Coordination of NO_2 to Cu and Mg in $M(NO_2)_2$ Complexes. A Theoretical Study

Luis Rodríguez-Santiago, Xavier Solans-Monfort, Mariona Sodupe,* and Vicenç Branchadell*

Departament de Química, Universitat Autònoma de Barcelona, Edifici Cn, 08193 Bellaterra, Spain

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The geometries, vibrational frequencies, and metal−ligand bond dissociation energies of 18 different structures of the $Cu(NO_2)_2$ complex have been studied. $Mg(NO_2)_2$ and $Cu(NO_3)_2$ have also been studied for comparison. The most stable structure of $Cu(NO_2)_2$ and $Cu(NO_3)_2$ corresponds to a D_{2h} one with a coplanar η^2-O,O coordination for the two NO_2 ligands. For $Mg(NO_2)_2$ the most stable structure is a D_{2d} one. The bonding in the D_{2h} and D_{2d} structures of $Cu(NO_2)_2$ is analyzed. For the MNO_2 systems the binding energy is very similar with both metals, while for the $M(NO_2)_2$ 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.

Introduction

Transition metal−ligand interactions have been the focus of great attention during the last years,[1] due to its great number of applications. These applications include many fields, such as biochemistry, environmental chemistry, development of new materials, and catalysis. The determination of accurate binding energies and geometries of the metal−ligand systems are of great interest for the development of these applications.[1a,2] 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 to understand 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 the ability of NO_2 to coordinate to a metal in different ways.[3] Each type of NO_2 coordination leads to different properties of the compound. Furthermore, nitrogen oxides (NO_x, $x = 1, 2$) are unwanted pollutants that take part in important chemical reactions in the atmosphere, and in corrosion. Thus, coordination of NO_2 to a metal as well as the interaction of successive NO_x ligands can provide important information for the understanding of these processes. The interaction of NO_2 with alkaline,[4−11] alkaline-earth,[12−16] and transition metals[17−20] has been studied by several authors both theoretically and experimentally.

Theoretical calculations for $M(NO_3)_2$ (M = Be, Mg, Ca) systems have been performed by Rossi et al. at the HF level.[21] The results obtained for the $Mg(NO_3)_2$ system were used for the assignment of the FT-IR matrix isolation spectrum of the $Cu(NO_3)_2$ stable gas-phase molecule. Based on this assignment, they conclude that both NO_3 groups are equivalent and lie in the same plane, in agreement with earlier electron diffraction studies.[22] On the other hand, experimental IR matrix studies have been carried out on the $Cu(NO_2)_2$ system by Worden and Ball.[17] 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.

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[23] with the correlation functional of Lee, Yang, and Parr[24]

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* Corresponding authors. E-mail: M.S., mariona@klingon.uab.es; V.B., vicenc@uab.es.

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(B3LYP). This method has proved to provide reliable geometries and harmonic vibrational frequencies compared to more computational demanding ab initio correlated methods.[2,25] 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 and a perturbative estimate of the triple excitations[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 (9s5p)/[4s2p] set developed by Dunning,[27] supplemented with a valence diffuse function ($\alpha_{sp} = 0.0639$ for nitrogen and $\alpha_{sp} = 0.0845$ 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.[28] The Cu basis set is a [8s4p3d] contraction of the (14s9p5d) primitive set of Wachter[29] supplemented with two diffuse p and one diffuse d function.[30] The Mg basis set is the (12s9p)/[6s5p] set of McLean and Chandler[31] supplemented with a d polarization function ($\alpha = 0.28$). The final basis sets are of the form (10s6p1d)/[5s3p1d] for N and O, (14s11p6d)/[8s6p4d] for Cu, and (12s9p1d)/[6s5p1d] 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 (14s11p6d3f)/[8s6p4d1f] basis set.[32] For Mg we have used the (16s12p3d2f)/[6s5p3d2f] basis set of Dunning referred as cc-pVQZ in the MOLPRO 96 program.[33] For N and O we have used the (10s5p2d1f)/[4s3p2d1f] basis set of Dunning augmented with one diffuse s and one diffuse p functions.[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[28] program and open shell calculations were based on a spin-unrestricted treatment, while the CCSD(T) results were performed with the MOLPRO[33] program and were based on a spin restricted formalism.

