Interaction of Y, Y_2, Mo, and Mo_2 with NH_3. A Density Functional Study

Ana Martínez*

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma México, Circuito Exterior s/n, Ciudad Universitaria, 04510 Coyoacán, México D.F., Mexico

Benoit Simard

Steacie Institute for Molecular Sciences, National Research Council Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada

Dennis R. Salahub

University of Calgary, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada

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The interaction of Y, Y_2, Mo, and Mo_2 with NH_3 is studied to understand the influence of the electronic configuration of the transition metal atoms and clusters on their reactions with ammonia. The interactions are investigated with the all-electron linear combination of Gaussian-type orbitals Kohn−Sham density functional theory (LCGTO-KS-DFT). The binding energies and harmonic frequencies characterize the equilibrium geometries. The reaction products investigated are MNH_3, MNH, M_2NH_3, M_2NH, and $M_2(NH)_2$. The binding energy indicates that the reaction of Y and Y_2 is possible. For Y, the stable products are YNH_3 and YNH with binding energies of 24.6 and 32.6 kcal/mol, respectively. For Y_2, the stable products of the reaction are Y_2NH_3, Y_2NH, and $Y_2(NH)_2$ (binding energies of 13.9, 55.5, and 110.2 kcal/mol, respectively). For Mo, the stable product is $MoNH_3$ with a binding energy of 8.5 kcal/mol. For MoNH, the binding energies indicate that the reactants (Mo + NH_3) are more stable than the products (MoNH + H_2) by 9.8 kcal/mol. For the $Mo_2[NH_3]$ complex, the binding energy is 17.9 kcal/mol, in good agreement with the experimental value of 14 kcal/mol previously reported. For Mo_2, there are no other stable products of the reaction because Mo_2NH and $Mo_2(NH)_2$ are less stable than the reactants (Mo_2 + NH_3) by 12.7 and 10.9 kcal/mol, respectively. The differences in the bonding are explained with molecular orbital pictures. For each metal, a relationship between the electronic configurations of the transition metals and the binding energies is reported.

Introduction

The theoretical study of the bonding in metal−ligand systems is challenging and has great importance in many fields.[1,2] There is a strong correlation between cluster−ligand chemistry, stereochemistry, structure, and surface−ligand simulations. Given this correlation, it is possible to learn much about metal-centered reactivity from studies of small, unligated metal clusters and their reactions with atoms and small molecules.[3]

The investigation of physisorption and chemisorption on clusters, as well as the incorporation of atoms and molecules into clusters[4−8] has been possible because of developments in theory and experiments that are providing valuable information on many properties of atomic aggregates. The theoretical study of 4d and 5d transition metal clusters includes both a large number of electrons and relativistic effects. In the density functional theory (DFT), scalar relativistic effects can be included efficiently using effective core potentials.[9] This theoretical approach has been used successfully in the study of transition metal atoms and clusters.[10]

The reactivity of clusters is a complicated subject. Understanding how the cluster electronic structure affects chemical reactivity can have an important influence in fields such as thin film coating and catalysis. For this reason, most of the work previously reported is devoted to the study of the reactivity of metal clusters as a function of the identity, as well as the cluster size.[11]

The reaction that we studied is yttrium and molybdenum with ammonia. Different transition metal atoms and clusters have different effects on the bonding situation. As an example, in a previous work, Simard et al.[12] reported results of the reaction of Y with NH_3. There, the reaction goes beyond the oxidative addition product to produce yttrium imide. Lian et al.[13] reported an experimental study for the reaction of Mo and Mo_2 with different ligands. They found no reaction of Mo with NH_3, while the dimer (Mo_2) reacts with NH_3 and produces the $Mo_2[NH_3]$ complex. The influence of the electronic configuration of the atoms and the dimers is also important in the study of the reactivity of transition metal clusters. Different transition metals could reflect different properties and bonding situations. In this context, and to explain the bonding and reaction of Y, Y_2, Mo, and Mo_2 interacting with ammonia, density functional studies on MNH_3, MNH, M_2NH_3, M_2NH, $M_2(NH)_2$ (M = Y and Mo) were performed. Bond distances, equilibrium geometries, binding energies, and Mulliken atomic charges are presented. The goal of this work is to understand the different bonding situations

* To whom correspondence should be addressed. Phone number: (5255) 5622-45-96. Fax number: (5255) 5616-12-01. E-mail address: martina@chip.iimatercu.unam.mx.

