

Relative Energies of Dioxo μ -Oxo Molybdenum Complexes from Various Fragmentation Strategies[‡]

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Abstract: A thiocyanatomolybdenum(vi) dioxo μ -oxo complex dimer bearing 4,4'-di-*t*Bu-2,2'-bipyridine ligands has shown exceptional oxidizing ability. It exists as a *meso* form (symmetrical) and a *d,l* pair (unsymmetrical) in the crystal unit cell and also in equilibrium in solution. Which oxygen atom and which configuration are predominantly involved in the process of oxygen atom transfer is a question whose answer would certainly help experimentalists. From ab initio theoretical calculations we analyzed the electronic differences between the two configurations. The large number of atoms (101) restricts

the choice of theoretical methods. We give results for second-order Møller–Plesset (MP2) and DFT with the hybrid functional B3LYP, with and without pseudopotentials, with double- ζ basis sets plus polarization functions. Although the structures of the two types of configurations are quite different, we show they have practically the

Keywords: ab initio calculations • density functional calculations • homogeneous catalysis • molybdenum • oxo ligands

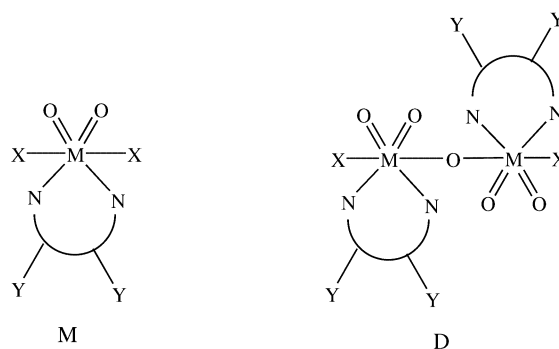
same energy. Similarly, no significant differences were found for electronic atomic populations on oxygen and surrounding atoms. To facilitate future studies on the process of oxygen atom transfer, we compare the entire molecules to smaller entities obtained by fragmentations or by so-called hybrid methods. We show that the *t*Bu groups, and even sometimes the pyridyl rings, play only a minor role in determining the electronic structure. Concerning the energy difference between the two configurations, the MP2 results appear more consistent than the B3LYP results.

Introduction

Metal oxo species are of utmost importance in catalytic oxidation processes. Many transition metals are involved in such reactions, for example, Ru, Cu, Fe, Co, and Ni.^[1] The metal oxo group exists in terminal (M=O) and bridging forms (M–O–M). Recently, molybdenum(vi) oxo compounds bearing thiocyanato groups and bipyridyl ligands were found to exhibit very interesting oxo-transfer properties. To better understand the reason for this high activity, we undertook a theoretical study.

The experimental studies concern two families of molybdenum oxo compounds, designated here for simplicity as M for monomer and D for dimer (Scheme 1). Besides being more active, the dimers have some unusual features.^[1] Thus when X is a NCS moiety and Y is a *t*Bu group, X-ray analy-

sis shows that three molecules are present in the unit cell of the dimer. At the center of the cell, the molecule is in the so-called *meso* configuration, in which the μ -O atom lies on a center of symmetry (i.e., Mo–O–Mo 180°). On each side the other two configurations *d* and *l* are unsymmetrical (Mo–O–Mo 155.7°). More details of these structures can be found in ref. [1]. More surprisingly, these different configurations also coexist in solution (in dichloromethane), as shown by NMR experiments.^[1] When the *t*Bu groups are replaced by OMe groups, only NMR signals corresponding to



Scheme 1. Definition of monomer and dimer molecules.

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the *meso* configuration are observed, whereas when the *t*Bu groups are replaced by benzyl groups only the bent forms occur.^[2] These unexpected observations, if somehow rationalized, could have important implications as far as reactivity is concerned, and could also give useful information on the mechanism of oxygen atom transfer.

Here we discuss the properties of the dimer. A molecule of the dimer with NCS and *t*Bu substituents contains 101 atoms. Accurate ab initio calculations are necessary, since we expect very small energy differences between the *meso* and *d,l* configurations. With our goal of better understanding the mechanism of oxygen-atom transfer in mind, modeling is clearly necessary for subsequent reactivity calculations. Although not a conclusive argument for reactivity, consideration of electronic density by atomic population analysis may help chemists as a first approximation.

We had two goals. First, we tried to determine whether electronic features can distinguish between the *d,l* and the *meso* configurations with regard to reactivity. At present, no experimental method exists for solving such a problem, and the size of the molecules makes ab initio calculations difficult. This leads to our second goal: to determine whether modeling (all-electron vs pseudopotentials, hybrid method vs fragmentation) can reproduce the best results obtained from a given quantum mechanical (QM) method.