Results and Discussion

Figure 1 shows the four different coordination modes of NO_2 to a metal atom considered in our study. NO_2 can act both as a monodentate ligand or as a bidentate ligand when interacting with a metal atom. As a monodentate ligand, NO_2 can interact with the metal through the oxygen (η^1-O) or through the nitrogen (η^1-N). As a bidentate ligand, it can interact with the two oxygens (η^2-O,O) or with one nitrogen−oxygen bond (η^2-N,O). In the present work we have investigated all the possible structures that can be obtained with two NO_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_2 ligands: coplanar and perpendicular.

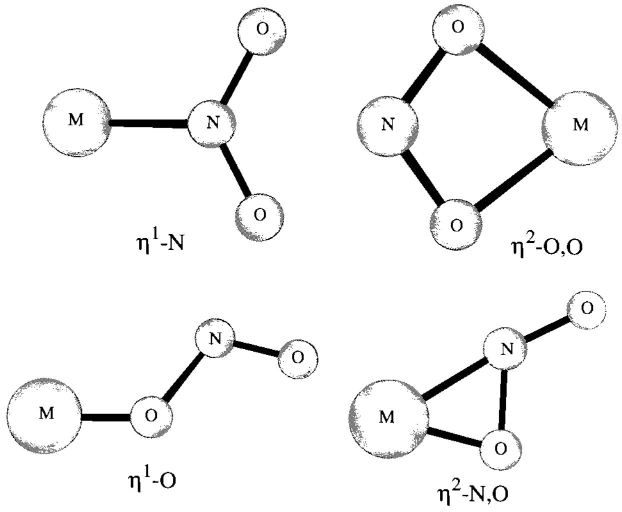

Figure 1. Coordination modes of one NO_2 to the metal atom.

Table 1. Computed Relative Energies of the Stationary Points found for $Cu(NO_2)_2$

	symmetry	state	$[NO_2]_1$	$[NO_2]_2$	ΔE/kcal mol^{-1}
AA	D_{2h}	$^2B_{3g}$	η^2-O,O	η^2-O,O ∥	0.0
AAp	D_{2d}	$^2B_2$	η^2-O,O	η^2-O,O ⊥	23.7
AAx	D_{2h}	$^2B_{1u}$	η^2-O,O	η^2-O,O ∥	31.5
AB	C_s	$^2A'$	η^2-O,O	η^2-N,O ∥	7.5
ABp	C_s	$^2A'$	η^2-O,O	η^2-N,O ⊥	18.3[a]
AC	C_s	$^2A'$	η^2-O,O	η^1-O ∥	12.4
ACp	C_s	$^2A''$	η^2-O,O	η^1-O ⊥	17.6[a]
AD	C_{2v}	$^2A_1$	η^2-O,O	η^1-N ∥	17.9[a]
ADp	C_{2v}	$^2A_1$	η^2-O,O	η^1-N ⊥	17.4[a]
BBt	C_s	$^2A'$	η^2-N,O	η^2-N,O ∥ trans	17.1
BBi	C_{2v}	$^2B_2$	η^2-N,O	η^2-N,O ∥ cis	16.9
BC	C_s	$^2A'$	η^2-N,O	η^1-O ∥	19.4[a]
BD	C_s	$^2A'$	η^2-N,O	η^1-N ∥	20.3[a]
BDp	C_s	$^2A'$	η^2-N,O	η^1-N ⊥	20.9[a]
CCi	C_s	$^2A'$	η^1-O	η^1-O ∥ cis	19.2
CDp	C_s	$^2A'$	η^1-O	η^1-N ⊥	27.5[a]
DD	D_{2h}	^2A_g	η^1-N	η^1-N ∥	26.4[b]
DDp	D_{2d}	$^2A_1$	η^1-N	η^1-N ⊥	26.3[b]

[a] First-order saddle points. [b] Second-order Saddle points.