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TABLE 1: Two Electronic Configurations of the Mo Atom and Their Energies (eV) Relative to the Ground State, Results with Different DFT Techniques and Effective Core Potentials (LANL2DZ) Compared to Experimental Data and Available Theoretical Results

					this work		
system	expt[a]	CI[b]	LSDA[c]	GGA[c]	BP86	B3LYP	BPW91
Mo [$4d^5 5s^1(^7S)$]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mo [$(4d^5 5s^1(^5S)$]	1.33	1.45	1.25	1.20	1.24	0.96	1.42

[a] Moore, C. E. *Atomic Energy Levels. As Derived from the Analyses of Optical Spectra*; United States Department of Commerce, National Bureau of Standards: Washington, DC, 1949. [b] Li, J.; Balasubramanian, K. *J. Phys. Chem.* **1990**, *94*, 545. [c] Martínez, A.; Köster, A. M.; Salahub, D. R. *J. Phys. Chem. A* **1997**, *101*, 1532.

in these systems. The bonding has been analyzed in terms of molecular orbitals.

Methodology

All calculations were performed using Gaussian 98[14] and three different functionals: (1) Becke's 1988 exchange functional, which includes the Slater exchange, along with the corrections involving the gradient of the density, with the gradient-corrected correlation functional of Perdew, along with his 1981 local correlation functional (BP86),[15] (2) the hybrid B3LYP functional,[16] and (3) Becke's 1988 exchange functional, coupled with Perdew and Wang's 1991 gradient-corrected correlation functional (BPW91).[17] These calculations were carried out with the LANL2DZ[18−20] atomic orbital basis functions. Full geometry optimization without symmetry constraints has been performed, starting from several initial geometries to locate different minima on the potential energy surface. Different spin multiplicities ($2S_z + 1$) were considered in all calculations to find the most stable spin state. To find the global minimum, one must consider several multiplicities and several initial structures for each adduct. Of course, one cannot exclude the possibility that true global minima were missed in the optimization procedure, but the number of different initial geometries and spin multiplicities that were considered is sufficiently high to lend confidence that the global minimum has been identified. Optimized geometries were verified by frequency calculations.

Five of the reactions that we studied present a negative binding energy, indicating that the products are more stable than the reactants. Two of these reactions are an association of the NH_3 molecule with the metal atom or dimer. For the other reactions, yttrium reacts with NH_3 and molecules of H_2 were formed. For these reactions, we tried to obtain the transition states with available methodology in the literature.[14] Many negative frequencies were achieved for these attempts. Several initial geometries were used, but we were unable to locate any transition states. Because the main interest of this study is to analyze the different bonding situations in these systems due to the different electronic configuration of the transition metals, we have not persisted.

Results and Discussion

Y, Y_2, Mo, and Mo_2. In Table 1 is presented the first excited electronic configuration of the Mo atom and its relative energy difference to the ground state. The comparison with other theoretical and experimental results is also shown. The electronic ground-state configuration is the same. With both BP86 and B3LYP, the calculated energy difference relative to the ^7S ground state is smaller than the experimental value.[21] When BPW91 is used, the relative energy is larger than its experimental counterpart. In this table, the comparison with configuration interaction (CI) calculations by Li and Balasubramanian[22] and with nonrelativistic density functional calculations by Martínez et al.[23] is also reported. Li and Balasubramanian used relativistic effective core potentials and multireference singles + doubles configuration interaction (MRSDCI) in their calculations. In Table 1, the results obtained with LANL2DZ and BPW91 are closer to the CI results than to the nonrelativistic density functional calculations (LSDA and GGA in the table). The error of the calculated energy differences lies between 0.08 and 0.2 eV (except for B3LYP, of which the error is approximately 0.4 eV). Hence, it is possible to consider that these errors are small enough for a reliable assignment of the atomic states of the Mo atom. The error of the CI calculations and of the present calculations are in the same acceptable range with respect to experiment. We realize that the "^5S" state is not a pure multiplet, as we have treated it in the single-determinantal Kohn−Sham approach. Indeed, different occupations of the various orbitals yield somewhat different energies. As a measure of the probable effect on the energy, we note that the 5 d orbital energies span a range of about 0.3 eV in our calculation. The main conclusion, that the ground state is ^7S and that the ^5S state is about 1 eV higher, seems well justified.