In the following we discuss the respective merits of different modeling strategies, the relative stabilities of the *meso* and *d,l* configurations and finally the atomic populations, mainly of the oxygen atoms and their neighbors, which are probably directly involved in oxidation reactions.

Methods of Calculation

Choice of methods: The evaluation of a given property of an electronic system by an ab initio method implies choosing all approximations needed to make the calculation feasible. This not only includes the theoretical method itself, which introduces more or less correlation energy, and the basis sets, but this also offers the opportunity of introducing pseudopotentials, solvent effects, and so on. Another type of approximation is the fragmentation of the entire molecule to discard uninteresting parts, if any. Until a few years ago the only way was to add end atoms, often H atoms, to the dangling bonds left by fragmentations. Now, QM/MM, or hybrid, methods provide a softer way to transform a large problem into a smaller one. We consider the application of all these approximations to our molecules.

Researchers working on charge distribution analysis typically perform their calculations at the MP2/6-31G* level.^[3] This is hard to achieve in our case for the entire molecules. However, when no densities are required, energies can be obtained at this level, and we were confident in the results, because we were looking for energy differences between similar entities. Other methods derived from DFT, especially B3LYP,^[4] have proven their adequacy for treating energy problems. Therefore, we also consider this method and finally give results at the Hartree–Fock (HF) level to allow for correlation effects. The 6-31G* basis set is an equally correct choice for our energy-difference calculations, since only neutral molecules in a singlet state will be encountered. Furthermore, this is a good compromise between computing time/feasibility and accuracy. For practical reasons the basis set for molybdenum was reduced to 3-21G*, in an all-electron calculation, and one f polarization function was optimized in the monomer molecule; we found $\zeta_f=0.60$. We do not regard this restriction in basis set as a real drawback in our case. Indeed, while this would be unacceptable in a calculation to determine very accurately the electronic structure of one given configuration, here we always consider

energy differences between quite similar configurations. This basis set is of double- ζ +polarization quality, as for the other atoms in our molecules. We do not think that the difference in the treatment of core electrons and in the valence number of primitive functions (versus the 6-31G* basis set) implies dramatic changes in these energy differences. Moreover, these configurations contain only two molybdenum atoms in a total of 101 atoms in the entire molecule. Deficiencies should tend to cancel each other out.

Concerning basis sets, the consideration of p polarization functions for H atoms and comparison of pure versus cartesian d and f functions are a priori necessary. However, we can foresee that these effects will only be second-order. The charges on H atoms and on C atoms directly linked to H atoms are of course affected by the introduction of p functions on H atoms, but these atoms lie far from the O atoms we are interested in, and the effect damps down very quickly. As for the choice of d and f functions, energies will be lower when the basis set is increased, but to a proportional amount in both configurations, so that the final effect on the energy difference is probably negligible.

For the dimer, which comprises two molybdenum atoms and almost fifty first- and second-row atoms, it is logical to consider the advantages of pseudopotentials. Two kinds of pseudopotentials and associated basis sets were considered: the Stuttgart/Dresden^[5] and the LanL2DZ combination, which uses the D95 basis sets of Dunning et al. on first-row atoms^[6a] and Los Alamos electron core pseudopotentials together with double- ζ basis sets for second-row atoms and atoms up to Bi.^[6b,c,d] The first type uses quite extended basis sets for transition metals, while in the second, basis sets for atoms of the second row and higher are of double- ζ quality. To decrease the size of calculations we used polarization functions only for sulfur ($\zeta_d=0.60$) and molybdenum atoms ($\zeta_f=0.47$). Although the introduction of polarization d functions for C and N atoms may lead to changes, both in density repartition and energy, their effect on the energy differences should be small, as for other choices in basis sets discussed above. The Gaussian 98 software^[7] was used throughout this work.

Regarding reasonable fragmentations of the molecules, the first obvious approach is to remove the *t*Bu groups. A further possible fragmentation is to break the pyridyl rings, that is, to remove C₃H₂*t*Bu groups. Finally, and less reasonably, all carbon atoms of the bipyridyl moiety can be removed, that is, leaving only N and O atoms bonded to Mo atoms. In the following, we respectively designate these fragmentations F1, F2, and F3, while F0 corresponds to the entire molecule without any fragmentation (Figure 1). It would not be reasonable to try to remove NCS groups, because they are too close to the oxygen atoms, the probable centers of the catalytic reaction.

