Rodríguez-Santiago, Branchadell, and Sodupe: Bonding of NO$_2$ to Cu and Ag

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40 The computed MP2(DF) geometrical parameters of NO$_2^+$ are $r(N-O) = 1.283(1.287)$ Å and $\angle ONO = 115.7(115.4)^\circ$. The experimental values are $1.25\pm0.02$ Å and $117.5^\circ$.41
42 The computed MP2(DF) geometrical parameters of NO$_2$ are $r(N-O) = 1.221(1.213)$ Å and $\angle ONO = 133.2(133.7)^\circ$. The experimental values are $1.194$ Å and $133.9^\circ$.43
INTRODUCTION

The study of metal–monoligand systems is of great interest, since it provides the most simple model for metal–ligand interactions. We have recently studied the complexes Sc–CO$_2$ (Ref. 1) and Cu–NO$_2$ (Ref. 2) using density functional methods in the geometry optimizations and frequency calculations, while the binding energies have been calculated at higher levels of calculation.

In the last years, density functional methods have been extensively used in the study of systems containing transition metals, yielding high quality results at a relatively low computational cost. However, the same level of accuracy is not generally achieved in the study of metal–monoligand systems. Recent work in this area has shown that, as a general trend, density functional methods yield reasonable molecular geometries and vibrational frequencies, but tend to overestimate binding energies. This fact has been related to the incorrect representation of atomic states arising from different electronic configurations of the metal. This overbinding is partially corrected when hybrid functionals, that incorporate contributions from the exact Hartree–Fock orbitals, which leads to a (14s 10p 6d)/[8s 6p 4d] basis set is of the form (14s 10p 6d)/[8s 6p 4d].

The purpose of the present paper is to study the Sc–CO$_2$ and Cu–NO$_2$ systems using different functionals in order to assess their validity in the study of geometries, vibrational frequencies, and binding energies. For this reason, the results provided by the different functionals will be compared with those obtained from high level conventional ab initio calculations.

COMPUTATIONAL DETAILS

Density functional (DF) calculations have been done using the two different gradient-corrected functionals: The exchange functional of Becke$^{23}$ with the correlation functional of Perdew$^{24}$ (B–P), and the same exchange functional along with the correlation functional of Lee, Yang, and Parr$^{25}$ (B–LYP). Moreover, the LYP exchange functional has also been used with two different hybrid exchange functionals: Becke’s half and half$^{26}$ (B1–LYP) and Becke’s three parameter functional$^{27}$ (B3–LYP). Conventional ab initio calculations have been carried out at the coupled cluster with single and double excitations level, with a perturbative estimate of the triple excitations [CCSD(T)]. Molecular geometries and harmonic vibrational frequencies have been determined at all these levels of calculation. In the geometry optimization at the CCSD(T) level of calculation we have correlated all electrons of N, C, and O except the 1s. For Sc and Cu we have correlated the 3d and 4s electrons. In the calculation of the binding energy of Sc–CO$_2$ we have also correlated the 3s and 3p electrons, since the correlation has a noticeable effect on the computed values (about 5.0 kcal mol$^{-1}$). For Cu–NO$_2$ we have observed that this effect is negligible (about 0.1 kcal mol$^{-1}$).

The same basis set has been used in all these calculations. The Cu and Sc basis set is a [8s 4p 3d] contraction of the (14s 9p 5d) primitive set of Wachters$^{29}$ supplemented with two diffuse p and one diffuse d functions. The final basis set is of the form (14s 11p 6d)/[8s 6p 4d]. For C, N, and O we use the (9s 5p)/[4s 2p] set developed by Dunning$^{31}$ supplemented with a valence diffuse function ($\alpha_{sp}$ = 0.0438 for carbon, $\alpha_{sp}$ = 0.0639 for nitrogen, and $\alpha_{sp}$ = 0.0845 for oxygen) and one 3d polarization function ($\alpha = 0.75$ for carbon, $\alpha = 0.80$ for nitrogen, and $\alpha = 0.85$ for oxygen). This basis set is referred to as D95+ in the GAUSSIAN 92$^{32}$ program system.

We have also carried out single point calculations using a larger basis set. In these calculations the metal basis set is further augmented by a single contracted set of polarization functions that is based on a three-term fit to a Slater-type orbital, which leads to a (14s 11p 6d 3f)/[8s 6p 4d 1f] basis.
TABLE I. Optimized geometry parameters of Sc–CO$_2$ and Cu–NO$_2$ computed at several levels of calculation.

<table>
<thead>
<tr>
<th>Level of calc.</th>
<th>$r$(M–O) (Å)</th>
<th>$r$(X–O) (Å)</th>
<th>A(OXO) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc–CO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B–P</td>
<td>1.927(−0.018)</td>
<td>1.372(−0.008)</td>
<td>111.7(1.4)</td>
</tr>
<tr>
<td>B–LYP</td>
<td>1.945(0.000)</td>
<td>1.375(−0.005)</td>
<td>111.3(1.0)</td>
</tr>
<tr>
<td>B3–LYP</td>
<td>1.928(−0.017)</td>
<td>1.358(−0.022)</td>
<td>110.8(0.5)</td>
</tr>
<tr>
<td>BH–LYP</td>
<td>1.918(−0.027)</td>
<td>1.342(−0.038)</td>
<td>110.8(−0.3)</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>1.945</td>
<td>1.380</td>
<td>110.3</td>
</tr>
<tr>
<td>Cu–NO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B–P</td>
<td>2.086(−0.007)</td>
<td>1.276(−0.006)</td>
<td>114.3(0.9)</td>
</tr>
<tr>
<td>B–LYP</td>
<td>2.112(0.019)</td>
<td>1.283(0.004)</td>
<td>114.3(0.9)</td>
</tr>
<tr>
<td>B3–LYP</td>
<td>2.090(−0.003)</td>
<td>1.284(−0.018)</td>
<td>114.2(0.8)</td>
</tr>
<tr>
<td>BH–LYP</td>
<td>2.077(−0.016)</td>
<td>1.245(−0.037)</td>
<td>114.0(0.6)</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>2.093</td>
<td>1.282</td>
<td>113.4</td>
</tr>
</tbody>
</table>

For both complexes, we have taken as reference the geometry parameters obtained at the CCSD(T) level of calculation. Table I shows that in all cases, DF geometries are very close to the ones obtained at the highest level of calculation. Regarding the bond lengths, the maximum deviation is produced for the X–O bond at the BH-LYP level: −0.038 Å for Sc–CO$_2$ (2.8% deviation) and −0.037 Å for Cu–NO$_2$ (2.9% deviation). With respect to bond angles, the largest deviation is produced in the OCO angle of Sc–CO$_2$ at the B–P level: 1.4° (1.3% deviation). DF bonds are generally shorter than the CCSD(T) ones, except for the B–LYP functional. B–P, B–LYP, and B3–LYP yield results in closer agreement with CCSD(T) than BH–LYP.

RESULTS AND DISCUSSION

The geometries of the Sc–CO$_2$ and Cu–NO$_2$ complexes are schematically represented in Chart 1.

They correspond to the most stable structures obtained in our previous work. Table I presents the geometries of Sc–CO$_2$ and Cu–NO$_2$ optimized at several levels of calculation.

TABLE II. Harmonic vibrational frequencies of Sc–CO$_2$ and Cu–NO$_2$ computed at several levels of calculation.

<table>
<thead>
<tr>
<th>Level of calc.</th>
<th>M–XO$_2$ in-plane (v$_2$)</th>
<th>M–XO$_2$ out-of-plane (v$_1$)</th>
<th>M–XO$_2$ stretch (v$_0$)</th>
<th>XO$_2$ bend (v$_1$)</th>
<th>XO$_2$ stretch (v$_0$)</th>
<th>XO$_2$ stretch (v$_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–NO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B–P</td>
<td>382(147)</td>
<td>317(−13)</td>
<td>940(−11)</td>
<td>1288(7)</td>
<td>1228(−54)</td>
<td></td>
</tr>
<tr>
<td>B–LYP</td>
<td>378(43)</td>
<td>296(−28)</td>
<td>826(−25)</td>
<td>1228(−45)</td>
<td>1194(−88)</td>
<td></td>
</tr>
<tr>
<td>B3–LYP</td>
<td>373(38)</td>
<td>319(−5)</td>
<td>874(22)</td>
<td>1335(62)</td>
<td>1311(29)</td>
<td></td>
</tr>
<tr>
<td>BH–LYP</td>
<td>360(25)</td>
<td>337(13)</td>
<td>926(73)</td>
<td>1437(164)</td>
<td>1445(163)</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>325</td>
<td>324</td>
<td>851</td>
<td>1273</td>
<td>1282</td>
<td></td>
</tr>
<tr>
<td>Sc–CO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B–P</td>
<td>371</td>
<td>312</td>
<td>479</td>
<td>942</td>
<td>998</td>
<td></td>
</tr>
<tr>
<td>B–LYP</td>
<td>347</td>
<td>312</td>
<td>463</td>
<td>740</td>
<td>912</td>
<td>977</td>
</tr>
<tr>
<td>B3–LYP</td>
<td>387</td>
<td>314</td>
<td>483</td>
<td>776</td>
<td>983</td>
<td>1054</td>
</tr>
<tr>
<td>BH–LYP</td>
<td>432</td>
<td>313</td>
<td>502</td>
<td>820</td>
<td>1057</td>
<td>1146</td>
</tr>
</tbody>
</table>

In cm$^{-1}$. In parentheses values relative to CCSD(T).

in the functional produces an increase in the values of all computed frequencies except the $b_1$ wagging. With the B3-LYP functional most of the frequencies are larger than the corresponding CCSD(T) ones, while BH-LYP frequencies are always larger than the B3-LYP ones. There is a variation in the ordering of the two N–O stretching frequencies. According to all the functionals except BH–LYP the asymmetric N–O stretching vibration appears at a higher frequency than the symmetric stretching, as in NO$_2$.\(^{37}\) On the other hand, the ordering is inverted in the BH–LYP and CCSD(T) calculations, leading to the same ordering observed in NO$_2$.\(^{38}\)

In spite of reproducing the CCSD(T) ordering, the BH–LYP N–O stretching frequencies are too large, with an error relative to CCSD(T) of about twice the error produced by the other functionals. The asymmetric N–O stretching frequency computed at the CCSD(T) level is only 53 cm$^{-1}$ larger than the experimental value of 1220 cm$^{-1}$.\(^{39}\)

As a summary of this comparison between DF and CCSD(T) frequencies, we can say that all functionals, except BH–LYP, yield frequencies within less than 100 cm$^{-1}$ of the CCSD(T) ones. Regarding the frequencies of Sc–CO$_2$, we obtain very similar results with the first three functionals, while BH–LYP frequencies are generally larger. According to the results obtained for Cu–NO$_2$, we expect the BH–LYP results to be less accurate than the results obtained using the other functionals.

The bond dissociation energies computed for the Cu–NO$_2$ and Sc–CO$_2$ complexes are presented in Table III. If we take the CCSD(T) values as the reference, we can see that DF calculations on Sc–CO$_2$ and Cu–NO$_2$ have different behavior. For Sc–CO$_2$ all DF methods except BH–LYP overestimate the binding energy, while for Cu–NO$_2$ the DF binding energies are lower than the CCSD(T) value. When comparing the different functionals, in all cases, BH–LYP yields the best result, i.e., the closest to CCSD(T). By comparing the three calculations that only differ in the exchange functional (B–LYP, B3–LYP, and BH–LYP), one can observe that the inclusion of the exact HF exchange into the functional leads to an improvement of the result, this being specially important for Sc–CO$_2$. As the contribution of exact exchange increases, the computed binding energies approach the CCSD(T) values.

The different behavior of Sc–CO$_2$ and Cu–NO$_2$ when changing the exchange functional shows that DF calculations overestimate the stabilizing contribution of exchange in the Sc–CO$_2$ complex with respect to the fragments. On the contrary, for Cu–NO$_2$ the stabilizing contribution of exchange is overestimated in the fragments. This tendency has also been observed in pilot calculations in which we have computed the binding energies at the HF level (exact exchange) and the DF level, using the Becke’s exchange potential and no correlation potential (B-null).

We have shown in our previous studies\(^{1,2}\) that both complexes have an important ionic character. According to this fact, the different behavior of the DF and CCSD(T) methods should be related to the computed values of the first ionization energy of the metal and of the electron affinity of the ligand. Tables IV and V present, respectively, the computed values of first ionization energies and adiabatic electron affinities.

For the first ionization energy of Sc, all theoretical results are lower than the experimental value. CCSD(T) provides the lowest value, 0.25 eV below the experimental one. The inclusion of exact exchange in the DF calculations does not show any systematic variation when the results are compared with CCSD(T). Regarding the first ionization energy of Cu, Table IV shows that CCSD(T) overestimates it by almost 0.7 eV. DF calculations with no hybrid functionals yield first ionization energies higher than the experimental value. The inclusion of exact exchange leads to a systematic lowering of the computed values, approaching the CCSD(T) result.

### Table III. Bond dissociation energies of Cu–NO$_2$ and Sc–CO$_2$ computed at several levels of calculation.

<table>
<thead>
<tr>
<th>Level of calc.</th>
<th>Sc–CO$_2$</th>
<th>Cu–NO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B–P</td>
<td>40.9(+21.0)</td>
<td>49.5(-7.8)</td>
</tr>
<tr>
<td>B–LYP</td>
<td>37.3(+17.4)</td>
<td>47.8(-9.5)</td>
</tr>
<tr>
<td>B3–LYP</td>
<td>29.4(+9.5)</td>
<td>49.2(-8.1)</td>
</tr>
<tr>
<td>BH–LYP</td>
<td>17.3(-2.6)</td>
<td>52.1(-5.2)</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>19.9(0.0)</td>
<td>57.3(0.0)</td>
</tr>
</tbody>
</table>

*In kcal mol$^{-1}$. In parentheses values relative to CCSD(T).

