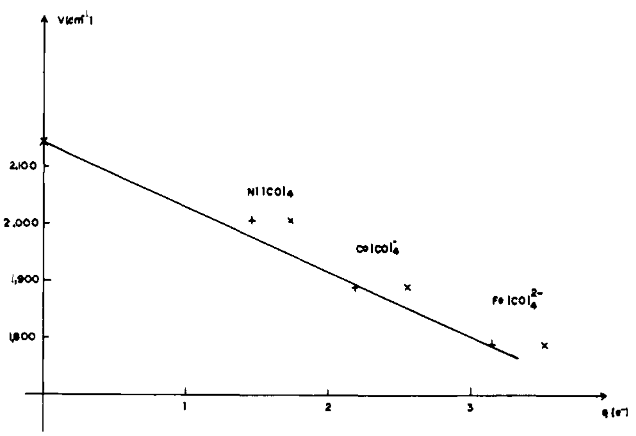

Figure 8. CO stretching frequency ν as a function of back-donated charge q for tetrahedral carbonyls: +, our results; ×, results using the d populations of ref 4.

Conclusion

We find a somewhat larger back-bonding for $Ni(CO)_4$ than for $Ni(N_2)_4$. For the Co and Fe complexes back-bonding becomes increasingly important but about the same for the CO and N_2 complexes. The magnitude of the back-donated 3d charge correlates well with the decrease in the N_2 and CO stretching frequencies. The 4s, 4p bonding seems to be important particularly for the carbonyls but does not change significantly with metal.

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