Besides the usual Mulliken population analysis we also considered analysis from natural orbitals^[8] and methods which fit the electrostatic potential to selected points around atoms: the Merz–Kollman–Sing (MKS) procedure^[9] and the ChelpG method of Breneman et al.^[10] The atoms in

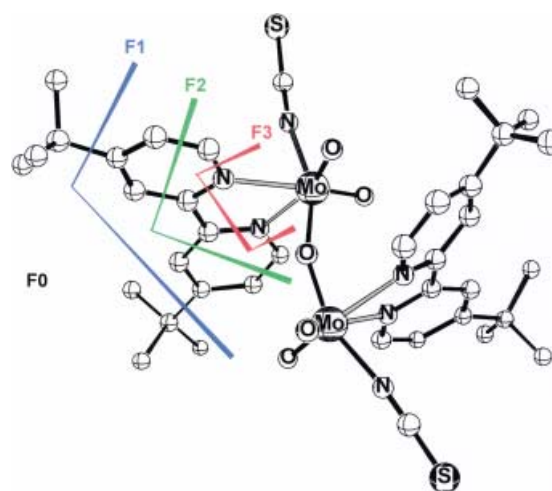


Figure 1. Fragmentation schemes of the *d,l* configuration.

molecules (AIM) method of Bader,^[11] based on the topology of the electron density and implemented in Gaussian98,^[12] was tried but found inappropriate for the cases of unusual topology in our molecules. Default size limitations in the natural bond order (NBO) package^[8] in Gaussian98 concern the number of atoms (99) and the number of basis functions (500); we encountered these limits in some of our calculations.

Another modeling process concerns the final geometry optimization of our molecules. Owing to their large size, it is hopeless to obtain acceptable low-energy minima on the potential energy surface simultaneously for both configurations. Convergences to stationary points, which could be arbitrarily far from the absolute minimum and which may not even be well defined (for reasons of computing time, frequency calculations are inappropriate), could introduce spurious effects for our purpose. Furthermore, fragmentations would have no sense if optimizations of geometries were accomplished independently. Therefore, for comparing the energies of the two configurations, we only used geometries provided by X-ray structure analysis.

Preliminary tests of methods and charge definitions: We have no experimental information on the dipole moments of our molecules. Furthermore, in order to have some idea about the relevance of various charge definitions used to describe atomic populations, it would be instructive to connect these various electronic population analyses to some experimental property, such as dipole moment, for a small test molecule. The dipole moment of the HCN molecule, which includes the NC sequence present in the apical branches of our complexes, is known and has widely been studied theoretically. Table 1 lists comparative values for HCN, obtained with the methods, basis sets, and charge definitions used throughout in this paper. The best values for the dipole moment are obtained from MP2/double- ζ and MP2/LanL2DZ calculations. The results obtained by B3LYP and RHF are worse. The corresponding MP2/double- ζ distributions of charges appear correct. Indeed, the central C atom, which accepts electrons from the H atom and donates electrons to the N atom, has only a small positive charge. The pseudopotential calculation assigns

a slightly greater attracting power to the N atom. In fact, all distributions of charges have the same qualitative behavior except one, namely, the Mulliken definition associated with the LanL2DZ pseudopotential calculation, for which the negative charge on the carbon atom needs some comments. It is well known that Mulliken charges are dependent on basis set. The optimization of d functions in this case ($\zeta_d^C=0.72$; $\zeta_d^N=0.94$) leads to the Mulliken charges +29 (H), -26 (C), and -4 (N) (unit: $10^{-2}e^-$) and $\mu=2.98$ D for the dipole moment. As another example, with the ChelpG definition of charges, we obtain +19 (H), +16 (C), -35 (N) (unit: $10^{-2}e^-$) and $\mu=2.90$ D. Clearly the effect observed in Table 1 is not due to the basis set; instead, it is a combination of the effects of the pseudopotential and the definition of charges. In fact, the differences observed with and without the introduction of d functions lie within the range of values obtained from other definitions of charges shown in Table 1. When discussing the electronic population analysis of our complexes, we shall mainly refer to results obtained from MP2 calculations, and caution must be taken with some results (especially those from the Mulliken definition) obtained from pseudopotential calculations.