TABLE 2: Ionization Potentials (in eV) of Y, Y_2, Mo, and Mo_2 with Three Different DFT Techniques and Effective Core Potentials (LANL2DZ) and Available Experimental Results

system	BP86[a]	B3LYP[b]	BPW91[c]	exptl[d]
Y	7.24	7.11	7.06	6.22
Y_2	5.27	4.86	5.10	4.96
Mo	7.49	7.14	7.36	7.09
Mo_2	7.28	7.74	7.07	6.95

[a] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. [b] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. Mielich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. [c] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244. [d] For ytrium, Jakubek, Z. J.; Simard, B. *J. Phys. B: At. Mol. Opt. Phys.* **2000**, *33*, 1827. For Y_2, Yang, D. S.; Simard, B.; Hackett, P. A.; Bérces, A.; Zgierski, M. Z. *Int. J. Mass. Spectrom. Ion Processes* **1996**, *159*, 65. For molybdenum, Rayner, D. M.; Mitchell, S. A.; Bourne, O. L.; Hackett, P. A. *J. Opt. Soc. Am. B* **1987**, *4*, 900. For Mo_2, Simard, B.; Lebeault-Dorget, M. A.; Marijnissen, A.; ter Meulen, J. J. *J. Chem. Phys.* **1998**, *23*, 9668. Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049.

In Table 2, ionization potentials of Y, Y_2, Mo, and Mo_2 are presented. Available experimental results[24] are also shown. The results are in good agreement with the experimental values. Taking into account the four systems, the results with BPW91 are in better agreement with experiment than the values obtained with the other functionals. The biggest difference is for the Y atom, the experimental ionization potential of which is around 0.8 eV lower than the calculated BPW91 value.

Table 3 presents experimental and theoretical[25] bond distances (in angstroms) for Mo_2. It is important to mention that the correct description of the Mo_2 complexes depends strongly on the correct description of the Mo−Mo bond. The equilibrium geometry of the molybdenum dimer is very sensitive to the theoretical methods and the basis sets employed. The calculations for Mo_2 can be used as a performance test for relativistic effective core potentials. The LANL2DZ effective core potential used for these calculations was generated considering explicitly the outermost core electrons along with the valence electrons. For this reason, it is possible to reproduce correctly the Mo−Mo bond distance, as seen in Table 3. The results with LANL2DZ are in very good agreement with CI and experi-

TABLE 3: Theoretical and Experimental Bond Distances (in Å) for Mo_2

							this work[g]		
	expt[a]	CASSCF[b]	SCF + ECP[c]	SCF[d]	CI[e]	MCSCF[f]	BP86	B3LYP	BPW91
Mo−Mo	1.929	1.923	1.87	1.88	1.97	2.1	1.99	1.97	1.99

[a] Efremof, Y. M.; Samoliova, A. N.; Kozhukhovsky, V. B.; Gurvich. L. V. *J. Mol. Spectrosc.* **1978**, *73*, 430. [b] Roszak, S.; Balasubramanian, K. *Inorg. Chem.* **1994**, *33*, 4169. [c] Miyoshi, E.; Sakai, Y. *J. Comput. Chem.* **1988**, *9*, 719. [d] McLean, A. D.; Liu, B. *Chem. Phys. Lett.* **1983**, *101*, 199. [e] Bursten, B. E.; Cotton, F. A.; Hall, M. B. *J. Am. Chem. Soc.* **1980**, *102*, 6348. [f] Wood, C.; Doran, M.; Hillier, I. A.; Guest, M. F. *Symp. Faraday Soc.* **1980**, *14*, 159. [g] Our calculations were performed with effective core potentials (LANL2DZ).

