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A Comparison of Quantitative Theoretical Results of the Bonding in $Ni(CO)_4$ and $Ni(N_2)_4$

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Using non-empirical calculations the details of bonding in $Ni(CO)_4$ and in the analogous $Ni(N_2)_4$ are investigated.

For $Ni(CO)_4$ some previous results are confirmed. In the calculation on $Ni(N_2)_4$ the close resemblance with $Ni(CO)_4$ is quite remarkable. The main difference is contained in the fact that carbon has a lower π-electron density than nitrogen and that therefore the π^*-orbital in CO is lower in energy and geometrically more favourable for back donation.

From the calculations we find a difference in metal-ligand bond energy between the carbonyl complex and the dinitrogen complex of approximately 18 kcal/mol.

Key words: $Ni(CO)_4$ – $Ni(N_2)_4$ – Carbonyl and dinitrogen complexes, relative stability of

1. Introduction

It is well known that complexes containing molecular nitrogen are rather unstable [1]; the first complexes were discovered only a couple of years ago [2] and at this moment only a small number of these complexes have been described in literature [3]. On the other hand, many stable complexes are known containing carbon monoxide [4, 5], a ligand that is iso-electronic with molecular nitrogen.

We therefore want to discuss here the complex formation properties of CO and N_2 by comparing the complexes $Ni(CO)_4$ and $Ni(N_2)_4$.

$Ni(CO)_4$ is a stable tetrahedrical system. $Ni(N_2)_4$ has been discovered recently [6] and has a structure similar to that of $Ni(CO)_4$. The model for the bonding in the carbonyl complexes [7, 5], also assumed for the dinitrogen complexes, is the following: a donation from a σ-type carbon lone pair orbital to central atom *s*- and *p*-orbitals and a backdonation from central atom *d*-orbitals to empty ligand orbitals of π^*-type.

Although there are quite a number of experimental data on the bonding in the carbonyl complexes, the conclusions on the extent of σ- and π-bonding are often contradicting [1, 8–12]. Furthermore there are theoretical investigations on $Ni(CO)_4$ [13, 14], on $Cr(CO)_6$ [14–16] and on dinitrogen complexes [17, 18] but these also do not lead to sharp conclusive results about the σ- and π-bonding in complexes with CO and N_2.

The method used for the calculations described here, is the standard non-empirical Hartree-Fock method in the Roothaan scheme for closed shell molecules. For the interatomic distances in $Ni(CO)_4$ experimental distances are used ($R_{Ni-C} = 3.44$ a.u., $R_{C-O} = 2.135$ a.u.). From these also the geometrical parameters for $Ni(N_2)_4$ are derived ($R_{Ni-N} = 3.44$ a.u., $R_{N-N} = 2.075$ a.u.). The basis set used is a relatively small basis set of Gaussian functions, in which more freedom is given to valence shell electrons than to core electrons [18–20]. Therefore total energies are relatively high, but the ordering of the orbital energy levels agrees completely with other calculations (e.g. for $Ni(CO)_4$ Ref. [13]) and bonding effects are reliably described with such a basis [21].

2. Results and Discussion

2.1. Stabilities

Since we are interested in the relative stabilities of the carbonyl- and dinitrogen-complexes, let us first study the total energies given in Table 1. From this table we see that there is a considerable gain in total energy for both systems. The ground state of atomic nickel, however, is not the d^{10}-configuration but $3d^8 4s^2 (^3F)$ and the energy difference between these states calculated with our basis set is 0.495 a.u. As a consequence, when we compare the total energies of $Ni(CO)_4$, $Ni(N_2)_4$, Ni, CO, and N_2 in their ground states, we do not find positive binding energies between Ni and CO or N_2.

We must be aware, however, that we have not incorporated any correction for the change in correlation energy and that even with a calculation that is closer to the Hartree-Fock limit, no positive binding energy is obtained.

The experimental bond energy for a bond between Ni and CO is 34.6 kcal/mol. As for this moment, there is no experimental information on the binding energy in $Ni(N_2)_4$. There is a study on the bond energy of molecular nitrogen in which the difference in bond energy of CO and N_2 in $[Ru(NH_3)_5CO]^{2+}$ and $[Ru(NH_3)_5N_2]^{2+}$ resp. is found to be 17.8 ± 2 kcal/mol [9].

From our calculations we find an energy difference of 17.1 kcal/mol. Although this agreement may be fortuitous, it may also indicate that a comparison of the systems on the basis of relative results is very well possible.

2.2. Charge Distribution

Before trying to analyse the differences in binding energy of these systems, we first will consider the charge distribution as found with a Mulliken population analysis. In Table 2 gross atomic charges and atom-atom overlap populations

Table 1. Total energies (a.u.)