### Table IV. First ionization energy* of Sc and Cu computed at several levels of calculation.

<table>
<thead>
<tr>
<th>Level of calc.</th>
<th>Sc</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>B–P</td>
<td>6.436(+0.143)</td>
<td>8.285(+1.124)</td>
</tr>
<tr>
<td>B–LYP</td>
<td>6.358(+0.065)</td>
<td>8.189(+1.128)</td>
</tr>
<tr>
<td>B3–LYP</td>
<td>6.490(+0.197)</td>
<td>8.030(+0.969)</td>
</tr>
<tr>
<td>BH–LYP</td>
<td>6.333(+0.040)</td>
<td>7.502(+0.441)</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>6.293(0.0)</td>
<td>7.061(0.0)</td>
</tr>
<tr>
<td>Exp.</td>
<td>6.54*</td>
<td>7.726*</td>
</tr>
</tbody>
</table>

*In eV. In parentheses values relative to CCSD(T)."
The first ionization energy of Sc is reasonably well represented by all theoretical levels, so that this factor does not explain the different values of the binding energy of Sc–CO$_2$. On the other hand, the computed values of the first ionization energy of Cu vary within a range of 1.2 eV. DF calculations tend to overestimate the first ionization energy of Cu, while CCSD(T) underestimates it. These results are in good agreement with the fact that CCSD(T) binding energy is larger than any of the values computed using DF.

The different accuracy of DF methods in the determination of the first ionization energies of the first row transition metals has already been discussed by several authors. Ziegler and Li have rationalized the results in terms of the overestimation of the exchange contributions of the s–d exchange–correlation energy contribution due to electrons of the same spin. This term is absent in the Sc (4s$^2$3d$^1$) to Sc$^+$(4s$^1$3d$^1$) ionization, while it is important for Cu. The fact that the inclusion of exact exchange in the DF calculations leads to lower values of the first ionization energy of Cu confirms this analysis.

Let us now consider the electron affinities of the ligands. Table V shows that CCSD(T) underestimates the adiabatic electron affinities of CO$_2$ and NO$_2$ by 0.1 and 0.2 eV, respectively. B–P and B–LYP calculations overestimate the electron affinity of CO$_2$ by 0.4–0.5 eV, while the values corresponding to NO$_2$ are very reasonable. The inclusion of exact exchange does not lead to any systematic improvement, although for CO$_2$, the BH–LYP result is clearly closer to the experimental value than any of the other DF results. The computed value of the electron affinity of CO$_2$ would be very sensitive to the choice of the exponent of the most diffuse basis functions. As these functions become more diffuse, the computed value would approach zero. We have used the standard exponents implemented in the GAUSSIAN 94 program$^{22}$ both for C and O and our computed electron affinities are only used to interpret the variation of the binding energy of Sc–CO$_2$ with the level of calculation.

The formation of a complex of essentially ionic nature between a metal M and a ligand L can be conceptually decomposed into two steps. The first one consists of the formation of the M$^+$ and L$^-$ ions. In the second step both ions interact to yield the complex. The energy associated with the first step would be $E_p(M) - E_a(L)$. This term will be referred to as $\Delta E_1$. Table VI presents the values of this term computed for Sc–CO$_2$ and Cu–NO$_2$.

For Sc–CO$_2$, the CCSD(T) value of $\Delta E_1$ is in very good agreement with the experimental result, while the DF calculations lead to lower values, due to the overestimation of the electron affinity of CO$_2$ (see Table V). The inclusion of exact exchange in the functional leads to results in closer agreement with CCSD(T).

Regarding Cu–NO$_2$, CCSD(T) underestimates $\Delta E_1$ by 0.5 eV. This is mainly due to the underestimation of the first ionization energy of Cu (see Table IV). DF calculations lead to considerably larger values of this term, due to the overestimation of the first ionization energy. The use of hybrid functionals approaches the DF results to the CCSD(T) one.

The variation of $\Delta E_1$ with the level of calculation qualitatively agrees with the variation of the values of the computed binding energies (see Table III). For Sc–CO$_2$ the DF calculations yield binding energies larger than the CCSD(T) value and for Cu–NO$_2$ the DF values are lower than the CCSD(T) one. However, while the computed binding energies differ by more than 20 kcal mol$^{-1}$ for Sc–CO$_2$ and by less than 10 kcal mol$^{-1}$ for Cu–NO$_2$ (see Table III), the differences in $\Delta E_1$ are less than 10 kcal mol$^{-1}$ for Sc–CO$_2$ and more than 25 kcal mol$^{-1}$ for Cu–NO$_2$, so that there is another factor that has to be taken into account.

The ionization of Sc leads to Sc$^+$ with a ground state electronic configuration 3d$^1$ 4s$^2$. The 3d electron is the one that participates in the bonding with CO$_2$, while the 4s electron remains in the metal. In order to minimize the repulsion with the incoming ligand, this electron has to polarize away from the ligand through $sd$ hybridization. The energetic cost of this polarization can be related to the 3d–4s promotion energy of Sc$^+$. Several authors have computed this promotion energy using both DF$^{14,15,17,44}$ and conventional ab initio methods.$^{46}$ These studies show that DF methods generally underestimate this promotion energy. This fact can be attributed to the tendency of the current exchange functionals to overbind d electrons.$^{44}$ The use of hybrid exchange functionals partially corrects this underestimation.$^{14,15,17}$ On the other hand, conventional ab initio methods tend to overestimate this promotion energy.$^{46}$ The difference between the value computed by Russo et al.$^{44}$ at the BLYP level (0.18 eV) and the QCISD(T) value reported by Raghavachari and Trucks$^{46}$ (1.12 eV), with basis sets of similar quality, is more than 20 kcal mol$^{-1}$. This fact may play a role in the difference between the values of the binding energy of Sc–CO$_2$ computed using density functional and CCSD(T) methods. This polarization, related to a 4s–3d promotion, is absent in Cu–NO$_2$, since Cu$^+$ has no s electron and the 3d shell is full.

Up to now we have compared the results obtained at several levels of calculation using in all cases the same basis set. We will now discuss the basis set effect on the computed binding energies. Table VII presents the values of the binding energies of Sc–CO$_2$ and Cu–NO$_2$ computed using the larger basis set.

For Sc–CO$_2$ the use of a larger basis set produces a diminution of the computed binding energy in all DF calculations (see Table III for comparison). This result can be
related to the variation of the $\Delta E_1$ term when going from the smaller to the larger basis set. This term increases by 0.15 eV due to a diminution of the computed electron affinity of CO$_2$. The CCSD(T) calculation using the larger basis set has not been possible, so that we have examined the basis set effect at the MCPF level. This level of calculation gives a binding energy of 18.7 kcal mol$^{-1}$ with the smaller basis set, very similar to the CCSD(T) value of 19.9 kcal mol$^{-1}$ (see Table III). The value of the binding energy computed at the MCPF level with the larger basis set is 5.5 kcal mol$^{-1}$ larger than the value corresponding to the smaller basis set. When going from the smaller to the larger basis set, $\Delta E_1$ increases by 0.13 eV at the MCPF level, so that one could expect a decrease in the computed binding energy. However, the computed value increases. This result can be related to the diminution of the $s$-$d$ promotion energy computed by Raghavachari and Trucks$^{36}$ at the QCISD(T) level for Sc$^+$ using a basis set without f functions (1.2 eV) and with f functions (0.69 eV).

If we assume that the difference between MCPF and CCSD(T) binding energies computed with the larger basis would be about the same as the one calculated with the smaller basis set, we could predict the CCSD(T) binding energy with the larger basis set would be about 25 kcal mol$^{-1}$. This value is very similar to the one obtained at the B3-LYP level. On the other hand, the value obtained at the BH-LYP level is much lower, while this functional lead to the close value to CCSD(T) with the smaller basis set (see Table III). The fact that with the larger basis set the DF (B3-LYP) and CCSD(T) values seem to converge to similar values leads us to conclude that our best estimate for the binding energy of Sc-CO$_2$ is 25 kcal mol$^{-1}$. This value is somewhat larger than our previous result of 17 kcal mol$^{-1}$.$^1$ The difference between both results is due to the fact that in the previous calculation the $3s$ and $3p$ electrons of Sc were not correlated.

For Cu-NO$_2$, the basis set effect is smaller than for Sc-CO$_2$. The use of a larger basis set produces the same effect on the computed binding energy at all levels of calculation, so that the difference between the DF and CCSD(T) results does not change. The functional that leads to the closest result to CCSD(T) is BH-LYP, as it was the case with the smaller basis set (see Table III). The value of the first ionization energy of Cu with the larger basis set is 7.16 eV, very similar to the value obtained with the smaller basis set, and notably smaller than the experimental value (see Table IV). Values closer to the experiment are obtained only with larger basis sets.$^{46}$ According to this fact, we expect the value of the binding energy of Cu-NO$_2$ computed at the CCSD(T) level with our larger basis set to be slightly overestimated. On the contrary, for Cu-NO$_2$, the binding energy computed using density functional methods is always lower than the CCSD(T) value. In both cases, the introduction of exact exchange in the functional lowers the difference between the DF and CCSD(T) computed binding energies. The different behavior of both systems on the level of calculation has been rationalized in terms of two contributions. The first one is the difference between the first ionization energy of the metal and the electron affinity of the ligand involved in the formation of complexes with an important ionic character. This factor is determinant in Cu-NO$_2$, since the first ionization energy of Cu is greatly overestimated by the nonhybrid density functionals. For Sc-CO$_2$ the discrepancy between DF and CCSD(T) results has also been attributed to an underestimation of 4s-3d promotion energy in Sc$^+$ by the nonhybrid functionals. The use of hybrid exchange functionals partially corrects these deficiencies, but the development of new functionals seems necessary to obtain fully satisfactory results.

**CONCLUDING REMARKS**

The structure, binding energy, and vibrational frequencies of Sc-CO$_2$ and Cu-NO$_2$ have been determined using density functional and coupled cluster methods. All levels of calculation lead to very similar equilibrium geometries and vibrational frequencies, while different results are obtained for the binding energy. In Sc-CO$_2$, density functional methods overestimate the binding energy with respect to the CCSD(T) value. On the contrary, for Cu-NO$_2$, the binding energy computed using density functional methods is always lower than the CCSD(T) value. In both cases, the introduction of exact exchange in the functional lowers the difference between the DF and CCSD(T) computed binding energies.

**ACKNOWLEDGMENTS**

This work has been financially supported by DGICYT (PB92-0621) and CRIT (GRQ93-2079). Computer time from the Centre de Supercomputació de Catalunya (CESCA) and Centre Europeu de Paral·lelisme de Barcelona (CEPBA) is gratefully acknowledged. L.R. gratefully acknowledges the Spanish Ministry of Education and Science for a doctoral fellowship.

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“Comparison of Density Functional and Coupled Cluster Methods”

Rodriguez-Santiago, Sodupe, and Branchadell: Density functional and coupled cluster methods

9971

5. “Coordination of NO$_2$ to Alkaline-Earth Metals. A theoretical Study”
The structure and harmonic vibrational frequencies have been determined for the alkaline-earth metal MNO₂ systems (M = Be, Mg, Ca, and Sr) using the B3LYP method. Binding energies have also been calculated using conventional ab initio methods, CCSD(T), and MCPF, with different basis sets. Four different coordination modes of NO₂ to the metal have been considered. The C₂v, η²-O,O coordination mode is the most stable one for all metals. However, for BeNO₂ the ground state is a A1g state while for the other metals the A1g state is the most stable one. Our best estimates for the D₂ binding energies are 77 kcal mol⁻¹ for BeNO₂, 53 kcal mol⁻¹ for MgNO₂, 69 kcal mol⁻¹ for CaNO₂, and 71 kcal mol⁻¹ for SrNO₂.

Introduction

The study of the bonding in metal—ligand systems is a very active area of research,¹ owing to their applications in many fields, such as homogeneous and heterogeneous catalysis, environmental chemistry or biochemistry. In particular, the study of alkaline-earth metals interacting with different kind of ligands has been the subject of many studies.²⁻¹¹ Nitrogen oxides are unwanted pollutants that take part in important chemical reactions in the atmosphere. Because metal—NO₂ systems are known to be involved in the decomposition of nitrogen oxides, the study of the coordination of NO₂ to metals is important for understanding these processes.

Experimental studies of alkali compounds and alkaline-earth metals with NO₂ suggest the existence of a long-lived MNO₂⁻ complex. For alkali metals, the IR data are consistent with a planar ring structure of C₂v symmetry with an η²-O,O bidentate coordination.¹²⁻¹⁵ The IR data for the alkaline-earth metal nitrates suggest a similar structure or a nonplanar one with a poorly defined position of the metal lying above NO₂⁻.

From a theoretical point of view, few calculations have been reported for MNO₂ systems.¹⁶⁻²¹ In agreement with the experimental results, the calculations for alkali metals show that the C₂v cyclic and the C₂ trans-ONO structures are energy minima, the C₂v being the most stable one. For the transition metal systems Cu—NO₂ and Ag—NO₂, the C₂v η²-O,O coordination mode was also found to be the ground-state structure.²⁴ Calculations on [MNO₂]⁺H₂O systems for alkaline-earth metals²⁵ have also recently been reported. To our knowledge no theoretical study has been performed for the neutral alkaline-earth—NO₂ complexes.

In this work we study the bonding in the MNO₂ systems for M = Be, Mg, Ca, and Sr. Calculations are done using both conventional ab initio methods and the density functional approach. One of the goals of the present work is to determine the ground-state structures and the vibrational frequencies for these systems. For this purpose we have studied four different coordination modes: the bidentate C₂v η²-O,O and C₂v η²-N,O and the monodentate C₂v η¹-N and η¹-O modes. The nature of the different bonding mechanisms and the relative stabilities of the different isomers are analyzed as well as the trends in the group. Another important goal of these studies is to provide accurate binding energies for the alkaline-earth metal nitrates.

Computational Details

Molecular geometries and harmonic vibrational frequencies have been determined using the density functional approach. In these calculations we have used the hybrid Becke’s three-parameter exchange functional²⁶ with the correlation functional of Lee, Yang, and Parr²⁷ (B3LYP). This functional has proved to provide reliable geometries and harmonic vibrational frequencies compared to more computational demanding ab initio correlated methods.²⁸⁻³⁰ However, to confirm the reliability of the B3LYP binding energies, we have also done single-point calculations at the coupled cluster level with single and double excitations with a perturbative estimate of the triple excitations (CCSD(T)) at the B3LYP equilibrium geometries. In the calculations at the CCSD(T) level we have correlated all the electrons of Be and 10 electrons for Mg, Ca, and Sr. For Na, we have correlated the 2s and 2p electrons.