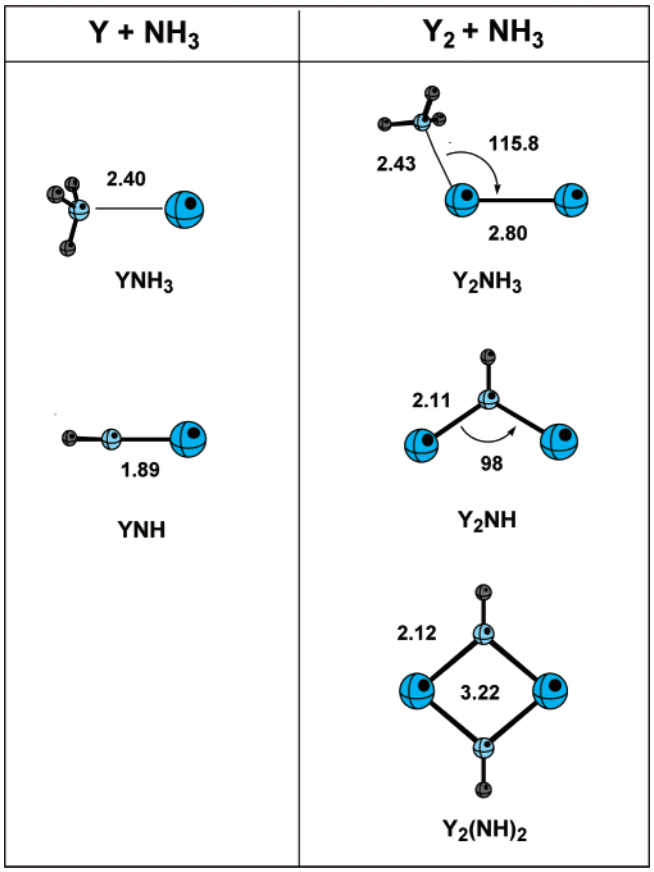

Figure 1. Optimized geometries for YNH_3, YNH, Y_2NH_3, Y_2NH, and $Y_2(NH)_2$.

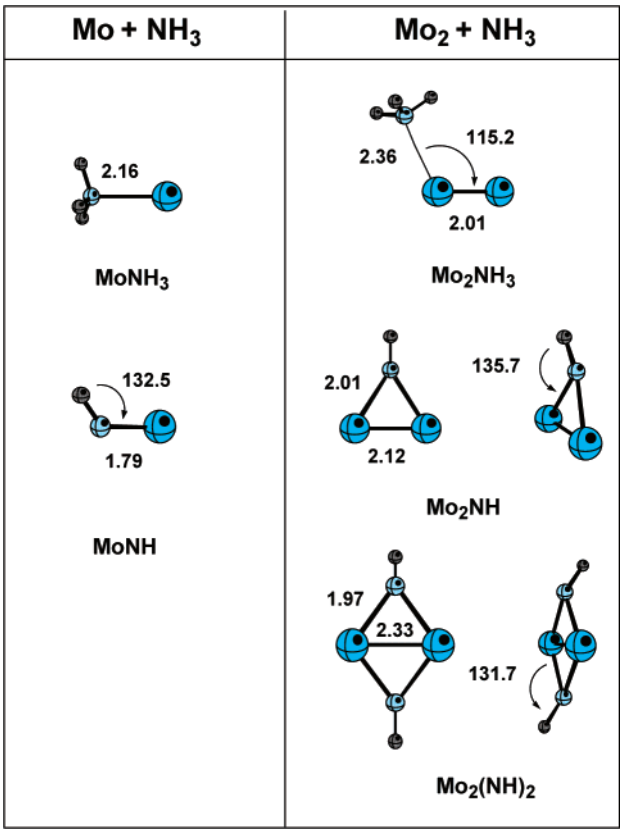

Figure 2. Optimized geometries for $MoNH_3$, MoNH, Mo_2NH_3, Mo_2-NH, and $Mo_2(NH)_2$.

mental values. Note that the Mo−Mo bond distance is not sensitive to the functional used, that is, for BP86, B3LYP, and BPW91 the Mo−Mo bond length is almost the same.

The binding energy of Y_2 was well described (1.8 eV, the experimental value is around 1.6 eV[24]). The binding energy of Mo_2 (and its congener Cr_2) has been the subject of much study and no little controversy,[24] revolving around the ability of (single-determinantal) Kohn−Sham theory to describe what are, from the point of view of traditional ab initio theory, highly correlated multideterminantal systems. Broken symmetry solutions involving localized orbitals are sometimes obtained. We will not dwell on these issues here because the processes of interest do not involve dissociation of the Mo−Mo bond.