Ni $(d^{10} - {}^1S)$	-1493.342
Ni $(d^8 s^2 - {}^3F)$	-1493.837
CO	-111.858
$Ni(CO)_4$	-1941.137
N_2	-108.149
$Ni(N_2)_4$	-1926.192
$\Delta E\{Ni(d^{10}) + 4CO - Ni(CO)_4\}$	0.363
$\Delta E\{Ni(d^{10}) + 4N_2 - Ni(N_2)_4\}$	0.254

Table 2. Gross atomic charges, atom-atom overlap populations and gross set populations

	$Ni(CO)_4$	$Ni(N_2)_4$
Q (Ni)	−0.317	−0.492
Q (C; N1)	0.173	0.216
Q (O; N2)	−0.094	−0.092
P (Ni–C; Ni–N1)	0.335	0.331
P (C–O; N1–N2)	0.725	0.718
N(Ni 4s)	0.459	0.457
N(Ni 4x)	0.500	0.482
N(Ni x^2)	1.244	1.272
N(Ni xy)	1.577	1.626
N(C; N1 2s)	1.571	1.578
N(C; N1 x)	0.752	1.068
N(O; N2 2s)	1.989	2.009
N(O; N2 x)	1.368	1.028

are given. From this table we see that due to complex formation the electronic structure of the ligand changes in such a way that there is a charge density shift from the atom adjacent to the nickel towards both the nickel atom and to the atom farther away. The charge at nickel in $Ni(CO)_4$ is in good agreement with photo-electron experiments [22] that indicate a small negative charge at nickel, in absolute value most probably smaller than 0.7 electron. There is little difference in the gross atomic charges between the carbonyl and the molecular nitrogen complex, in the latter one only the nickel atom being somewhat more negative. In the same way, the overlap populations are very similar. More interesting are the set populations, the gross populations split up into the contributions of the various sets of atomic orbitals, also given in Table 2. Apart from the differences, caused by the differences in nuclear charge of C and N, and of O and N respectively, we may remark a difference in the nickel $3d$ occupancy (which is smaller in the carbonyl complex) and in the nickel $4p$ occupancy (which is larger in the carbonyl complex). Together they result in a larger negative charge on nickel in the dinitrogen complex as compared with the carbonyl complex.

In a more compact form the Ni-populations can be written for $Ni(N_2)_4$ as $3d^{8.69}\ 4s^{0.46}\ 4p^{1.34}$ ($Q = -0.49$) and for $Ni(CO)_4$ as $3d^{8.46}\ 4s^{0.46}\ 4p^{1.40}$ ($Q = -0.32$). We therefore can state that the nickel d-orbital occupancy in these systems is much closer to the free atom ground state (d^8s^2) than to the valence state configuration d^{10}, which is normally considered to be important in the formation of carbonyl and dinitrogen complexes. However, instead of having two electrons in the $4s$-orbital, we now may describe the valence state as a distribution of approximately two electrons in a set of sp^3 hyprid type orbitals. The resulting configuration for $Ni(CO)_4$ can be compared with the result of Demuynck and Veillard: $3d^{9.21}\ 4s^{-0.02}\ 4p^{0.57}$ ($Q = 0.24$) [18].

Veillard *et al.* [23] already showed that we should not attach too much significance to the absolute values calculated for the populations since they all are obtained using a Mulliken population analysis and therefore depend on the spatial extensiveness of the functions used in the calculations. In view of the

Table 3. Set populations in some symmetry blocks

	$Ni(CO)_4$	$Ni(N_2)_4$		no charge transfer	δ_{CO}	δ_{N_2}
A_1 symmetry						
Ni $1s+2s+3s$	5.992	5.992		6.000	−0.008	−0.008
Ni $4s$	0.467	0.465		0.000	0.467	0.465
Cs	0.842	0.844				
Os	0.996	1.007	σ	2.500	−0.115	−0.114
Cp	0.228	0.276				
Op	0.318	0.255				
E_ε symmetry						
Cp	0.182	0.268				
Op	0.352	0.256	π	0.500	0.034	0.023
Nid	0.933	0.954		1.000	−0.134	−0.092
$T_{2\xi}$ symmetry						
Cs	0.909	0.911				
Os	0.998	1.001	$\sigma+\pi$	3.000	−0.011	−0.018
Cp	0.399	0.541				
Op	0.683	0.528				
Ni $2p+3p$	3.966	3.965		4.000	−0.034	−0.035
Ni $4p$	0.500	0.482		0.000	0.500	0.482
Nid	1.577	1.626		2.000	−0.423	−0.374

photo-electron results, however, the distribution given by our calculation looks reasonable enough.