The same basis set has been used in these two levels of calculation. The N and O basis set is the (9s 5p)/(4s 2p) set developed by Dunning,³² supplemented with a valence diffuse function (α_N = 0.0639 for nitrogen and α_O = 0.0845 for oxygen) and one d polarization function (α = 0.80 for nitrogen and α = 0.85 for oxygen). This basis set is referred to as D95+ in the Gaussian 94 program. The Be basis set is the (11s 5p)/(4s 3p) set given by Krishnan et al.³⁴ supplemented with a valence diffuse function (α = 0.0207) and one d polarization function (α = 0.255). The Mg basis set is the (12s 9p)/(6s 5p) set of McLean and Chandler³⁵ supplemented with a d polarization function (α = 0.28). The Ca basis sets is the (12s 6p)/(8s 4p) set given by Roos, Veillard, and Vinatier³⁶ supplemented with two diffuse p functions (0.09913 and 0.03464) and five d functions contracted (311) to three functions.³⁷ For Sr we have used the relativistic effective core potential (RECP) of Hay and Wadt³⁸ in which the 4s, 4p, and 5s orbitals are included in the valence space. We have used their (5s 6p) valence basis set. With use of a general contraction, the inner three s functions are contracted to two functions, the outermost two s functions are uncontracted, and the six p functions are contracted (321). Five d functions contracted (311) to three functions have been added.³ The final basis sets are

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Coordination of NO₂

Figure 1. Studied coordination modes of NO₂ to the metal.

of the form (10s 6p 1d)/(5s 3p 1d) for N and O, (12s 6p 1d)/(5s 4p 1d) for Be, (12s 9p 1d)/(6s 5p 1d) for Mg, (12s 8p 5d)/(8s 6p 3d) for Ca, and (5s 6p 5d)/(4s 3p 3d) for Sr.

Single-point calculations using a larger atomic natural orbital (ANO) basis set have been carried out for the most stable isomer of each compound. These calculations have been performed using the modified coupled pair functional (MCPF) method. The same electrons as in the CCSD(T) calculations have been correlated. For N and O we have used the (10s 5p 2d 1f)/(4s 3p 2d 1f) basis set of Dunning augmented with one diffuse s and one diffuse p functions. This basis set, augmented with one diffuse d and one diffuse f functions, is referred to as aug-cc-pVTZ in the Gaussian 94 program. For Be and Mg we have used the (14s 9p 4d 3f)/(5s 4p 3d 2f) and the (17s 12p 5d 4f)/(6s 5p 4d 3f) ANO basis sets of Widmark et al., respectively. For Ca and Sr we have used the (20s 15p 8d 6f)/(8s 7p 5d 3f) and (26s 19p 14d 4f)/(110s 10p 7d 3f) ANO basis set described in detail in reference 9.

The B3LYP and CCSD(T) calculations were performed using the Gaussian 94 program, and open shell calculations were based on a spin-unrestricted treatment. The MCPF all-electron calculations were performed using the MOLCAS program, while those calculations with Sr using pseudopotentials were performed using the SWEDEN-MOLECULE program. In the MCPF case, the open shell calculations were based on a spin-restricted formalism.

Results and Discussion

Figure 1 shows the four different coordination modes of NO₂ to the metal that we have studied. For the NO₂-O structures we have considered two different electronic states, the 2A₁ and the 2B₁ states. For the other coordinations we have only considered the ground state, that is, the 2A₁ state for the C₂v structures and the 2'A for the C₂ structures. The B3LYP optimal geometries and the B3LYP and CCSD(T) relative energies for the MNO₂ complexes are shown in Tables 1 and 2, respectively.

Table 2 shows that in all cases the most stable coordination mode is the NO₂-O one. For BeNO₂, the ground state is the 2B₁ state, while for the other metals the 2A₁ state is the most stable one. The computed B3LYP relative energies are in quite good agreement with the CCSD(T) values, the only exception being the 2B₁ state for all metals due to the different nature of the bonding (see below). The ordering of stabilities between the different isomers is the same for Mg, Ca, and Sr, while for Be the NO₂-N structure is more stable than the NO₂-O one.

The bonding mechanism between an alkaline-earth metal and NO₂ is believed to be initiated by long-range electron transfer from the metal to the NO₂ ligand, which leads to a charge-transfer MNO₂⁻ complex. Our calculations show an important ionic character for the MNO₂⁻ complexes studied. In all cases except the Be₂⁻ state of the NO₂-O structure, the last doubly occupied orbital of the complex is mainly the 6ai orbital of NO₂. This orbital, which is schematically represented in Figure 2, is the single occupied orbital in the MNO₂⁻ fragment in the NO₂ coordination (2A₁ state) is in all cases very similar to that obtained for free NO₂⁻.

In the NO₂-N coordination the geometrical parameters of the ligand are between those obtained for free NO₂⁻ and NO₂.
Coordination of NO₂ to Alkaline-Earth...

indicating that for this coordination the covalent interaction between the metal and the ligand is larger than in the bidentate \( \eta^2 \)-O,O structure. In the C structure the interpretation of the geometrical parameters is more difficult because the symmetry between the two NO bonds has been broken. However, it can be observed that the ON angle is much closer to NO₂⁺ than to NO₂⁻.

The ionic interaction is maximized in the \( \eta^2 \)-O,O coordination mode by the approach of the metal atom along the C2 axis between the two oxygen atoms. Thus, this coordination is the most stable one. The second most favorable ionic interaction takes place in the \( \eta^1 \)-O structure. For the \( \eta^1 \)-N,O structure the ionic stabilization is somewhat less favorable owing to the M—N—O structure. For the \( \eta^1 \)-N isomer the ionic interaction is very inefficient. This is the order observed for Be complexes, since the differences between the ionic interactions are more important when the metal—ligand distances are smaller. However, in the case of Mg, Ca, and Sr, the \( \eta^2 \)-N,O structure is slightly more stable than the \( \eta^1 \)-O one. In these cases the more favorable overlap between the 6a₁ orbital of NO₂ (see Figure 2) and the orbitals of the metal determines the order of stability of the \( \eta^1 \)-O and \( \eta^2 \)-N,O isomers.

The bonding mechanism corresponding to the \( ^2 \)B₁ state of the \( \eta^2 \)-O,O coordination is different. The Mulliken population analysis shows that the charge over the metal is always larger than in the \( ^2 \)A₁ state. In this complex the last doubly occupied molecular orbital is mainly the 6a₁ orbital of free NO₂ (as in the \( ^2 \)A₁ state) but now the open shell corresponds to an orbital that is mainly the 2b₁ orbital of NO₂ (see Figure 2). This 2b₁ orbital would be the first virtual orbital in free NO₂. Consistent with this, the Mulliken population analysis shows that in the \( ^2 \)B₁ state the unpaired electron is completely located in the NO₂ fragment of the complex. The nature of these orbitals shows that in the \( ^2 \)B₁ state there is some ionic M⁺NO₂⁻ contribution to the bonding. As in the case of the \( ^2 \)A₁ state, in addition to the electron-transfer mechanism there is also important backdonation from the occupied orbitals of NO₂ to the empty p and d orbitals of the metal atom. It can be observed in Table 1 that the geometrical parameters of the NO₂ fragment in the \( ^2 \)B₁ state are now more similar to those obtained at the same level of calculation for NO₂⁺. The M—O distances are shorter than in the \( ^2 \)A₁ state because the s orbital of the metal is empty and the repulsion with the ligand is smaller. The N—O distances are larger because now the antibonding 2b₁ orbital of NO₂ is occupied.

Table 2 shows that the energy difference between the \( ^2 \)A₁ and the \( ^2 \)B₁ states of the \( \eta^2 \)-O,O coordination varies significantly with the level of calculation. It is observed that the \( ^2 \)B₁ state is more stabilized with respect to the \( ^2 \)A₁ state at the B3LYP level than at the CCSD(T) one, the largest difference being determined for Ca and Sr. The use of the larger basis set reduces the difference between B3LYP and CCSD(T) results. However, for Ca both methods still differ by 9.1 kcal mol⁻¹. Part of this error may arise from the fact that the s—d excitation in Ca⁺ is underestimated at the B3LYP level compared to CCSD(T). Considering that the d population is larger in the \( ^2 \)B₁ state than in the \( ^2 \)A₁ one, it is not surprising that Ca and Sr, which have low-lying d orbitals, show the largest differences.

It has already been mentioned that for all the alkaline-earth metals considered the most stable structure corresponds to the \( \eta^2 \)-O,O coordination. However, although for Be the ground state is the \( ^2 \)B₁ state, for the rest of the metals the \( ^2 \)A₁ state is the lowest one. The Be atom has the smallest atomic radius; its inner electron shell contains only the 1s electrons, and so the closed shell repulsion with the ligand is smaller than in the rest of the alkaline-earth metals considered. This fact allows Be to get closer to the ligand, and thus, the stabilizing interactions are stronger for the Be complexes. Therefore, in the case of Be the \( ^2 \)B₁ state becomes more stable than the \( ^2 \)A₁ state because these strong interactions compensate the cost of transferring a second electron to the ligand. This is not the case with the other alkaline-earth metals studied, where the metal—ligand distances are larger than for Be complexes. For the other coordination modes of the BeNO₂ complex, the electronic state equivalent to the \( ^2 \)A₁ state is always more stable than the one involving the occupation of the 2b₁ orbital of NO₂.

The harmonic vibrational frequencies computed for the most stable electronic state of each coordination are presented in Table 3. All coordination modes have been found to be minima on the potential energy surface except the \( \eta^1 \)-N structure for all metals and the \( \eta^1 \)-O isomer of MgNO₂. The \( \eta^1 \)-N structure is a transition state connecting two equivalent \( \eta^2 \)-N,O minima. For MgNO₂, the \( \eta^1 \)-O transition state connects the \( \eta^2 \)-O,O and the \( \eta^2 \)-N,O minima. It can be observed in Table 3 that the first frequency of the \( \eta^1 \)-O coordination, which corresponds to the bending of the MON angle, is very low for all metals except Be, indicating that the potential energy surface is very flat. Therefore, the only structures that one would expect to detect in experiments are the \( \eta^2 \)-N,O and \( \eta^2 \)-O,O structures.

Let us consider the largest three frequencies of each case that correspond to the vibrations of the NO₂ fragment. If one compares the frequencies associated with the NO₂ fragment of the same coordination mode but for the different metals, it can be observed that they are always very similar, especially for Mg, Ca, and Sr compounds. This indicates that the nature of the NO₂ fragment remains more or less the same regardless of

**Table 2: Relative Energies of MNO₂ Complexes Computed at Several Levels of Calculation**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta^1 )-N</td>
<td>25.6</td>
<td>28.5</td>
<td>22.6</td>
<td>26.2</td>
</tr>
<tr>
<td>( \eta^1 )-O</td>
<td>1.9</td>
<td>3.2</td>
<td>13.9</td>
<td>15.0</td>
</tr>
<tr>
<td>( \eta^2 )-O(O(( ^2 )A₁))</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( \eta^2 )-O(O(( ^2 )B₁))</td>
<td>-13.7</td>
<td>-7.8</td>
<td>24.9</td>
<td>31.4</td>
</tr>
<tr>
<td>( \eta^1 )-O,O</td>
<td>6.5</td>
<td>8.2</td>
<td>10.8</td>
<td>11.8</td>
</tr>
</tbody>
</table>

- Relative to the \( ^2 \)A₁ state of the \( \eta^2 \)-O,O structure. In kcal mol⁻¹.
Coordination of NO₂

TABLE 3: Harmonic Vibrational Frequencies* Computed at B3LYP Level

<table>
<thead>
<tr>
<th>Coordination</th>
<th>NO₂</th>
<th>NO₂</th>
<th>NO₂</th>
<th>NO₂</th>
<th>NO₂</th>
<th>NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>M—NO₂ in-plane wag</td>
<td>1901</td>
<td>403</td>
<td>621</td>
<td>896</td>
<td>1516</td>
<td>1438</td>
</tr>
<tr>
<td>M—NO₂ out-of-plane wag</td>
<td>1164</td>
<td>311</td>
<td>344</td>
<td>790</td>
<td>1486</td>
<td>1368</td>
</tr>
<tr>
<td>M—NO₂ stretch</td>
<td>1801</td>
<td>214</td>
<td>288</td>
<td>790</td>
<td>1462</td>
<td>1406</td>
</tr>
<tr>
<td>NO₂ bend</td>
<td>1651</td>
<td>173</td>
<td>231</td>
<td>784</td>
<td>1452</td>
<td>1401</td>
</tr>
</tbody>
</table>

* In cm⁻¹.

the metal considered. It can also be observed that for the η²-O,O coordination in the ²A₁ state (Mg, Ca, and Sr) the frequencies resemble more those of free NO₂ than those of free NO₂ or NO₂⁻, confirming again the η²NO₂⁻ character in these complexes. In the η²O state of the η²-O,O coordination of BeNO₂ the values of the two NO stretchings are smaller than in the rest of the η²O,O structures, approaching the values of NO₂⁻.

In the η¹-N coordination mode the two NO stretching values are always larger than in the η²O,O isomers, proving the larger covalent contribution to the bond in this coordination. Moreover, the relative ordering values in this coordination between the two NO stretchings are the same as in NO₂ and the opposite in NO₂⁻. In the C₃ structures, η²-N,O and η¹-O, the values of the two NO stretching frequencies are very different. This is due to the fact that in this coordination the C₃ₙ symmetry has been lost with a lengthening of the NO bond interacting with the metal and a shortening of the terminal NO bond compared to free NO₂.

Tevault and Andrews reported an experimental value of 1244 cm⁻¹ for the frequency corresponding to the asymmetric stretching of the NO₂ fragment in the CaNO₂ and SrNO₂ complexes in rare-gas matrices and another value of 1223 cm⁻¹ only for SrNO₂ complex. They suggested a nonplanar structure of the complex with a poorly defined position of M⁺ above the plane of the ligand associated with the first value and a coplanar structure associated with the second one. All our attempts to calculate a nonplanar η²O,O structure collapsed to the planar one. In any case, both experimental values are in very good agreement with the values computed for the NO asymmetric stretching of CaNO₂ and SrNO₂ (1249 and 1257 cm⁻¹, respectively).