Geometry Optimization of MNH_3, MNH, M_2NH_3, M_2NH, and $M_2(NH)_2$ (M = Y and Mo). To explain the bonding and reaction of Y, Y_2, Mo, and Mo_2 interacting with ammonia, density functional calculations on MNH_3, MNH, M_2NH_3, M_2-NH, and $M_2(NH)_2$ (M = Y and Mo) were performed. Figures 1 and 2 show the optimized geometries for the most stable structures that were considered. In Table 4, the results of the geometry optimization for YNH_3 and $MoNH_3$ with other available theoretical results are presented for comparison. As can be seen in this table, there is a good agreement with the

TABLE 4: Results of the Geometry Optimization, Including M−NH_3 Bond Distance (R_e), Spin Multiplicity ($2S_z + 1$), and Binding Energies (D_0), and Available Theoretical Results

	YNH_3	$MoNH_3$
BPW91/LANL2DZ[a]		
R_e (Å)	2.40	2.60
$2S_z + 1$	2	7
D_0 (kcal/mol)	−24.6	−8.5
MCPF[b]		
R_e (Å)	2.54	2.75
$2S_z + 1$	2	7
D_0 (kcal/mol)	−19.2	−9.3
ASED-MO (Modified Extended Hückel)[c]		
R_e (Å)	2.47	2.52
$2S_z + 1$	2	5
D_0 (kcal/mol)	−19.8	−12.57

[a] Our calculations were performed with BPW91 and effective core potentials (LANL2DZ). [b] Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *Inorg. Chem.* **1993**, *32*, 4218. [c] Tsipis, A. C. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 11.

modified coupled-pair functional (MCPF) method.[26] The agreement is also very good with the semiempirical ASED-MO[27] values for YNH_3. Our results for $MoNH_3$ agree with the MCPF results reported before. For $MoNH_3$, the disagreement with atom

TABLE 5: Reaction Energies (eV [kcal/mol]) for Different Products of the Reaction of Y and Y_2 with NH_3 and Net Atomic Charges from Mulliken Population Analysis

reaction	ΔE	atomic charges and $2S_z + 1$
$Y + NH_3 \rightarrow YNH_3$	−1.1 [−24.6]	YNH_3 ($2S_z + 1 = 2$) Y = − 0.17 N = + 0.17
$Y + NH_3 \rightarrow YNH + H_2$	−1.4 [−32.6]	YNH ($2S_z + 1 = 2$) Y = +0.4 N = −0.4
$Y_2 + NH_3 \rightarrow Y_2NH_3$	−0.6 [−13.9]	Y_2NH_3 ($2S_z + 1 = 1$) Y = −0.10, −0.05 N = +0.14
$Y_2 + NH_3 \rightarrow Y_2NH + H_2$	−2.4 [−55.5]	Y_2NH ($2S_z + 1 = 3$) Y = +0.26 N = −0.52
$Y_2 + 2NH_3 \rightarrow Y_2(NH)_2 + 2H_2$	−4.8 [−110.2]	$Y_2(NH)_2$ ($2S_z + 1 = 1$) Y = +0.53 N = −0.53

TABLE 6: Reaction Energies (eV [kcal/mol]) for Different Products of the Reaction of Mo and Mo_2 with NH_3 and Net Atomic Charges from Mulliken Population Analysis

reaction	ΔE	atomic charges and $2S_z + 1$
$Mo + NH_3 \rightarrow MoNH_3$	−0.4 [−8.5]	$MoNH_3$ ($2S_z + 1 = 7$) Mo = −0.12 N = +0.12
$Mo + NH_3 \rightarrow MoNH + H_2$	0.4 [9.8]	MoNH ($2S_z + 1 = 5$) Mo = +0.32 N = −0.32
$Mo_2 + NH_3 \rightarrow Mo_2NH_3$	−0.8 [−17.9]	Mo_2NH_3 ($2S_z + 1 = 1$) Mo = +0.05, −0.21 N = +0.16
$Mo_2 + NH_3 \rightarrow Mo_2NH + H_2$	0.5 [12.7]	Mo_2NH ($2S_z + 1 = 3$) Mo = +0.24 N = −0.48
$Mo_2 + 2NH_3 \rightarrow Mo_2(NH)_2 + 2H_2$	0.5 [10.9]	$Mo_2(NH)_2$ ($2S_z + 1 = 3$) Mo = +0.52 N = −0.52