Among all the possible structures, only 18 have been found as stationary points on the potential energy surface of the $Cu(NO_2)_2$ 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_{2h} symmetry and corresponds to the two NO_2 ligands bonded to the Cu atom with the η^2-O,O coordination in the same plane (AA structure). The D_{2d} structure with the two NO_2 ligands acting with η^2-O,O coordination in perpendicular planes (AAp structure) is 23.7 kcal mol^{-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 η^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 (η^1-N coordination).

The geometry parameters of the η^2-O,O moiety in all structures are very similar to those computed for free NO_2^-

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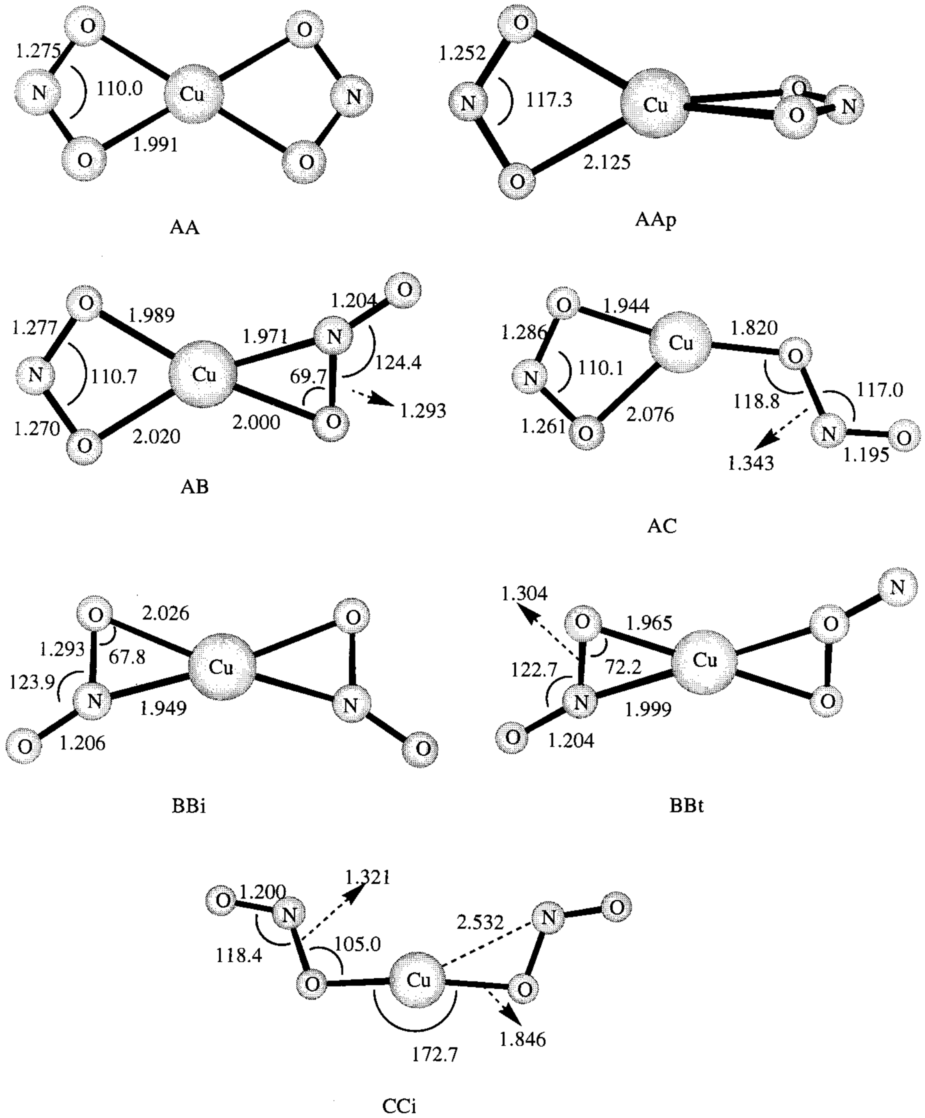