TABLE 4: D₃h Binding Energies for the Ground States of the MNO₂ Complexes

<table>
<thead>
<tr>
<th></th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>80.8</td>
<td>47.2</td>
<td>70.1</td>
<td>67.9</td>
</tr>
<tr>
<td>CCSD</td>
<td>70.2</td>
<td>50.4</td>
<td>68.1</td>
<td>71.3</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>68.7</td>
<td>48.9</td>
<td>66.0</td>
<td>69.3</td>
</tr>
<tr>
<td>MCFF</td>
<td>69.8</td>
<td>49.8</td>
<td>67.1</td>
<td>70.6</td>
</tr>
<tr>
<td>MCFF (a)</td>
<td>78.8 (77.2)</td>
<td>53.4 (52.6)</td>
<td>69.1 (68.7)</td>
<td>71.4 (71.1)</td>
</tr>
</tbody>
</table>

* In kcal mol⁻¹, † Smaller basis set. ‡ Larger basis set. In parentheses are shown the D₃h binding energies computed using the B3LYP harmonic frequencies.
In all cases, the MCPF binding energies computed with the larger basis set are in good agreement with the initial values obtained at the B3LYP level with the smaller basis set; the main difference can be observed in the case of the Mg complex (6.2 kcal mol\(^{-1}\)). Therefore, one can conclude that for these alkaline-earth metal complexes the values of the binding energies computed at the MCPF level using a large basis set seem to be good enough when compared with those values computed at the MCPF level using a large basis set.

Let us now consider the variation of the binding energy when changing the metal. The Be complex presents the strongest bond, while the binding energies corresponding to Mg, Ca, and Sr complexes increase when going down in the group. The values computed for Ca and Sr are very similar, while for Mg the binding energy is notably smaller. The binding energy of a complex with an important ionic nature can be formally decomposed into two contributions. The first one, \( \Delta E_1 \), would involve the formation of the \( M^+ \) and \( NO_2^- \) ions from the neutral fragments. The second contribution, \( \Delta E_2 \), would correspond to the interaction between both ions.

\[
\Delta E = (\Delta E_1 + \Delta E_2)
\]

\( \Delta E_1 \) includes the first ionization potential of the metal atom and the adiabatic electron affinity of \( NO_2^- \). This second term remains constant along the group so that the variation of \( \Delta E_1 \) is determined by the ionization potential of the metal. \( \Delta E_2 \) is the formation energy of \( NO_2^- \) relative to the \( M^+ \) and \( NO_2^- \) ions. Figure 3 represents the variation of \( \Delta E_2 \) with respect to the inverse of the \( M-O \) bond distance for the studied complexes. The observed linear variation corresponds to what is expected for complexes with an important ionic nature. The variation of \( \Delta E_2 \) for Mg, Ca, and Sr complexes is determined by the \( \Delta E_2 \) term. 

Conclusions

The structure, binding energies, and vibrational frequencies of different coordination modes have been determined for the M\( NO_2 \) system (\( M = Be, Mg, Ca, Sr \)). The \( \eta^1\cdot\cdot\cdot O \) coordination is the most stable one for all the metals studied, as was previously found for the alkali and the Cu and Ag nitrite complexes. In the case of Mg, Ca, and Sr, the ground state is a \( \tilde{A}_1 \) state while for Be it is a \( \tilde{B}_1 \) state. This \( \tilde{B}_1 \) state presents a different bonding mechanism, and it is geometrically very different from the \( \tilde{A}_1 \) state. The B3LYP values for the binding energy obtained with a double-\( \zeta \) plus polarization quality basis set are very similar to those obtained at the MCPF level with a large ANO basis set. Our best calculation for the \( D_0 \) binding energies are 77 kcal mol\(^{-1}\) for Be\( NO_2 \), 53 kcal mol\(^{-1}\) for Mg\( NO_2 \), 69 kcal mol\(^{-1}\) for Ca\( NO_2 \), and 71 kcal mol\(^{-1}\) for Sr\( NO_2 \). The variation of the binding energies agrees with a metal-\( \cdot \)-ligand bond of basically ionic character.

Acknowledgment. This work has been financially supported by DGICYT (PB95-0640) and CIRIT (SGR95-00401). Computer time from the Centre de Supercomputació de Catalunya (CESCA) is gratefully acknowledged. L.R. gratefully acknowledges the Spanish Ministry of Education and Science for a doctoral fellowship.

References and Notes


Coordination of NO$_2$


(43) SWEDEN-MOLECULE is an electronic structure program written by the following: Almlof, J.; Bauschlicher, C. W.; Blomberg, M. R. A.; Chong, D. P.; Heilver, A.; Langhoff, S. R.; Malmqvist, P. A.; Rendell, A. P.; Siegbahn, P. E. M.; Taylor, P. R.


6. "Coordination of NO$_2$ to Cu and Mg in M(NO$_2$)$_2$ Complexes. A Theoretical Study"
Coordination of $\text{NO}_2$ to $\text{Cu}$ and $\text{Mg}$ in $M(\text{NO}_2)_2$ Complexes. A Theoretical Study$^1$

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Abstract

The geometries, vibrational frequencies and metal-ligand bond dissociation energies of 18 different structures of the $\text{Cu}(\text{NO}_2)_2$ complex have been studied. $\text{Mg}(\text{NO}_2)_2$ and $\text{Cu}(\text{NO}_3)_2$ have also been studied for comparison. The most stable structure of $\text{Cu}(\text{NO}_2)_2$ and $\text{Cu}(\text{NO}_3)_2$ corresponds to a $D_{2h}$ one with a coplanar $\eta^2$-O,O coordination for the two $\text{NO}_2$ ligands. For $\text{Mg}(\text{NO}_2)_2$ the most stable structure is a $D_{2d}$ one. The bonding in the $D_{2h}$ and $D_{2d}$ structures of $\text{Cu}(\text{NO}_2)_2$ is analyzed. For the $\text{MNO}_2$ systems the binding energy is very similar with both metals, while for the $M(\text{NO}_2)_2$ complexes the difference when changing the metal is very important. This behavior is related to the first and second ionization potentials of Cu and Mg. The computed vibrational frequencies are in good agreement with the available experimental data.

$^1$Enviado a Inorg. Chem.
Introduction

Transition metal-ligand interactions have been the focus of great attention during the last years, due to its great number of applications. These applications include many fields, such as biochemistry, environmental chemistry, development of new materials or catalysis. The determination of accurate binding energies and geometries of the metal-ligand systems are of great interest for the development of these applications. Computational chemistry methods have proved to be very efficient in obtaining binding energies and geometries. Moreover, the critical step in catalysis is often the breaking of the first bond of a small metal cluster, but in experimental studies the energy that is frequently determined is the average metal-ligand bond energy. So, it is important the understanding of how the bonding changes with the number of ligands.

Nitrite coordination complexes have been very studied from the earliest days of coordination chemistry due to this ability of NO₂ to coordinate to a metal in different ways. Each type of NO₂ coordination leads to different properties of the compound. Furthermore, nitrogen oxides (NOₓ, x=1,2) are unwanted pollutants that take part in important chemical reactions in the atmosphere, and in corrosion. Thus, coordination of NO₂ to a metal as well as the interaction of successive NOₓ ligands can provide important information for the understanding of these processes. The interaction of NO₂ with alkaline, alkaline-earth and transition metals, have been studied by several authors both, theoretically and experimentally.

Theoretical calculations for M(NO₂)₂ with M=Be, Mg and Ca systems have been
performed by Rossi et al. at the HF level. The results obtained for the Mg(NO$_3$)$_2$ system were used for the assignment of the FT-IR matrix isolation spectrum of the stable gas phase molecule Cu(NO$_3$)$_2$. From this assignment, they conclude that both NO$_3$ groups are equivalent and lie in the same plane, in agreement with earlier electron diffraction studies. On the other hand, experimental IR matrix studies have been carried out on the Cu(NO$_2$)$_2$ system by Worden and Ball. This system is very similar to Cu(NO$_3$)$_2$, and one would expect both molecules to have the same structure. However, the authors consider that the most probable structure for Cu(NO$_2$)$_2$ implies two different NO$_2$ groups.

In order to elucidate the structure of Cu(NO$_2$)$_2$, we have performed calculations using density functional and conventional ab initio methods. We have studied all the possible coordination modes of two NO$_2$ molecules to a Cu atom. The bonding mechanism of the most stable structure has been analyzed. We have also performed calculations on the Cu(NO$_3$)$_2$ and Mg(NO$_2$)$_2$ systems in order to compare them with the Cu(NO$_2$)$_2$ complex.

**Computational details**

Molecular geometries and harmonic vibrational frequencies have been determined using the density functional approach. In these calculations we have used the hybrid Becke’s three parameter exchange functional with the correlation functional of Lee Yang and Parr (B3LYP). This method has proved to provide reliable geometries and harmonic vibrational frequencies compared to more computational demanding ab initio correlated methods. However, in order to confirm the reliability of the B3LYP binding energies, we have also done single point calculations at the coupled cluster level with single and double excitations and a
perturbative estimate of the triple excitations\textsuperscript{26} (CCSD(T)) at the B3LYP equilibrium geometries. In the calculations at the CCSD(T) level we have correlated the 3d and 4s electrons of Cu and the 2s, 2p and 3s electrons of Mg. For N and O we have correlated the 2s and 2p electrons.

The same basis set has been used in these two levels of calculation. The N and O basis set is the (9s 5p)/[4s 2p] set developed by Dunning,\textsuperscript{27} supplemented with a valence diffuse function ($\alpha_o=0.0639$ for nitrogen and $\alpha_o=0.0845$ for oxygen) and one d polarization function ($\alpha=0.80$ for nitrogen and $\alpha=0.85$ for oxygen). This basis set is referred to as D95+* in the GAUSSIAN-94 program.\textsuperscript{28} The Cu basis set is a [8s 4p 3d] contraction of the (14s 9p 5d) primitive set of Wachter\textsuperscript{29} supplemented with two diffuse p and one diffuse d function.\textsuperscript{30} The Mg basis set is the (12s 9p)/[6s 5p] set of McLean and Chandler\textsuperscript{31} supplemented with a d polarization function ($\alpha=0.28$). The final basis sets are of the form (10s 6p 1d)/[5s 3p 1d] for N and O, (14s 11p 6d)/[8s 6p 4d] for Cu and (12s 9p 1d)/[6s 5p 1d] for Mg.

Single-point CCSD(T) calculations using a larger basis set have also been carried out for the most stable structure of each complex. In these calculations the Cu basis set is further augmented by a single contracted set of f polarization functions that is based on a three-term fit to a Slater-type orbital, which leads to a (14s 11p 6d 3f)/[8s 6p 4d 1f] basis set.\textsuperscript{32} For Mg we have used the (16s 12p 3d 2f)/[6s 5p 3d 2f] basis set of Dunning referred as cc-pVQZ in MOLPRO 96 program.\textsuperscript{33} For N and O we have used the (10s 5p 2d 1f)/[4s 3p 2d 1f] basis set of Dunning augmented with one diffuse s and one diffuse p functions.\textsuperscript{34} This basis set, augmented with one diffuse d and one diffuse f functions, is referred to as aug-cc-pVTZ.
The B3LYP calculations were performed using the GAUSSIAN-94\textsuperscript{28} program and open shell calculations were based on a spin unrestricted treatment, while the CCSD(T) results were performed with the MOLPRO\textsuperscript{33} program and were based on a spin restricted formalism.

**Results and discussion**

Figure 1 shows the four different coordination modes of NO\textsubscript{2} to a metal atom considered in our study. NO\textsubscript{2} can act both as a monodentate ligand or as a bidentate ligand when interacting with a metal atom. As a monodentate ligand, NO\textsubscript{2} can interact with the metal through the oxygen (\(\eta^1\)-O) or through the nitrogen (\(\eta^1\)-N). As a bidentate ligand, it can interact with the two oxygens (\(\eta^2\)-O,O) or with one nitrogen-oxygen bond (\(\eta^2\)-N,O). In the present work we have investigated all the possible structures that can be obtained with two NO\textsubscript{2} molecules coordinated to a Cu atom combining the four coordination modes shown in Figure 1 and considering for each case two different orientations for the NO\textsubscript{2} ligands: coplanar and perpendicular.

Among all the possible structures, only 18 have been found as stationary points on the potential energy surface of the Cu(NO\textsubscript{2})\textsubscript{2} system. The B3LYP relative energies of these structures are shown in Table 1. Figure 2 shows the B3LYP geometrical results for the structures characterized as energy minima. It can be observed in Table 1 that the most stable structure has D\textsubscript{2h} symmetry and corresponds to the two NO\textsubscript{2} ligands bonded to the Cu atom with the \(\eta^2\)-O,O coordination in the same plane (AA structure). The D\textsubscript{2d} structure with the two NO\textsubscript{2} ligands acting with \(\eta^2\)-O,O coordination, in perpendicular planes (AAp structure) is 23.7 kcal mol\textsuperscript{-1} above the AA structure. In general, the most stable structures are those in which one
of the two NO$_2$ fragments acts with the $\eta^2$-O,O coordination. The less stable structures are, in general, those with one of the two NO$_2$ fragments coordinated through the N atom ($\eta^1$-N coordination).

The geometry parameters of the $\eta^2$-O,O moiety in all structures are very similar to those computed for free NO$_2$ ($r$(NO)=1.270 Å and $\angle$ONO=116.4°). In the fragments with $\eta^2$-N,O and $\eta^1$-O coordination the symmetry between the two NO bonds of each NO$_2$ has been broken, however, we can see that the ONO angle in the $\eta^1$-O coordinations is close to the value of this angle in NO$_2^-$, while in the $\eta^2$-N,O coordinations the ONO angle lies within the values obtained for NO$_2^-$ and NO$_2$ ($\angle$ONO=133.7°). This shows that the bonding between the Cu atom and the two NO$_2$ molecules has an important ionic contribution. Thus, the most favorable structure for the ionic interaction is the AA structure where the metal atom interacts with the four oxygen atoms. The second most favorable ionic interaction takes place in the $\eta^1$-O coordination. The few exceptions to this general observation are due to the differences in the metal-ligand covalent interactions.