superposition-electron delocalization−molecular orbital (ASED-MO) method is due to the different spin multiplicity. While for us the septet is the ground state, Tsipis[27] did not report results for the septet state. We performed the calculations of the quintuplet, but the energy is higher than the energy of the septuplet. It seems that the septuplet was missed during the optimization procedure with ASED-MO. Other theoretical results that we can use for the comparison is for YNH. For this system, Das and Balasubramanian reported high-level ab initio calculations.[28] They found a Y−N bond length of 2.12 Å for a $^2\Sigma+$ state. We obtained a shorter bond distance but the same lowest-lying electronic state. Hence, it is possible to consider this structure for the explanation of the reactivity between yttrium and ammonia, as we will show below.

For all of the structures presented in Figures 1 and 2, the Mo−N bond distance is shorter than the Y−N bond length. Also, the Y−Y bond length is larger than the Mo−Mo bond distance. The compounds with Y are linear or planar structures, while with Mo they are out of the plane or they present an angle different from 180°; for example, for MoNH, the H−N−Mo bond angle is equal to 132.5°.

The reactions that were taken into account for this study are presented in Tables 5 and 6. For the analysis of the structures, it is important to remember the electronic configuration of the metal atoms ($[Kr]4d^15s^2$ for Y and $[Kr]4d^55s^1$ for Mo) and the molecular configuration of Y_2 (single bond (2.94 Å), quintet spin state) and Mo_2 (multiple bond (1.99 Å), singlet spin state). The analysis of the yttrium compounds with ammonia shows that there is a charge-transfer process from the ammonia to the Y atom, as seen in Table 5 with the atomic charges. However, the situation is different for YNH. In this compound, the charge transfer is from the Y atom to the NH molecule. In both cases, the binding energy indicates that the products of the reaction are more stable than the reactants. For the dimer, a comparison of the Y−Y bond distance of the dimer with the Y−Y bond length of the compounds shows that for Y_2NH_3, the Y−Y bond distance is shorter than that for the dimer without NH_3. For Y_2NH and $Y_2(NH)_2$, the Y−Y bond distance is very large. Analyzing the atomic charges reported in Table 5 shows that for Y_2NH_3 there is a charge-transfer process from the NH_3 to Y_2. As a result, the Y−Y bond length decreases as a consequence of the charge transfer being to a bonding orbital of the Y−Y dimer. On Y_2NH and $Y_2(NH)_2$, the atomic charges indicate a charge-transfer process from the dimer to the molecule. In these cases, the charge transfer is stronger than that with ammonia. As seen below, Y−Y bonding orbitals become unoccupied, and for this reason, the Y−Y bond length is larger than that on Y_2NH_3. It appears that for Y and Y_2, there is a relation between the charge-transfer process (to the metal or from the metal) and the binding energy, namely, as the charge transfer increases the binding energy also increases.

Analyzing the molybdenum compounds, Martínez et al.[23] reported that the Mo atom can only react as an electron donor because the electron pairing on the Mo atom is energetically unfavorable because of the Coulombic interaction. The experimental observation[13] indicates that Mo atoms show no reactivity toward electron donors such as NH_3. Table 6 shows that the interaction of the Mo atom with NH_3 is thermodynamically favorable with a binding energy of 8.5 kcal/mol, while for NH it is thermodynamically unfavorable because the products of the reaction are less stable than the reactants by 9.8 kcal/mol. For $MoNH_3$, the charge transfer is from the NH_3 to the Mo atom, and it is unfavorable because of the Coulombic interaction. For this reason, the binding energy is smaller than that for the dimer. In the case of MoNH, the charge transfer is from Mo to NH, but this charge transfer is not enough to stabilize the system, as can be seen from the binding energy. It is perhaps possible that the ground state of MoNH was missed during the optimization procedure, but the number of different initial geometries and spin multiplicities that were considered is sufficiently high to feel confident that the global minimum has been identified.