Figure 2. Computed structures of the different energy minima determined for the $Cu(NO_2)_2$ complex. Distances are in angstroms, and angles are in degrees.

(r(NO) = 1.270 Å and ∠ONO = 116.4°). In the fragments with η^2-N,O and η^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 η^1-O coordinations is close to the value of this angle in NO_2^-, while in the η^2-N,O coordinations the ONO angle lies within the values obtained for NO_2^- and NO_2 (∠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 η^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 $^2B_{3g}$ ground state of the most stable D_{2h} structure, AA, and in the $^2B_2$ state of the D_{2d} structure, AAp. 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 $^2D(d^9)$ state of Cu^{2+} and the $(NO_2)_2^{2-}$ fragment. It can be observed in Figure 3 that the unpaired electron is described by an orbital arising from the antibonding combination between the $4b_{3g}$ orbital of $(NO_2)_2$ 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 $(NO_2)_2^-$ fragment. The metal Mulliken population analysis shows a situation between both descriptions. The metal population is $4s^{0.75}\ 3d^{9.39}$, and the unpaired electron is distributed 0.6 in the metal and 0.4 in the ligands. In the $^2B_2$ state of the D_{2d} structure, the unpaired electron occupies an orbital arising from the antibonding combination between the d_{xy} orbital of the metal and the b_2 combination of the $6a_1$ orbitals of NO_2, and that there is also an important donation from the ligands to the 4s orbital of Cu^{2+}.

The orbital of NO_2 that has the larger overlap with the metal is the $4b_2$ orbital. Thus the orbitals of the $(NO_2)_2$ 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 $(NO_2)_2$ 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, while the