Let us now analyze the bonding in the $^2$B$_{3g}$ ground state of the most stable $D_{2h}$ structure, AA, and in the $^2$B$_2$ state of the $D_{2d}$ structure, AA$^p$. Figure 3 shows a schematic orbital interaction diagram between Cu and two NO$_2$ molecules both for the $D_{2h}$ and $D_{2d}$ structures. The bonding in the $D_{2h}$ structure can be described as the interaction of the $^2$D($d^9$) state of Cu$^{2+}$ and the (NO$_2$)$_2$$^2$- fragment. It can be observed in Figure 3 that the open shell in this structure arises from a three-electron interaction between the $b_{3g}$ symmetry adapted combination of the 4b$_2$ orbitals of the NO$_2$ molecules and the $d_{yz}$ orbital of the metal. Moreover, there is a very important donation from the $a_g$ combination of the 6a$_1$ orbitals of NO$_2$ to the 4s metal orbital.
The bonding can also be viewed as the interaction of the \( ^3D \) \((d^9s^1)\) state of Cu\(^+\), where there is a 3d-4s promotion in the metal in order to reduce repulsion with the ligands, and the \((\text{NO}_2)_2\) fragment. The metal Mulliken population analysis shows a situation in between both descriptions. The metal population is \( 4s^{0.75} \) 3d\(^{0.39}\) and the unpaired electron is distributed 0.6 in the metal and 0.4 in the ligands. If we consider the \(^2B_2\) state of the \(D_{2d}\) structure, it can be observed that the open shell arises from a three-electron interaction of the \(d_{xy}\) orbital of the metal and the \(b_2\) combination of the \(6a_1\) orbitals of \(\text{NO}_2\), and that there is also an important donation from the ligands to the 4s orbital of Cu\(^{2+}\).

The orbital of \(\text{NO}_2\) that has the larger overlap with the metal is the \(4b_2\) orbital. Thus the orbitals of the \((\text{NO}_2)_2\) fragment that interact more strongly with the metal atom are \(4b_{3g}\) and \(4b_{2u}\) in the \(D_{2h}\) structure, and \(5e\) in the \(D_{2d}\) one. The energy difference between both structures mainly arises from the interaction of these orbitals with the metal. For the \(D_{2d}\) structure the \(5e\) orbitals of the \((\text{NO}_2)_2\) fragments form two destabilizing four-electron interactions. On the other hand, in the \(D_{2h}\) structure the \(4b_{3g}\) orbital forms one three electron interaction, and the \(4b_{2u}\) orbital remains in the complex as a non bonding orbital. So, the \(D_{2d}\) structure is destabilized with respect to the \(D_{2h}\) one due to a larger repulsive metal-ligand interaction involving the 3d electrons of the metal.

The examination of the orbital interaction diagram of the \(D_{2d} \text{Cu(\text{NO}_2)}_2\) complex shows that it is possible that the ground state is not the one considered but a \(^2E\) state in which the open shell orbital would be one of the \(7e\) orbitals while the \(7b_2\) orbital would be doubly occupied. We have carried out the calculation of the \(^2E\) state starting from the geometry of the \(^2B_2\) state. At this geometry, the \(^2E\) state is 1.5 kcal mol\(^{-1}\) higher in energy than the \(^2B_2\) state.
Geometry relaxation reduce the $D_{2d}$ symmetry to $C_{2v}$. The optimization leads to a structure corresponding to a $^2B_2$ state in $C_{2v}$ symmetry that is 16 kcal mol$^{-1}$ higher in energy than the global $D_{2h}$ minimum. This $C_{2v}$ structure has an imaginary frequency associated to a rotation that connects two equivalent $D_{2h}$ minima. In any case, both if the ground state of the $D_{2d}$ structure is a $^2B_2$ or a $^2E$ state, the discussion about the interactions of the (NO$_2$)$_2$ fragment with the metal based on the orbital interaction diagram presented in Figure 3 would be similar.

Let us now consider a system where the metal atom has no d occupied orbitals, such as the Mg(NO$_2$)$_2$ complex. Figure 4 shows the B3LYP optimized geometries for the $D_{2h}$ and $D_{2d}$ structures of the Mg(NO$_2$)$_2$ system. The computed values for the geometrical parameters are almost identical for both structures. In contrast to the Cu(NO$_2$)$_2$ system for Mg(NO$_2$)$_2$ the $D_{2d}$ structure is the global minimum, the $D_{2h}$ structure being a transition state that connects two equivalent $D_{2d}$ minima. The energy difference between both structures is only 2.5 kcal mol$^{-1}$ at the B3LYP level. In the Mg(NO$_2$)$_2$ complex there are no occupied d orbitals on the metal and, therefore, the order of stability is determined by the steric repulsion between the ligands. This repulsion is slightly larger in the $D_{2h}$ structure than in the $D_{2d}$ one.

The only experimental data available for Cu(NO$_2$)$_2$ correspond to vibrational frequencies measured in Ar matrix by Worden and Ball. These authors suggest that in the Cu(NO$_2$)$_2$ complex the two NO$_2$ ligands would be coordinated in different ways. On the other hand, the gas phase structure of Cu(NO$_3$)$_2$ determined from electron diffraction experiments shows a $D_{2h}$ structure in which the coordination mode of the two NO$_3$ ligands is the same. We have calculated the $D_{2h}$ structure for the Cu(NO$_3$)$_2$ molecule and the obtained geometry is shown in Figure 5. We can see that the computed results are in very good agreement with the
gas phase experimental geometry of the Cu(NO$_3$)$_2$ molecule. The ground state of this molecule is a $^2B_{3g}$ state, as in Cu(NO$_2$)$_2$, and the bonding mechanism is the same in both cases. Thus, one can conclude that the most stable structure of the Cu(NO$_2$)$_2$ system should also have $D_{2h}$ symmetry, with two equivalent NO$_2$ ligands, as determined by our calculations.

The harmonic vibrational frequencies computed for the ground state structure of Cu(NO$_2$)$_2$ and Mg(NO$_2$)$_2$ complexes are presented in Table 2. It can be observed that for both systems the values for the NO symmetric stretching are larger than the values for the NO asymmetric stretching, the difference between both frequencies being small. The same behavior is observed for free NO$_2^-$, while for NO$_2$ the ordering between both NO stretching frequencies is reversed and the difference between them is large. These facts confirm again that the NO$_2$ fragments of the complex have an important NO$_2^-$ character.

Worden and Ball reported the infrared spectra of NO$_2$ reacting with vaporized Cu and condensed together in Ar matrices. Three frequencies were assigned to the Cu(NO$_2$)$_2$ system: 1214, 1192 and 1173 cm$^{-1}$. Three possible structures are considered: Cu$^{2+}$(NO$_2$)$_2$, Cu$^+(N_2O_4)$, and Cu$^+(NO_2)NO_2$, where both NO$_2$ molecules are not equivalent. The IR data do not allow to discriminate between them, but these authors consider the later as the most probable one. Thus, they assign the frequency of 1214 cm$^{-1}$ to the asymmetric NO stretching of NO$_2^-$, while the other two frequencies are assigned to the same absorption but shifted due to structural isomerism of the NO$_2$ units or due to matrix effects. We have performed calculations on the Cu$^+(N_2O_4)$ system and the results show that all the possible structures lie higher in energy than the Cu(NO$_2$)$_2$ $D_{2h}$ structure (between 36.8 kcal mol$^{-1}$ and 50.9 kcal mol$^{-1}$, depending on the coordination). On the other hand, the structures shown in Table 1 with both NO$_2$ molecules
coordinated in different ways lie also higher in energy. The same assignment made by Worden and Ball for the three observed frequencies would be valid for a \( \text{Cu}^{2+}(\text{NO}_2)_2 \) structure. So, our results in favor of a \( D_{2h} \) structure with two equivalent \( \text{NO}_2 \) ligands for the \( \text{Cu}(\text{NO}_2)_2 \) system can be compatible with the IR results reported by Worden and Ball. Our calculated value for the asymmetric NO stretching, 1254 cm\(^{-1}\), is in excellent agreement with the experimental value. Moreover, for \( \text{Cu}(\text{NO}_3)_2 \), the computed vibrational frequencies presented in Table 3 are in excellent agreement with the experimental values reported by Rossi et al.\(^{21}\)

Table 4 presents the binding energies computed with respect to the neutral fragments of the ground state structure of the complexes \( \text{Cu}(\text{NO}_2)_2 \), \( \text{Cu}(\text{NO}_3)_2 \) and \( \text{Mg}(\text{NO}_2)_2 \). The binding energies are computed both at the B3LYP and CCSD(T) levels. By comparing the B3LYP and CCSD(T) values obtained with the same basis set, one can observe that the computed values at the CCSD(T) level are always larger than the B3LYP ones. However, the behavior of Cu and Mg complexes is different. For \( \text{Mg}(\text{NO}_2)_2 \), the difference between the B3LYP and CCSD(T) values is very small while in the case of the Cu complexes, the differences are larger. As we have shown in our previous study,\(^{20}\) these differences in Cu complexes are due to the different description of the first and second ionization potentials of Cu at the B3LYP and CCSD(T) levels.

Table 4 shows that the values of the metal-ligand bond dissociation energy of \( \text{CuNO}_2 \) and \( \text{MgNO}_2 \) are very similar, while the value for \( \text{CuNO}_3 \) is much larger. The formation of an ionic complex between two fragments, M and L, can be conceptually decomposed in two steps. The first one consists on the formation of the \( M^+ \) and \( L^- \) ions. In the second step both ions interact to yield the complex. The energy associated with the first step would be \( E_1(M)- \)
E_{eq}(L). Table 5 shows the ionization potentials of Cu and Mg and the electron affinities of NO_{2} and NO_{3}. It can be observed that the first ionization potentials of Mg and Cu are very similar, so that the energy necessary to ionize the fragments will be very similar in both cases. Moreover, as we have already shown,^{16} the interaction energy between M^{+} and L^{-} is also very similar in both cases. As a result, the M-NO_{2} dissociation energies of CuNO_{2} and MgNO_{2} are quite similar. The difference between the metal-ligand bond dissociation energies of CuNO_{2} and CuNO_{3} can be understood from the fact that the electron affinity of NO_{3} is larger than that of NO_{2} (see Table 5).

For the total binding energy of the M(NO_{X})_{2} complexes, we must consider the sum of the first and second ionization potentials of the metal and twice the electron affinity of NO_{X}. The total M-(NO_{X})_{2} binding energies show important differences between Cu(NO_{2})_{2} and Mg(NO_{2})_{2}. The reason for this difference is that the second ionization potential of Cu is much larger than the one corresponding to Mg. However, the difference between the second ionization potentials of Cu and Mg (about 100 kcal mol^{-1}) is notably larger than the difference between the total binding energy of Cu(NO_{2})_{2} and Mg(NO_{2})_{2} (less than 50 kcal mol^{-1}). This fact indicates that the M^{2+}-2L^{-} interaction term has to be larger for Cu(NO_{2})_{2} than for Mg(NO_{2})_{2}. This is mainly due to a larger ligand to metal charge transfer in the Cu complex. The Mulliken population analysis shows that the net charges on the metal in the M(NO_{2})_{2} complexes are 0.45 for Cu and 0.90 for Mg at the B3LYP level of calculation. The Cu-(NO_{3})_{2} binding energy increases with respect to the Cu-(NO_{2})_{2} value, again due to the larger electron affinity of NO_{3}. As a consequence of these considerations, the binding energy for the second NO_{X} (see Table 4) in the Cu complexes is smaller than the value for the first one, while in Mg(NO_{2})_{2} the value is much larger.
Let us now consider the basis set effect on the computed binding energies. Table 4 shows also the CCSD(T) values obtained with the larger basis set. It can be observed that the change in the metal-ligand bond dissociation energy of M-NO$_2$ is small when going from the smaller to the larger basis set. On the other hand, the values of the total binding energy of M(NO$_2$)$_2$ show larger differences. For Cu(NO$_2$)$_2$ the decrease of the energy is mainly due to the increase of the ionization potentials of Cu with the size of the basis set (see Table 5).

From this considerations, we can conclude that in Cu complexes the binding energies at B3LYP level are underestimated due to the large value of the ionization potentials of Cu. However, at CCSD(T) level the values are overestimated due to an underestimation of the ionization potential. This underestimation is partially corrected when increasing the size of the basis set, the CCSD(T) and B3LYP values approaching to each other.

**Conclusions**

The structure, binding energies and vibrational frequencies of the different coordination modes of Cu(NO$_2$)$_2$ and of the most stable structures of Mg(NO$_2$)$_2$ and Cu(NO$_3$)$_2$ have been determined. The D$_{2h}$ structure, with the NO$_2$ groups showing coplanar η$^2$-O,O coordination, is the most stable one for Cu(NO$_2$)$_2$, as in the case of Cu(NO$_3$)$_2$ for which experimental data are available. For Mg(NO$_2$)$_2$ the D$_{2d}$ structure is the most stable one. The different stability of the D$_{2h}$ and D$_{2d}$ structures in Cu(NO$_2$)$_2$ arises from the different interaction of the fragments with the d orbitals of Cu. The difference in Mg(NO$_2$)$_2$ is only due to steric interactions between the ligands since Mg does not have occupied d orbitals to interact with the NO$_2$ ligands. The computed frequencies are in good agreement with the experimental values. The binding
energies obtained at the B3LYP level with a relatively small basis set are in good agreement with the values obtained at the CCSD(T) level using a larger basis set.

Acknowledgments

This work has been financially supported by DGICYT (PB95-0640) and CIRIT (SGR95-00401). Computer time from the Centre de Supercomputació de Catalunya (CESCA) is gratefully acknowledged. L.R. gratefully acknowledges the Spanish Ministry of Education and Science for a doctoral fellowship.
References


1992, 1, 190.


Table 1: Computed relative energies of the stationary points found for \( \text{Cu(NO}_2\text{)}_2 \).

<table>
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<tr>
<th>Symmetry</th>
<th>State</th>
<th>([-\text{NO}_2\text{]}_1)</th>
<th>([-\text{NO}_2\text{]}_2)</th>
<th>(\Delta E/\text{kcalmol}^{-1})</th>
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<tr>
<td>AA</td>
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<td>(^2\text{B}_g)</td>
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<td>(\eta^2\text{-O, O} )</td>
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<td>(\eta^2\text{-N, O})</td>
<td>(\eta^2\text{-O, O} )</td>
</tr>
<tr>
<td>A Ax</td>
<td>(\text{D}_{2h})</td>
<td>(^2\text{B}_{1u})</td>
<td>(\eta^2\text{-O, O})</td>
<td>(\eta^2\text{-O, O} )</td>
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<td>(\eta^2\text{-O, O})</td>
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<td>ACp</td>
<td>(\text{C}_s)</td>
<td>(^2\text{A}'')</td>
<td>(\eta^2\text{-O, O})</td>
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\(^a\)First order saddle points.

\(^b\)Second order Saddle points
Table 2: Computed harmonic vibrational frequencies* for M(NO$_2$)$_2$, NO$_2$ and NO$_2^-$ in cm$^{-1}$.