The Mo_2NH_3 complex is quasi-linear, as can be seen in Figure 2. The binding energy is 17.9 kcal/mol and indicates a thermodynamically favorable process. This binding energy agrees with the experimental values of Lian et al,[13] who reported a binding energy of approximately 14 kcal/mol. There is a charge transfer from the ammonia to the dimer. The Mo−Mo bond is elongated. In this case, the dimer can react as an electron acceptor because the metal−metal multiple bonds can accept some charge. For the dimer, the only compound that is thermodynamically favorable is Mo_2NH_3. For Mo_2NH and $Mo_2(NH)_2$ the charge transfer is from the metal dimer to the molecules. With the charge transfer, the Mo−Mo bonds increase. The lengthening of the Mo−Mo bond distance destabilizes the system because the sextuplet bond of Mo−Mo is quite stable. For the molybdenum compounds, the relation between the charge transfer and the binding energy is different from the situation with the yttrium compounds. While for the yttrium compounds it is irrelevant whether the charge transfer is from the metal to the molecule or vice versa, for the molybdenum compounds the process is thermodynamically favorable only if the charge transfer is from the molecule to Mo or Mo_2. If the Mo atom or the dimer transfer charge to the molecules, the process is thermodynamically unfavorable.

As was reported before,[13,23,26] the results of the interactions of Y and Mo with NH_3 can be rationalized in terms of attractive and repulsive interactions between the metal electrons and the lone pair of the ammonia. For Y, this interaction is attractive due to the presence of empty 4d orbitals. For Mo, this interaction is less attractive because of the spherical symmetry arising from the half-filled orbitals. In this case, the electron pairing is unfavorable because of the Coulombic interaction.

For the dimers with ammonia, the repulsion between the lone pair of ammonia and those of the dimer is reduced by polarization of the charge. Bagus et al.[29] reported the importance of charge polarization within the metal fragment. The polarization of the metal dimer in Mo_2NH_3 is bigger than that for Y_2NH_3. This is reflected on the binding energy because for Mo_2NH_3 it is bigger than for Y_2NH_3.

The molecular orbitals of Y_2 show that bonding or antibonding orbitals (formed with d + s atomic orbitals) can be occupied with a charge transfer. When Y_2 transfers charge to a molecule, bonding or antibonding orbitals may be emptied. Both processes are energetically favorable. Molecular orbitals of Mo_2 show that, if the charge transfer is to the Mo_2, an antibonding orbital (formed with d + s orbitals) will be occupied. If the charge transfer is from the dimer, a bonding orbital will be unoccupied. This effect, in addition to the high stability of a closed shell, is reflected in an energetically unfavorable process when the charge transfer is from the dimer to the molecule.

Conclusions

To explain the bonding and reaction of Y, Y_2, Mo, and Mo_2 interacting with NH_3, density functional calculations on MNH_3, MNH, M_2NH_3, M_2NH, and $M_2(NH)_2$ (M = Y and Mo) were performed. For Y, the stable products are YNH_3 and YNH. For Y_2, the stable products of the reaction are Y_2NH_3, Y_2NH, and $Y_2(NH)_2$. The binding energy indicates that the reaction of Y and Y_2 is possible. For Mo, the stable product is $MoNH_3$. For MoNH, the binding energies indicate that the reactants (Mo + NH_3) are more stable than the products (MoNH + H_2). For the $Mo_2[NH_3]$ complex, the binding energy is 17.9 kcal/mol, in good agreement with the experimental value of 14 kcal/mol previously reported. For Mo_2, there is no other stable products of the reaction because Mo_2NH and $Mo_2(NH)_2$ are less stable than the reactants (Mo_2 + NH_3).

The results of the interactions of Y and Mo with NH_3 can be rationalized in terms of attractive and repulsive interactions between the metal electrons and the lone pair of the ammonia. For Y, this interaction is attractive because of the presence of empty 4d orbitals. For Mo, this interaction is less attractive because of the presence of many open 4d orbitals. In this case, the electron pairing is unfavorable because of the Coulombic interaction.

For the dimers with ammonia, the repulsion between the lone pair of NH_3 and those of the dimer is reduced by polarization of the charge. The polarization of the metal dimer in Mo_2NH_3 is bigger than that for Y_2NH_3. This is reflected on the binding energy because for Mo_2NH_3 it is bigger than for Y_2NH_3.

The differences in the bonding are correlated with the differences in the molecular orbital occupation. For each metal, a relationship between the electronic configurations of the transition metals and the binding energies is reported.

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