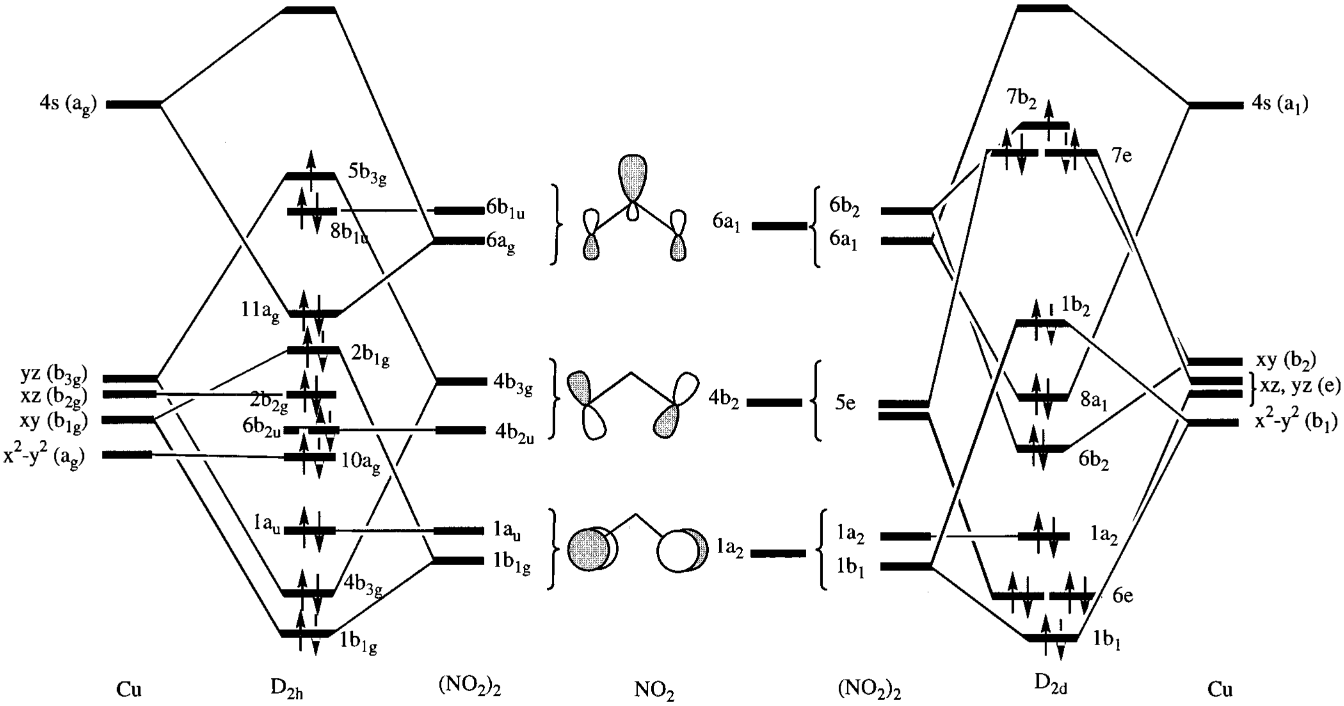

Figure 3. Diagram of the most important orbitals involved in the formation of the D_{2h} and D_{2d} structures of $Cu(NO_2)_2$.

$4b_{2u}$ orbital remains as a non bonding orbital in the complex. 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} $Cu(NO_2)_2$ 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} due to Jahn−Teller instability. 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 that 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, whatever the ground state is, 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 occupied d 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.[17] 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 a similar compound, $Cu(NO_3)_2$, determined from electron diffraction experiments[22] shows a D_{2h} structure in which the coordination mode of the two NO_3 ligands is the same. For this reason, 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.

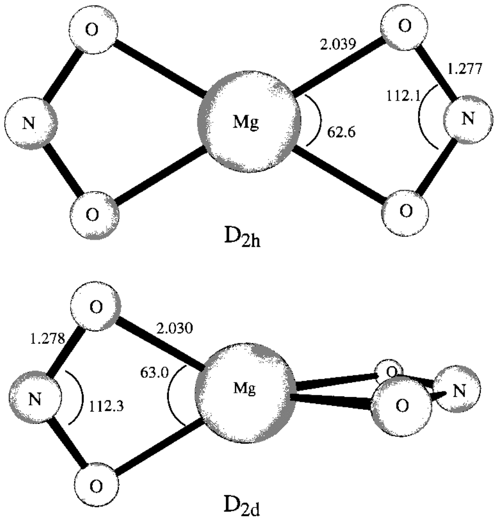

Figure 4. Computed D_{2d} and D_{2h} structures $Mg(NO_2)_2$. Distances are in angstroms, and angles are in degrees.

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

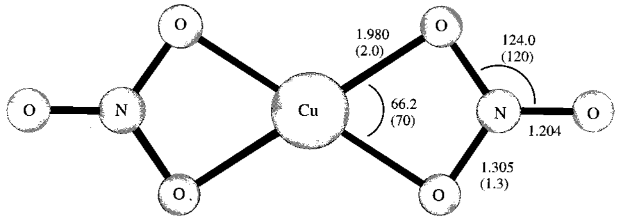

Figure 5. Computed D_{2h} structure of $Cu(NO_3)_2$. In parentheses are shown the experimental values.[22] Distances are in angstroms, and angles are in degrees.