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<th>NO sym.</th>
<th>NO sym.</th>
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<td>895(0)</td>
<td>1225(0)</td>
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<td>1348(60)</td>
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<td>Mg(NO$_2$)$_2$</td>
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<td>886(21)</td>
<td>1287(476)</td>
<td>1336(23)</td>
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<td>NO$_2^-$</td>
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<td>NO$_2^-$ exp.$^c$</td>
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*In parenthesis, the IR intensity of each frequency in km mol$^{-1}$.

$^b$Reference 36.

$^c$Reference 37.
Table 3: Harmonic vibrational frequencies\(^a\) for Cu(NO\(_3\))\(_2\) in cm\(^{-1}\).

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<tr>
<td>771(111)</td>
<td></td>
<td>NO(<em>2) def. (B(</em>{1u}))</td>
</tr>
</tbody>
</table>

\(^a\)In parenthesis, the IR intensity of each frequency in km mol\(^{-1}\).

\(^b\)O' indicates the terminal oxygen of the NO\(_3\) fragments.

\(^c\)Reference 21.
Table 4: Metal-ligand binding energies of $M(NO_x)_n$ complexes (in kcal mol$^{-1}$) computed at different levels of calculation.

<table>
<thead>
<tr>
<th></th>
<th>successive</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M-NO_x$</td>
<td>$MNO_x-NO_x$</td>
</tr>
<tr>
<td></td>
<td>B3LYP CCSD(T)$^a$</td>
<td>B3LYP CCSD(T)$^a$</td>
</tr>
<tr>
<td>$Cu(NO_2)_2$</td>
<td>49.2</td>
<td>72.3</td>
</tr>
<tr>
<td></td>
<td>57.2(56.1)</td>
<td>83.9(85.2)</td>
</tr>
<tr>
<td>$Cu(NO_3)_2$</td>
<td>37.4</td>
<td>71.6</td>
</tr>
<tr>
<td></td>
<td>43.8(36.9)</td>
<td>75.9</td>
</tr>
<tr>
<td>$Mg(NO_2)_2$</td>
<td>86.6</td>
<td>143.9</td>
</tr>
<tr>
<td></td>
<td>101.0(93.9)</td>
<td>159.8</td>
</tr>
</tbody>
</table>

$^a$In parentheses are shown the CCSD(T) values with the larger basis set.
Table 5: Computed ionization potential for the metals and adiabatic electron affinities of NO₅.

<table>
<thead>
<tr>
<th>metal</th>
<th>B3LYP</th>
<th>CCSD(T)ᵃ</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.03</td>
<td>7.06(7.15)</td>
<td>7.73ᵇ</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>20.80</td>
<td>19.62(20.00)</td>
<td>20.29ᵇ</td>
</tr>
<tr>
<td>Mg</td>
<td>7.73</td>
<td>7.54(7.58)</td>
<td>7.65ᵇ</td>
</tr>
<tr>
<td>Mg⁺</td>
<td>15.46</td>
<td>14.80(14.87)</td>
<td>15.03ᵇ</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NO₂, Eₑ/eV</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>2.36</td>
<td>2.12(2.13)</td>
<td>2.28ᶜ</td>
</tr>
<tr>
<td>NO₃</td>
<td>4.04</td>
<td>3.82(3.92)</td>
<td>3.92±0.2ᵈ</td>
</tr>
</tbody>
</table>

ᵃIn parentheses are shown the CCSD(T) values with the larger basis set.
ᵇReference 38.
ᶜReference 39.
ᵈReference 40.
Figure captions

Figure 1: Coordination modes of one NO$_2$ to the metal atom.

Figure 2: Computed structures of the different energy minima determined for the Cu(NO$_2$)$_2$ complex. Distances are in Angstroms and angles in degrees.

Figure 3: Diagram of the most important orbitals involved in the formation of the $D_{2h}$ and $D_{2d}$ structures of Cu(NO$_2$)$_2$.

Figure 4: Computed $D_{2d}$ and $D_{2h}$ structures Mg(NO$_2$)$_2$. Distances are in Angstroms and angles in degrees.

Figure 5: Computed $D_{2h}$ structure of Cu(NO$_3$)$_2$. In parentheses are shown the experimental values.$^{35}$ Distances are in Angstroms and angles in degrees.
"Coordination of NO$_2$ to Cu and Mg in M(NO$_2$)$_2$ ..."

Figure 1

\[ \eta^1\text{-N} \]

\[ \eta^1\text{-O} \]

\[ \eta^2\text{-O,O} \]

\[ \eta^2\text{-N,O} \]
Figure 2

"Coordination of NO₂ to Cu and Mg in M(NO₂)₂..."
"Coordination of NO\textsubscript{2} to Cu and Mg in M(No\textsubscript{2})_2 ..."
Figure 4
Figure 5
7. "Coordination of Cu\textsuperscript{+} Ions to Zeolite Frameworks Strongly Enhances their Ability to Bind NO\textsubscript{2}. An ab initio Density Functional Study"
Coordination of Cu\(^+\) Ions to Zeolite Frameworks Strongly Enhances Their Ability To Bind NO₂. An ab Initio Density Functional Study

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Received September 11, 1997. Revised Manuscript Received December 5, 1997

Abstract: Comparison is made of the interaction of NO₂ with Cu\(^+\) ions in the gas phase and inside zeolites using density functional theory (B3LYP functional). The zeolite is represented by a tritetrahedra model embedded in the periodic structure of zeolite ZSM-5 and by a free space cluster model. Both models yield virtually the same results. Cu\(^+\) is coordinated to two oxygen atoms of the zeolite framework only. For the complexes with NO₂, several minima and transition structures on the potential energy surfaces are localized. The naked Cu\(^+\) ion preferentially binds NO₂ in the \(\eta^1\)-O trans mode, while in zeolites the Cu\(^+\) site binds NO₂ in a \(\eta^2\)-O,O coordination. For the \(\eta^2\)-O,O structure the binding is three to four times stronger in the zeolite (43 kcal/mol) than in the gas phase which is due to a three-body zeolite framework—Cu\(^+\) ion—NO₂ interaction. \(d^{10}\)–\(s^1d^0\) promotion leads to a more favorable orbital interaction between Cu\(^+\) and NO₂ in the \(\delta^+\) state and, due to reduced repulsion, to a stronger electrostatic interaction between Cu\(^+\) and the zeolite framework.

1. Introduction

Transition metal cations show catalytic activity in different systems ranging from heterogeneous over homogeneous to biological. In recent years, it became possible to study the reactivity of naked (noncoordinated) transition metal cations. Despite a fascinating chemistry revealed by these studies, catalytic activity could be observed in exceptional cases only, see, e.g., refs 2 and 3. An example is the role that Cu\(^+\) ions play in the catalytic decomposition of NO₂—a mixture of NO and NO₂ of obvious environmental significance. Cu-exchanged zeolites, in particular Cu-ZSM-5, show a high and sustained activity. Many studies reached the conclusion that the Cu\(^+\) ion is in the core of the active sites of these catalysts.3–8 In contrast, Schwarz and co-workers did not find any catalytic activity when investigating the [Cu\(^+\), N, O] system in the gas phase.9 This highlights the important role that ligands play in activating transition metal cations.

Some activation of Cu\(^+\) and other transition metal ions by ligands has been observed before. The second water ligand was found to bind more strongly than the first one,10 in contrast to alkaline metal ions, for which the energies for adding the next ligand are steadily decreasing when adding an increasing number of ligands. Confirmation came from ab initio calculations11–13 which also provided the explanation:12 The unique feature of transition metal ions is their ability to reduce metal—ligand repulsion by sda hybridization. Since sda hybridization reduces the charge density along the \(\sigma\) axis, the second ligand binding energy can be larger than the first, because both ligands benefit from reduced repulsion while sharing the energetic cost of hybridization.12 We will show below that the much stronger activation of Cu\(^+\) ions by zeolite frameworks has a similar origin.

We study the interaction of NO₂ with Cu\(^+\) ions in the gas phase and in zeolites. We localize several stationary points on the potential energy surfaces by ab initio methods employing density functional theory (DFT). We find a dramatic increase of the binding energy of NO₂ on the Cu\(^+\) ion inside the zeolite compared with the naked Cu\(^+\) ion. For a realistic description of this effect it is vital to have a valid model of the active site. In agreement with previous theoretical studies14,15 we find that the Cu\(^+\) ion is coordinated to two lattice oxygen atoms of the zeolite framework only, in contrast to the Cu\(^2+\) ion which prefers a higher coordination. Two is an unusually low coordination number for Cu\(^+\), but it is confirmed by EXAFS studies on activated Cu-exchanged zeolites.16,17 Our description includes...
Figure 1. Predicted structures for the Cu⁺ site in zeolites (left) and for its complex with NO (right): (a) tritetrahedra model embedded into the periodic ZSM-5 structure and (b) zeolite framework represented by the shell-1.5 model.

The full periodic structure of the MFI framework (MFI is the common code for the framework type of ZSM-5 catalysts) for which we adopt the shell-model ion pair potential. We then determine the local structure of the Cu⁺ site by embedding a model consisting of three tetrahedra (Figure 1a) into the periodic MFI structure and treat it quantum mechanically. We use for this purpose a recently developed combined quantum mechanics/interatomic potential approach (QM-pot).18,19 We finally show that a virtually identical structure of the active site is obtained when using a nonembedded cluster model consisting of a central AlO₄ tetrahedron and two neighbored SiO₄ tetrahedra (Figure 1b). This model, shell-1.5, proved successful in previous studies20,21 and is used for the majority of structure predictions of the complexes of NO₂ with Cu⁺ in zeolites. We finally show that the effect of the zeolite framework as ligand is special. The increase of the binding energy predicted for the zeolite is by far larger than that predicted for Cu⁺ with two water molecules as ligands, even if we simulate the spatial arrangement of the two oxygen binding sites of zeolite frameworks by constraining the two water ligands to a bent configuration.

There is an increasing number of experimental and theoretical studies of the direct catalytic decomposition and the selective catalytic reduction of NOₓ. This is not the place to give a complete account, nor is our aim to study the whole mechanism. We focus here on NO₃, which is of interest not only as a pollutant itself but also as the product of the catalytic oxidation of NO.22 Moreover, among several proposed mechanisms for the NO direct decomposition, the formation of the ZCu-NO₂ complex has been suggested by several authors.23,24 It can react with NO to form the ZCu(NO₂)NO intermediate which decomposes into molecular nitrogen and oxygen.

Among the computational studies devoted to the problem,14,15,25-32 two are of particular relevance to our study. The DFT study of Yokomichi et al. compares the binding of NO to the naked Cu⁺ ion and to the [HO₂Al(OH)₂]⁻Cu⁺ model for the Cu⁺ site in zeolites.30 They find enhanced binding although by far not as dramatic as found for NO in the present study. They explain the effect by destabilization of d-orbitals due to interactions with the oxygen atoms of the zeolite skeleton. As...
part of their comprehensive analysis of possible intermediates in the NO\textsubscript{2} decomposition process, Trout et al. study several isomers of the complex of NO\textsubscript{2} with a model of the Cu\textsuperscript{+} ion in ZSM-5.\textsuperscript{14} Their and our results for the structures and binding energies are remarkably similar, although there are some differences in the method used and the model adopted. Trout et al. use the local density approximation (LDA) and a different basis set. Their cluster model has the central Al\textsubscript{2}O\textsubscript{3} tetrahedron surrounded by four SiO\textsubscript{2} tetrahedra, and the terminating OH groups are fixed at observed atomic positions.

2. Details of Calculations

DFT (density functional theory) calculations have been performed using the B3LYP functional which proved successful for a broad class of problems including transition metals,\textsuperscript{33,35} and which is a major improvement compared to LDA. The following basis sets optimized by Ahlrichs and co-workers have been adopted:\textsuperscript{36} Cu – double-\textgamma augmented with a p function (exponent 0.155 065), i.e., \([8s6p3d]\); NO\textsubscript{2} – triple-\textgamma; zeolite models – triple-\textgamma on oxygen and double-\textgamma on all other atoms. Polarization functions with exponents 0.25, 0.30, 1.2, 1.0, and 0.8 are added to all Si, Al, O, N, and H atoms, respectively. DFT calculations are made using the TURBODFT code.\textsuperscript{37} The coupled cluster CCSD(T) calculations follow in all details the description in ref 35 and use the GAUSSIAN code.\textsuperscript{38}

Our calculations on the Cu(\textsubscript{2}H\textsubscript{2})O and Cu(\textsubscript{2}H\textsubscript{2}O\textsubscript{2}) complexes yield 43.8 and 44.6 kcal/mol for the binding of the first and second water ligand, respectively—slightly larger values than computed with the MCPF method by Bauschlicher et al. (40.5 and 41.3 kcal/mol)\textsuperscript{12} or than inferred from experiments by Mangera et al. (35 \pm 3 and 39 \pm 3 kcal/mol).\textsuperscript{10} We correctly reproduce the increased binding energy for the second ligand.

For describing the periodic zeolite structure both in the combined QM-pot approach and in the pure potential function energy minimizations the shell-model ion pair potential\textsuperscript{39} is used. The combined QM-pot calculations make use of the TURBODFT\textsuperscript{37} and the GULP\textsuperscript{40} codes in the quantum and the shell-model ion pair potential part, respectively. The parameters for the ions of the anionic zeolite framework have been found by a fit to DFT data obtained with the same basis set as used here.\textsuperscript{41}

The parameters for Cu\textsuperscript{+} are taken from ref 42. The parameters used are summarized in the Supporting Information.

3. Results and Discussion

3.1. Structure of the Cu\textsuperscript{+} Site

First we performed a lattice energy minimization using the shell-model ion pair potential alone to determine the structure of the Cu\textsuperscript{+} site in a periodic ZSM-5 environment. One Al atom per unit cell was substituted into the T12 position of the orthorhombic structure of MFI (96 T0\textsubscript{2}O\textsubscript{2} formula units, hence the Si/Al ratio is 95).\textsuperscript{43} This position was also considered before,\textsuperscript{14} and there is no reason to believe that the results will critically depend on the substitution site. It was found that the relative energies differ by no more than 5 kcal/mol when substituting Al in any of the 24 different sites. The T12 site was found only about 2.5 kcal/mol above the minimum energy substitution site. The lattice energy minimization was made in P1 symmetry and resulted in a monoclinic structure. The Cu\textsuperscript{+} ion is found coordinated to two lattice oxygen atoms only. Even if the optimization was started with structures in which the Cu\textsuperscript{+} ion was inside a five-membered ring the same 2-fold coordinated structure was found.