2.3. Donation and Back Donation

Looking closer into the electron distribution, we can analyse the electron shifts in the various symmetry blocks of the tetrahedral systems, as presented in Table 3.

In the A_1 block which contains central atom s-orbitals, we find in both complexes the same charge transfer, 0.115 for a carbonyl and 0.114 for a dinitrogen group; comparing these data with the results found for the protonation of the diatomic systems [18], we see that the charge shift per ligand is about the same on protonation and on complex formation.

In the T_1 block only ligand π-orbitals are present. Here for the dinitrogen complex a very small charge shift to N1 occurs and no shift at all for the carbonyl complex.

The compensation for the σ-shift in the π-system in the complexes is found in the E block orbitals: a shift from nickel d-orbitals to ligand π-orbitals. In this symmetry block we notice a remarkable difference between the two systems. In fact the shift in the dinitrogen complex is much smaller than in the carbonyl complex. In both cases the electrons are accepted by a ligand π-orbital of antibonding character that is mainly concentrated on the atom adjacent to the nickel atom. The carbonyl π^* orbital is approximately of such a type but it differs clearly from the symmetrical dinitrogen π^*-orbital. Therefore backdonation to the carbonyl is more favourable than to the dinitrogen. In the T_2 block we find both

Table 4. Charge transfer (δN) per ligand (Ni → L) and changes in overlap population (δP)

		$Ni(CO)_4$		$Ni(N_2)_4$	
		δN	δP_{C-O}	δN	δP_{N-N}
A_1	σ	−0.115	0.082	−0.114	0.040
E_ε	π	0.034	−0.011	0.023	−0.010
$T_{2\zeta}$	σ	−0.061	−0.020	−0.048	0.013
	π	0.050	−0.003	0.029	−0.013
Total	σ	−0.298	0.022	−0.257	0.130
	π	0.218	−0.013	0.134	−0.059

the σ- and the π-effect and furthermore some shift from nickel 3*d*- to nickel 4*p*-orbitals.

Now reviewing the total situation in Table 4, we see that the σ-donation is in both complexes approximately equally large (in the dinitrogencomplex somewhat smaller). This charge transfer stabilizes the ligand σ-bond by removing the antibonding effect of the lone pair. The backdonation into π^* labalizes the bond within the ligand. In the carbonyl complex the charge shift of this backdonation almost completely compensates the σ charge transfer. In the dinitrogen complex the backdonation is smaller, but the weakening influence on the N–N bond is nevertheless relatively large.

3. Conclusions

We now can formulate a number of effects that, from a theoretical point of view, favour the bonding in $Ni(CO)_4$ and in general in carbonyl complexes.

First of all, according to our calculations, the nickel atom adopts in the complex a configuration ($3d^{8.46}\ 4s^{0.46}\ 4p^{1.40}$), that is rather close to the ground state configuration ($3d^8 4s^2$). The only difference is that the 4*s* orbital is replaced by some set of sp^3-type orbitals.

Furthermore, carbon monoxide is a rather good σ-donor because, as a result of the donation of carbon lone pair electrons to nickel, the C–O bond is stabilized. The donation properties are enhanced if the σ-electron shift can be compensated in some way or another.

On protonation, this compensation takes place by a shift of π-electrons from oxygen to carbon. In tetrahedral complexes, however, it mainly occurs by the back donation from nickel 3*d*-orbitals to a CO π^*-orbital. This back donation is favourable because carbon monoxide has a π^*-orbital with a relatively low energy, that is mainly concentrated on carbon. It is this well fitting combination of donating and accepting possibilities that causes the stability of carbonyl complexes.

The resemblance between the bonding in the complex with dinitrogen and the carbonyl complex is very close. However, there are differences, and they all make the dinitrogen complex somewhat less favourable.

The π^*-orbital of N_2 is much higher in energy than that of CO and it is symmetrically distributed over the two nitrogen atoms. This together makes it less favourable to donate metal $d\pi$-electrons into such an orbital for reasons of energy and geometry.

As a consequence there are also somewhat less σ-electrons donated towards the nickel. Furthermore electrons in the symmetrical π^*-orbital of N_2 have a stronger antibonding influence on the N–N bond than electrons in a CO-π^*-orbital (mainly concentrated on carbon) will have on the C–O bond.

All these effects add up to a difference of approximately 18 kcal/mol in the bond energy of nickel with CO and N_2 resp., thus making the carbonyl complex considerably more stable than the molecular nitrogen analogue.

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