Table 2. Computed Harmonic Vibrational Frequencies[a] for $M(NO_2)_2$, NO_2, and NO_2^- (in cm^{-1})

	NO_2		NO asy.		NO sym.	
	def. (B_{1u})	def. (A_g)	str. (B_{3g})	str. (B_{2u})	str. (B_{1u})	str. (A_g)
$Cu(NO_2)_2$	882(114)	895(0)	1225(0)	1254(564)	1348(60)	1350(0)

	NO_2		NO asy.	NO sym.	
	def. (A_1)	def. (B_2)	str. (E)	str. (B_2)	str. (A_1)
$Mg(NO_2)_2$	882(0)	886(21)	1287(476)	1336(23)	1336(0)

	NO_2 def. (A_1)	NO sym. str. (A_1)	NO asy. str. (B_2)
NO_2	741(6)	1388(0)	1703(416)
NO_2 exp.[b]	750	1325	1634
NO_2^-	780(3)	1339(13)	1322(722)
NO_2^- exp.[c]	821	1332	1240

[a] In parentheses, the IR intensity of each frequency in km mol^{-1}. [b] Reference 35. [c] Reference 36.

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 matrixes. 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 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 $Cu^{2+}(NO_2^-)_2$ structure. So, our results in favor of a D_{2h} structure with two equivalent NO_2 ligands for the $Cu(NO_2)_2$ 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 $Cu(NO_3)_2$, the computed vibrational frequencies presented in Table 3 are in excellent agreement with the experimental values reported by Rossi et al.[21]

Table 3. Harmonic Vibrational Frequencies[a] for $Cu(NO_3)_2$ (in cm^{-1})

computed[b]	exp.[c]	description
1683(0)		NO′ str. (A_g)
1668(1328)	1615	NO′ str. (B_{1u})
1247(460)	1205	NO asy. str. (B_{2u})
1233(0)		NO asy. str (B_{3g})
1020(0)		NO sym. str. (A_g)
1018(65)	965	NO sym. str. (B_{1u})
778(20)		NO_3 def. (B_{3u})
777(0)		NO_3 def. (B_{2g})
774(0)		NO_2 def. (A_g)
771(111)		NO_2 def. (B_{1u})

[a] In parentheses, 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 presents the binding energies computed with respect to the neutral fragments of the ground-state structure of the complexes $Cu(NO_2)_2$, $Cu(NO_3)_2$, and $Mg(NO_2)_2$. 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 $Mg(NO_2)_2$, 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 $CuNO_2$ and $MgNO_2$ are very similar, while the value for $CuNO_3$ 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 $E_i(M)-E_{ea}(L)$. 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 differ-

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Table 4. Metal-Ligand Binding Energies of $M(NO_x)_n$ Complexes (in kcal mol^{-1}) Computed at Different Levels of Calculation

	successive				total	
	$M-NO_x$		MNO_x-NO_x		$M-(NO_x)_2$	
	B3LYP	CCSD(T)[a]	B3LYP	CCSD(T)[a]	B3LYP	CCSD(T)[a]
$Cu(NO_2)_2$	49.2	57.2 (56.1)	37.4	43.8 (36.9)	86.6	101.0 (93.9)
$Cu(NO_3)_2$	72.3	83.9 (85.2)	71.6	75.9	143.9	159.8
$Mg(NO_2)_2$	47.2	49.2 (51.5)	88.5	93.5 (96.1)	135.7	142.7 (147.6)

[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 NO_x

	B3LYP	CCSD(T)[a]	exp.
		metal E_I/eV	
Cu	8.03	7.06 (7.15)	7.73[b]
Cu^+	20.80	19.62 (20.00)	20.29[b]
Mg	7.73	7.54 (7.58)	7.65[b]
Mg^+	15.46	14.80 (14.87)	15.03[b]
		NO_x E_{ea}/eV	
NO_2	2.36	2.12 (2.13)	2.28[c]
NO_3	4.04	3.82 (3.92)	3.92 ± 0.2[d]

[a] In parentheses are shown the CCSD(T) values with the larger basis set. [b] Reference 37. [c] Reference 38. [d] Reference 39.

ences 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 $M-NO_x$ 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.

Conclusion

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.

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