Our observations are slightly at variance with the report of Sayle et al.\textsuperscript{44} A more comprehensive simulation of a large variety of different Cu sites in ZSM-5 by a shell-model potential with parameters slightly different from ours also yielded dicoordinated Cu\textsuperscript{+} sites, but the majority of Cu\textsuperscript{+} sites had a larger coordination number. Note that the simulations of Sayle et al. also allowed OH\textsuperscript{−} species to coordinate to the Cu\textsuperscript{+} ion. Next we defined a triitetrahedra cluster (T3), \([\text{H}_{2}\text{O}]\text{SiO}\text{(OH)}_{2}\text{Si(OH)}_{3}\text{]+}^{-}\), around the Cu\textsuperscript{+} site (Figure 1a), and a structure refinement was made using the combined QM-pot approach. The 2-fold coordination remained unchanged, and the Cu\textsuperscript{+}−Al and Cu\textsuperscript{+}−O distances changed to 2.8 and 2.05 Å, respectively. Trout et al. also found a 2-fold coordinated structure with slightly shorter bond distances. The Al−O distance was 2.4 Å, and two slightly different Cu−O bond distances of 1.95 and 1.86 Å were obtained. Hartner−Fock calculations on cluster models\textsuperscript{15} also yield a 2-fold coordination of Cu\textsuperscript{+} with Cu−O distances of 2.10 and 2.16 Å. These results are in agreement with the experimental structure information available. From \(37\text{Al}^{16}\text{Cu}\) SEDOR NMR experiments on Cu−ZSM5 a Cu−Al distance of 2.3 ± 0.2 Å has been inferred.\textsuperscript{45} The EXAFS experiments of Yamashita et al.\textsuperscript{17} and Lambert et al.\textsuperscript{16} yield Cu−O distances of 1.94 and 2.00 Å, respectively. Other EXAFS and XANES data imply a coordination number of 2.1 and a mean Cu−O distance of 1.94 Å.\textsuperscript{46,47}

Figure 1b shows the structure of the CuZ site obtained by DFT calculations when the zeolite is represented by the shell-1.5 model. The binding energy of Cu\textsuperscript{+} to the shell-1.5 model is 160 kcal/mol. This model is OH terminated at the central Al atom, but H-terminated at the Si atoms. The tri-tetrahedra model adopted in the embedded cluster calculation is OH terminated on both the Al and the Si atoms. There is good agreement between this free cluster optimization and the embedded cluster calculations. Embedding has two effects. It constrains the relaxation of the cluster atoms (since they "feel" that they are part of the zeolite framework) and it adds long-range interactions. Comparison of parts a and b of Figure 1 shows that this has little effect on the coordination type and on the strength of the interaction. The Cu−O distances shrink by 2−3% only. We conclude that the shell-1.5 model without embedding provides a reasonable first information on the effect of coordinating the Cu\textsuperscript{+} ion to the MFI framework.
Table 1. Binding Energies of NO₂ (kcal/mol), Relative Energies w.r.t. the Most Stable Structure Are Given in Parentheses

<table>
<thead>
<tr>
<th>structure</th>
<th>CCSD(T)/B3LYP</th>
<th>B3LYP</th>
<th>ZCu-NO₂ this work</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>η₁⁻O trans</td>
<td>19.6 (0.0)</td>
<td>26.4 (0.0)</td>
<td>30.3 (12.4)</td>
<td></td>
</tr>
<tr>
<td>η₁⁻O cis</td>
<td>17.1 (2.4)</td>
<td>24.3 (2.1)</td>
<td>30.0 (12.7)</td>
<td></td>
</tr>
<tr>
<td>η₁⁻N</td>
<td>7.7 (11.9)</td>
<td>16.4 (10.0)</td>
<td>25.1 (17.6)</td>
<td></td>
</tr>
<tr>
<td>η₂⁻NO₂</td>
<td>7.1 (12.5)</td>
<td>14.4 (10.0)</td>
<td>35.8 (6.9)</td>
<td></td>
</tr>
<tr>
<td>η₂⁻O,O</td>
<td>10.4 (9.1)</td>
<td>14.0 (12.4)</td>
<td>10.7 (32.0)</td>
<td></td>
</tr>
<tr>
<td>η₂⁻N,O</td>
<td>2A₁</td>
<td>10.5 (15.9)</td>
<td>42.7 (0.0)</td>
<td></td>
</tr>
<tr>
<td>η₂⁻O,O</td>
<td>2B₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Results of Mulliken Population Analysis and, in Parentheses, a Population Analysis Based on Occupation Numbers (Ref 48)

<table>
<thead>
<tr>
<th></th>
<th>charge</th>
<th>spin density</th>
<th>metal orbital population</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZCu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>η₁⁻O,O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>η₁⁻N</td>
<td>2A₁</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>ZCuNO₂</td>
<td>2A'</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>η₁⁻N</td>
<td>2B₂</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>η₁⁻N</td>
<td>2A''</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>ZCuNO₂</td>
<td>2A''</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>η₁⁻N</td>
<td>2B₂</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>ZCuNO₂</td>
<td>2A''</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

Different coordination modes have been found: the bidentate η₁⁻O,O and η₁⁻N,O coordinations and the monodentate η¹⁻O (cis and trans) and η¹⁻N coordinations. Only the η₁⁻O and η₁⁻N modes are minima on the ground-state potential energy surface. The most stable isomer is η₁⁻O (trans), with η₁⁻O (cis) being only 2.1 kcal/mol higher in energy. The η₁⁻O state is the transition state connecting the two equivalent η¹⁻O cis isomers, while the η₁⁻N one corresponds to the η₁⁻O (trans) → η₁⁻N isomerization. The η₁⁻N structure is a very shallow minimum with almost the same energy as the η₁⁻N transition structure. Comparison is made with CCSD(T) single point results. The binding energies are reduced in all cases, but the relative stability of the local minima is maintained and the transition structures remain above the minima they connect. The bonding in the ground state (2A' and 3A₁) is mainly noncovalent and arises from the interaction of the 1s(10s) state of Cu⁺ and the 2A₁ ground state of NO₂. The relative stability of the different isomers can be understood in terms of metal−ligand repulsion and electrostatic attraction. Table 2 shows for the η₁⁻O,O and η₁⁻N,O transition structures that—in agreement with this view—the metal orbital population stays close to d¹⁰s⁰, the unpaired electron remains localized on NO₂, and the positive excess charge remains on Cu. Consistently, the positive of the NO₂ fragment in the complex is very similar to that of the 2A₁ state of free NO₂ at the same level of calculation (Table 3). The 2B₂ state of the η₁⁻O,O coordination is a minimum on an excited potential energy surface. It can be viewed as the interaction of the 1s(10s) state of Cu⁺ with the 2B₂ state of NO₂. The geometric structure of the NO₂ fragment in this state is very similar to that of the 2B₂ state of free NO₂ (Table 3). The left-hand side of Figure 3 shows the most relevant orbitals involved in the bond between Cu⁺ and NO₂. The orbital occupation is given for the 2A₁ ground state of NO₂. In the 2B₂ excited state the 4b1 orbital is singly occupied, while the 6a1 orbital is doubly occupied. This opens the possibility for an electron donation from the doubly occupied 6a1 orbital of...
“Coordination of Cu⁺ Ions to Zeolite ...”

**Table 3. Bond Distance (Å) Bond Angle (deg), and Electron Affinity (EA, eV) for NO₂⁻**

<table>
<thead>
<tr>
<th></th>
<th>r(NO)</th>
<th>∠ONO</th>
<th>EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂⁻</td>
<td>1.194</td>
<td>134.2</td>
<td>42.0</td>
</tr>
<tr>
<td>obsd</td>
<td>(1.194)²</td>
<td>(133.9)²</td>
<td>(1.02)²</td>
</tr>
<tr>
<td>calc</td>
<td>(1.270)²</td>
<td>(100.6)²</td>
<td>(2.28)²</td>
</tr>
<tr>
<td>NO₂⁺</td>
<td>1.264</td>
<td>116.0</td>
<td>1.85</td>
</tr>
<tr>
<td>obsd</td>
<td>(1.25 ± 0.02)²</td>
<td>(117.5 ± 2.0)²</td>
<td>(2.28)²</td>
</tr>
</tbody>
</table>

* Reference 49. ² CCSD method, ref 50. ³ Reference 51. ⁴ Reference 52. ⁵ Observed results or other computed results in parentheses.

Figure 3. Diagram of the most important orbitals involved in the formation of the bond between the Cu⁺ site and NO₂⁻.

NO₂⁻ to the 4s orbital of Cu and some back-donation from the 3d orbital on Cu to the singly occupied 4b_
orbital on NO₂. In effect, there is some 3d—4s promotion (d-population about 9.5, cf. Table 2), and this state can also be described as bonding between Cu⁺ (d⁹) and the 2A₁ state of NO₂⁻.

3.3. Complexes of NO₂⁻ with Cu⁺ in Zeolites. Figure 4 shows the structures and Table 1 the binding energies for the complexes of NO₂⁻ with the Cu⁺ attached to the zeolite model (CuZ). When coordinated to the zeolite framework, the Cu⁺ ion interacts more strongly with NO₂⁻. In general, the distances between Cu and NO₂ are shorter, and the binding energies are larger. Major changes on the topology of the potential energy surfaces occur. The η¹-O minimum structures (cis and trans) and the η²-O,O transition structure (A₁ — A² states) show the least changes. In the former the bond becomes stronger, while the latter is further destabilized. For the η²-N,O structure the binding is significantly increased and it becomes a local minimum now, while it was a transition structure in the gas-phase complex. The η¹-N coordination is also stabilized but not as much as the η²-N,O structure. In the zeolite complex it becomes a transition structure connecting the two symmetrical η²-N,O minima, while it was a local minimum in the gas-phase complex.

A particular striking case is the 2B₂ state of the η²-O,O complex. In the gas phase it was least binding and an excited state. In the zeolite complex we also find the corresponding state, 2A'',. However, now it is the most stable one and represents the global minimum. It is four times more stable than the 2B₂ state and three times more stable than the 2A₁ state of the η²-O,O complex in the gas phase. Compared with the most strongly bound gas-phase complex (η¹-O trans) the binding energy increases by 62%. To confirm this unusually strong binding effect, we have investigated the η²-O,O complex of NO₂⁻ by the embedded cluster method. NO₂⁻ was interacting with the quantum part only, but relaxation of the positions of the nuclei of the embedded model was constrained by forces from all the atoms of the periodic zeolite framework. Figure 1a shows the structure found which is virtually identical with that of the complex involving the shell-1.5 model shown in Figure 1b. The binding energy, 42.0 kcal/mol, differs by less than 1 kcal/mol from the result in Table 1. It remains to be seen if this agreement between a free space cluster model which does not represent any specific site and a specific model (T12 site in ZSM-5) persists if additional sites of the MFI framework or different frameworks are considered. If so, there would be an interesting implication: The activation of Cu⁺ ions by zeolite frameworks for NO₂⁻ binding is not connected with a particular site in a particular framework. If, e.g., ZSM-5 proves to be a particular efficient Cu-containing catalyst, this may have other reasons than different intrinsic properties of the different Cu⁺(≡SiO₂)₂Al(OH)₃ sites.

Before, Yokomichi et al. found that Cu⁺ attached to a (OH)₂Al(OH)₃⁻ model of the zeolite framework binds NO more strongly than the naked Cu⁺ ion. The increase was from 38 to 51 kcal/mol—not as large as found here for NO₂⁻.

To analyze the dramatic effect of binding energy increase, we look at the relevant orbitals of NO₂⁻ and ZCu shown in Figure 3. Note that the orbital occupancies shown apply to only one of the different situations discussed below. Z in ZCu stands for the shell-1.5 zeolite model. In the ground state of ZCu the 20a'' orbital is the HOMO of Cu⁺ and doubly occupied. This orbital is mainly the dₓₒ orbital of Cu⁺ mixed with the 4pₒ orbital to polarize away from Z— to reduce repulsion. Thus, the side opposite to the zeolite surface is a high electron density region,
and there is an increased repulsion for the NO$_2$ ligand approaching the Cu$^+$ ion on the zeolite wall. The repulsion with all ligands can be reduced by 3d–4s promotion. In the ZCu model this promotion becomes much easier (1.9 eV) than in the naked Cu$^+$ ion (2.6 eV). We have already seen that the interaction of the naked Cu$^+$ ion in its d$^{10}$ ground state with NO$_2$ in its excited B$_2$ state results in a 3d–4s promotion. Since this promotion is also facilitated by an increased electrostatic attraction between the Cu$^+$ ion and the zeolite wall, there is a mutual enhancement. Due to the reduced repulsion between Cu$^+$ and Z$^-$ in the 2A' state of ZCuNO$_2$, the Cu$^+$...O(zeolite) distances shrink by 0.05 Å on NO$_2$ bonding, both for the embedded T3 model (Figure 1a) and the nonembedded shell-1.5 model (Figure 1b). This leads to a gain in the electrostatic energy between Cu$^+$ and Z$^-$. We can also start our consideration from the “opposite” situation, NO$_2$ in its 1A' ground state and a fully promoted Cu$^+$ state (d$^{10}$). Figure 3 shows the orbital occupancies for this situation. The 36 a' orbital of the ZCu system which was the LUMO in the d$^{10}$ ground state is now singly occupied. This orbital is mainly the 4s orbital of Cu$^+$. It interacts with the 6a$_1$ orbital of NO$_2$ which is singly occupied in the 2A' ground state to give a doubly occupied a' orbital (40a', Figure 5). The singly occupied 20a'' orbital (d$_{xy}$) on Cu$^+$ interacts with the doubly occupied 4b$_2$ orbital of NO$_2$ to yield the singly occupied 23a'' orbital above and the doubly occupied 18a'' orbital below the 40 a' orbital (Figure 5). Since this three-electron interaction is connected with some donation from the 4b$_2$ orbital of NO$_2$ to the 3d orbital on Cu (20a'') and some back-donation from the 4s orbital of Cu$^+$ to the 6a$_1$ orbital of NO$_2$, the NO$_2$ gets partially excited and the d$^{10}$ state gets less s and more d character. This view is supported by the observation that the structure of the CuNO$_2$ fragment in the 2A' state of the ZCuNO$_2$ complex is very similar to that of the 2A' state of the 3d-O$_2$Cu$^+$NO$_2$ gas-phase complex (see Figures 1b and 2). The picture of the bonding is further confirmed by the population analysis given in Table 2. The d occupation on Cu in ZCuNO$_2$ is 9.33—a decrease by 0.52 electrons compared to ZCu. In the gas-phase complex, in which 3d–4s promotion is not enhanced by the Cu$^+$–zeolite interaction, the 3d population is closer to the d$^{10}$ state, 9.55. Moreover, the Mulliken spin density indicates that the unpaired electron is mainly located on the metal ion since the most important contribution to the singly occupied orbital 23a'' comes from the Cu d$_{xy}$ orbital (20a'') of ZCu.

The 2A' electronic state of the 3d-O$_2$CuNO$_2$ complex lies 32 kcal/mol above the 4A' ground state. In this case the 40a' orbital is the open shell orbital and the 23a'' orbital that is antibonding between ZCu and NO$_2$ is doubly occupied (Figure 3). Since the Cu contribution to the former is mainly 4s and to the latter mainly 3d (Figure 3), the 3d population in the 2A' state is larger than in 2A'', while the 4s population is smaller (Table 2). Figure 3 also shows that the (18a'')$ightarrow$(40a')/23a''$^2$ occupation corresponds to the orbital occupation in the 2A' ground state of NO$_2$. Hence, in the 2A' state of 3d-O$_2$CuNO$_2$ the structure of the CuNO$_2$ fragment is closer to the 2A' state of gas-phase Cu$^+$NO$_2$ than to the 2B$_2$ state (Figure 2 and Table 3). Frequency calculations on the 2A' state show that this stationary point is a second-order saddle point. The movement associated with one of the imaginary frequencies leads to the 4a' structure (cis), while the other one corresponds to the NO$_2$ rotation. Since this structure has a very high energy and rotation of NO$_2$ is not expected to decrease the energy significantly, we have not studied this electronic state further.

For the 4a'-N,O coordination the binding energy of the ZCuNO$_2$ complex is twice as large as in the gas phase. The reason is that for this coordination mode the 6a$_1$ orbital of NO$_2$ has the proper local symmetry to interact with the HOMO of ZCu (20a''). The resulting three-electron interaction becomes a more stabilizing two-electron interaction when an electron is promoted from 3d (20a'') to 4s (36a''). This 3d–4s promotion on the Cu atom is much larger for ZCu than for Cu for the reasons discussed above. Note that due to reduced repulsion on 3d–4s promotion the Cu$^+$...O distance shrinks from 1.99 Å in ZCu (Figure 1b) to 1.95 Å in the ZCuNO$_2$ complex (Figure 4). The orbital occupation data of Table 2 support this view. The d population on Cu decreases from 9.85 and 9.83 in ZCu and 9.43 in n$_2$-N,O Cu$^+$NO$_2$, respectively, to 9.43 in n$_2$-N,O Cu$^+$NO$_2$. The population analysis (Table 2) shows that in Cu$^+$NO$_2$ the spin density is mainly located in the NO$_2$ fragment, while in ZCuNO$_2$ half of the spin is on Cu.

From the above considerations follows that the effect of a largely increased bond strength with Cu$^+$ in a zeolite is coupled to the presence of a singly occupied orbital available for bonding in the energy region where the Cu orbitals are found. When binding water instead of NO$_2$ to the CuZ complex, the binding energy calculated for the shell-1.5 model (27 kcal/mol—a similar value has been reported before$^{15}$) decreases compared to the Cu$^+$OH$_2$ gas-phase complex energy (43.8 kcal/mol).

To understand if the effect found is specific for zeolites as ligands of Cu$^+$ or may be also present with other oxygen ligands we have made additional calculations on the Cu$^+$(H$_2$O)$_3$NO$_2$ system (n$_2$-O$_2$ coordination, 3B$_2$ state). Figure 6 shows the optimized structure. The orbital interactions are the same as in the 2A' state of ZCuNO$_2$, and the structure of the CuNO$_2$ fragment is almost identical (cf. Figures 1 and 6). However, the binding energy computed with respect to the linear equilibrium structure of Cu$^+$(H$_2$O)$_3$ as reference,
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Figure 6. Predicted structure of the $(\text{H}_2\text{O})_2\text{Cu}^+\text{NO}_2$ complex.

i.e., with all structure parameters the same as in the $(\text{H}_2\text{O})_2\text{Cu}^+\text{NO}_2$ complex, a value of 23.5 kcal/mol is obtained—larger than for the naked $\text{Cu}^+$ ion but still far from that obtained for $\text{Cu}^+$ in zeolites (42.7 kcal/mol). Promotion from $d^{10}$ to $d^3s^1$ is found as costly (2.6 eV) as for the free $\text{Cu}^+$ ion.

We conclude that half of the activating effect that the zeolite framework has on $\text{Cu}^+$ ions is that it holds the oxygen ligands in the proper position. About the other half is due to the stronger bonding between the negatively charged zeolite surface and the positively charged $\text{Cu}^+$ ion in the presence of $\text{NO}_2$. When $3d$–$4s$ promotion reduces repulsion, the zeolite-$\text{Cu}$ distance can shrink and there is a gain in electrostatic energy. In contrast, the $\text{Cu}^+$–$\text{OH}_2$ distance is larger in the $(\text{H}_2\text{O})_2\text{Cu}^+\text{NO}_2$ complex (2.02 Å) than in the linear $\text{Cu}^+(\text{H}_2\text{O})_2$ system (1.98 Å). The $\text{Cu}^+$–$\text{OH}_2$ distance optimized for the bent structure of the $\text{Cu}^+(\text{H}_2\text{O})_2$ system ($\text{O}–\text{Cu}–\text{O}$ angle fixed to its optimum value in the $(\text{H}_2\text{O})_2\text{Cu}^+\text{NO}_2$ complex) is 2.05 Å. This indicates that with respect to the bent structure as reference there is some reduction of repulsion, but the gain in electrostatic energy (ion–dipole) is not as large as in the $\text{ZCuNO}_2$-system (ion-pair interaction).

This has implications for selecting models of the $\text{Cu}^+$ site in zeolites. Although the local structure of the active site of the zeolite and the bonding mechanism can be reasonably well represented by the most simple $\text{Cu}^+$–water models, the unusually strong binding energy of $\text{NO}_2$ (this work) and $\text{NO}$ (ref 30) changes significantly from such simple models to the more realistic ones studied in this and previous work (e.g. refs 14,15,28–30).

4. Conclusion

The coordination of $\text{Cu}^+$ to the zeolite framework results in a substantially stronger bonding of $\text{NO}_2$ and in different preferred coordination modes compared to the gas-phase complex between $\text{Cu}^+$ and $\text{NO}_2$. This effect is due to $d^{10}$–$d^3s^1$ promotion which reduces repulsion with all ligands of $\text{Cu}^+$. As a result orbital interactions between $\text{Cu}^+$ and $\text{NO}_2$ become more favorable and electrostatic interactions between $\text{Cu}^+$ and the negatively charged zeolite wall more attractive. Hence we observe a cooperative (three-body) effect in the system zeolite–$\text{Cu}^+\text{NO}_2$ which strengthens both the $\text{NO}_2–\text{Cu}^+$ and the $\text{Cu}^+$–zeolite interactions.

Acknowledgment. Most calculations for this study have been made when L.R. was at Humboldt-University. Financial support for his stay from the Spanish Minister of Education and Science is gratefully acknowledged. This work has also been supported by the “Fonds der Chemischen Industrie” and by the “Deutsche Forschungsgemeinschaft”.

IA973196K
8. Conclusiones
De acuerdo con los objetivos planteados, hemos dividido las conclusiones en dos grandes apartados: a partir del análisis de diferentes métodos de cálculo aplicados al estudio de sistemas metal-ligando podemos extraer las siguientes conclusiones de tipo metodológico:

1. Los métodos del funcional de la densidad proporcionan geometrías y frecuencias vibracionales comparables a las obtenidas con método CCSD(T). Sin embargo, en el cálculo de energías de enlace los resultados son más discrepantes.

2. Las diferencias entre las energías calculadas a nivel DFT y CCSD(T) se han analizado usando los sistemas ScCO₂ y CuNO₂. En el primer caso, las energías de enlace DFT están sobrestimadas respecto a las energías CCSD(T) debido a la subestimación de la promoción 4s-3d en el Sc⁺ por los funcionales actuales. En el sistema CuNO₂ las energías de enlace DFT están subestimadas respecto a las energías CCSD(T) debido a la sobrestimación del potencial de ionización del Cu con los funcionales actuales. Estas deficiencias se deben a la descripción incorrecta de los estados atómicos con los funcionales existentes y se solucionan parcialmente introduciendo el intercambio exacto en el funcional.

3. En el complejo CuNO₂ la energía de enlace calculada con el método CCSD(T) está sobrevalorada debido principalmente a la mala descripción del potencial de ionización del Cu. La energía de enlace exacta en este sistema estaría situada entre los valores obtenidos con los métodos del funcional de la densidad y con el método CCSD(T).
4. Los resultados obtenidos con el método QCISD(T) para el sistema CuNO₂ son muy diferentes de los obtenidos con el método CCSD(T). En este sistema el método QCISD(T) proporciona resultados incorrectos.

A partir de los resultados obtenidos también se pueden extraer las siguientes conclusiones respecto a la estructura y las propiedades de los diferentes sistemas estudiados:

1. La estructura más estable para el complejo MNO₂ corresponde, en todos los casos estudiados, al NO₂ coordinado al metal a través de los dos oxígenos (coordinación \( \eta^2 \)-O,O), que es la coordinación más favorable para la interacción iónica. El estado fundamental en los sistemas con M=Cu y Ag es un estado \(^1\text{A}_1\). En los sistemas con metales alcalinotérreos el estado fundamental es siempre un estado \(^2\text{A}_1\) excepto en el caso del Be donde el estado \(^2\text{B}_1\) es más favorable. Este estado presenta un mecanismo de enlace diferente y es geometricamente muy distinto al del estado \(^2\text{A}_1\). Todo ello es debido al menor radio atómico del Be.

2. La estructura más estable en el sistema Cu(NO₂)₂ es la estructura D\(_{2h}\) con los dos fragmentos NO₂ coordinados a través de los dos oxígenos (coordinación \( \eta^2 \)-O,O) en el mismo plano con un estado fundamental \(^2\text{B}_3\). En el sistema Mg(NO₂)₂ la estructura D\(_{2d}\), con los dos fragmentos NO₂ en planos perpendiculares, es más estable que la D\(_{2h}\). En este caso el estado fundamental es un \(^1\text{A}_1\). La mayor estabilidad de la estructura D\(_{2h}\) con respecto a la estructura D\(_{2d}\) en el caso del Cu(NO₂)₂ se debe a la diferente interacción de los orbitales de los ligandos con los orbitales d del metal. En el caso del sistema Mg(NO₂)₂ el metal no posee orbitales d ocupados para interaccionar con los ligandos y por tanto el orden de estabilidades se debe únicamente a las diferencias en las interacciones estéricas entre los ligandos.

3. Los valores de los parámetros geométricos optimizados y frecuencias vibracionales calculadas para los fragmentos NO₂, así como el análisis de población muestran que el enlace en los sistemas MNO₂ y M(NO₂)₂ estudiados presenta un carácter principalmente iónico tanto en el caso de metales de transición como en el de metales alcalinotérreos.
4. Las frecuencias vibracionales calculadas para los sistemas CuNO₂, CaNO₂, SrNO₂, Cu(NO₂)₂ y Cu(NO₃)₂ a nivel DFT están en muy buen acuerdo con los datos experimentales existentes.

5. La variación de las energías de enlace en los sistemas MNO₂ está de acuerdo con la presencia de un enlace metal-ligando de tipo básicamente iónico. En particular, el comportamiento de Cu y Mg es muy similar debido a que poseen un primer potencial de ionización muy similar. En los sistemas M(NO₂)₂ las energías de enlace totales M-(NO₂)₂, y por tanto las del segundo NO₂, M(NO₂)-NO₂, muestran importantes diferencias entre Cu(NO₂)₂ y Mg(NO₂)₂. Dichas diferencias se deben a que el segundo potencial de ionización del Cu es mucho mayor que el del Mg, lo que lleva a una energía de disociación total en el Cu(NO₂)₂ menor que en el Mg(NO₂)₂.

6. El modo de coordinación del NO₂ al Cu⁺ es diferente en el interior de una zeolita, representada por un modelo de cluster, que en fase gas. Mientras en fase gas la estructura más estable corresponde al NO₂ coordinado a través de un oxígeno (η¹-O trans), en la zeolita la coordinación más estable es la η²-O,O con el NO₂ coordinado a través de los dos oxígenos.

7. El mecanismo de enlace del NO₂ también varía cuando se introduce en la zeolita. En el [CuNO₂]⁺ libre el estado fundamental corresponde a la interacción del estado ¹S(d¹⁰) del Cu⁺ con el estado ²A₁ del NO₂. Cuando el NO₂ se coordina al Cu⁺ en el interior de la zeolita se produce una promoción 3d¹⁰→3d⁹4s¹ en el Cu⁺ para reducir la repulsión metal-NO₂. A su vez, también se reduce la repulsión entre el Cu⁺ y la zeolita con lo que las distancias Cu⁺-···O(zeolita) se acortan y la interacción electrostática del Cu⁺ con la zeolita, cargada negativamente, aumenta.

8. La energía de enlace del NO₂ al Cu⁺ en la zeolita, 42.7 kcal mol⁻¹, aumenta considerablemente respecto a la energía de enlace del NO₂ al Cu⁺ en fase gas, 26.4 kcal mol⁻¹. Esto se debe al incremento de la atracción entre la superficie de la zeolita y el Cu⁺ debido a la promoción 3d-4s en el Cu⁺. El análisis del sistema Cu⁺(H₂O)₂NO₂, donde la zeolita se representa mediante un modelo de moléculas de agua, proporciona
una energía de enlace del NO$_2$ de 23.5 kcal mol$^{-1}$. Por tanto, ni el Cu$^+$ aislado, ni el modelo de moléculas de agua representan correctamente la adsorción del NO$_2$ en la zeolita CuZSM-5.

9. La inclusión del efecto de toda la zeolita mediante un método que combina la mecánica cuántica y la mecánica molecular no produce cambios apreciables respecto a la geometría y a la energía de enlace obtenidas con el modelo de *cluster* para la coordinación más estable. Por tanto, el modelo que hemos utilizado parece, en principio, un buen modelo para continuar con el estudio del mecanismo de la descomposición de los óxidos de nitrógeno.
9. Referencias


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