Energies of Fragment Molecules

Atomization energies of the molecules with fragmentations F_n are listed in Table 2 for the d,l configuration. Results for the *meso* configuration are quite similar and are thus omitted. Of course, these values do not imply any kind of stability property, since no thermodynamic considerations were included, no reaction path was considered, and our structures, as stated, were not even optimized. Moreover, with regard to the above discussion on basis sets, our results must be discussed with caution. The interest merely lies in the compari-

Table 1. Atomic charge distributions [$10^{-2}e^-$] and dipole moments [D] of the HCN molecule from various definitions of charges. a: Mulliken; b: NPA^[8]; c: MKS^[9]; d: ChelpG^[10]

Method/basis	Charge type	H	C	N	μ
experiment		–	–	–	2.98 ± 0.03
MP2/double- ζ	a	+28	+2	-30	2.96
	b	+23	+7	-30	3.02
	c	+20	+14	-34	2.92
	d	+18	+17	-35	2.89
MP2/LanL2DZ	a	+26	-27	+1	3.07
	b	+20	+13	-33	3.12
	c	+15	+24	-40	3.00
	d	+14	+27	-41	2.95
B3LYPdouble- ζ	a	+25	+11	-36	2.90
	b	+23	+8	-31	2.90
	c	+21	+12	-33	2.87
	d	+19	+15	-34	2.85
RHF/double- ζ	a	+32	+6	-38	3.24
	b	+23	+12	-35	3.24
	c	+24	+11	-36	3.21
	d	+22	+15	-37	3.19

Table 2. Total atomization energies [kcal atom⁻¹] of d,l fragment molecules. Q: quintet state; T: triplet state; S: singlet state; If not indicated: singlet state. F_n fragmentations are defined in text.

F_n		DZE + polarization			LanL2DZ		
		HF	MP2	B3LYP	HF	MP2	B3LYP
F3	Q	40.8	84.1	89.3	36.3	77.5	84.9
	T	41.0	84.4	89.3	36.3	77.6	84.9
	S	30.3	84.2	86.7	25.7	77.6	82.2
F2		58.5	100.8	104.8	52.6	91.4	99.1
F1		74.3	114.1	117.6	68.1	103.0	111.4
F0		74.3	103.5	108.3	69.6	94.6	103.8

son, concerning methods and fragmentation processes, to energy differences given in the next chapter, but also in the discussion on the choice of pseudopotentials.

All molecules are bound, relative to complete dissociation, even at the HF level, and B3LYP and MP2 calculations give comparable results. For F3, apart from the meaningless HF calculations, the energies only slightly favor the quintet or triplet (where available) states in comparison to the singlet states. Another conclusion is that the pseudopotential LanL2DZ calculations give quite comparable results to the all-electron calculations. This is a first proof that our restricted basis set on Mo atoms in all-electron calculations was not completely unrealistic, since in the pseudopotential calculations no equivalent restriction is present. A calculation on the F2 molecule in its *d,l* configuration, performed with the Stuttgart pseudopotentials and basis sets,^[5] gave $59.6 \text{ kcal atom}^{-1}$ at the HF level and $102.2 \text{ kcal atom}^{-1}$ at the MP2 level. These results are in better agreement with the all-electron calculations than the LanL2DZ calculations. However, the latter, which already are in correct agreement, are somewhat smaller than the Stuttgart calculations, which use an extended basis set for metal atoms. Indeed, the numbers of basis functions in the case of the F2 molecules are 297, 440, and 466 for the LanL2DZ pseudopotential and basis, the 6-31G* basis and the Stuttgart pseudopotential and basis with more or fewer polarization functions, respectively. Since it would be very difficult (or even impossible) to obtain results for the F0 and F1 molecules in the last-named case, we only considered LanL2DZ for pseudopotential calculations. With the chosen unit (kcal atom^{-1}) we observe that the values, in all cases, increase regularly on going from F3 to F1 and then slightly decrease to F0. The behavior between F3 and F1, expected for homoatomic clusters, becomes operative here, probably as a consequence of similar structures when considering fragments of increasing size. Indeed, apart from F3, only C–H and C–C bonds are destroyed or created. The decrease in the atomization energies between F1 and F0 is probably an artefact resulting from both the consideration of heteroatomic molecules and the difference in the number of atoms, which is the greatest in that case in comparison to all other fragments. A 5% change would be sufficient to reverse this energetic order without altering the orders of the other fragments. In the context of this study, this is considered acceptable. In anticipation of the forthcoming discussion in the next section, let us emphasize the following points: B3LYP results are closer to MP2 rather than to HF results, both for all-electron and pseudopotentials calculations. As expected, HF results are not very satisfactory, as is the F3 fragmentation in all cases. The energy differences between the *meso* and *d,l* configurations are indicated by the points labeled fragmentations in Figures 2 and 3. A comparison with results obtained from QM/MM methods is provided in the next section.

QM/MM versus Fragmentation Methods

Let us divide the molecules into two parts, A and B, where A is at the center of the molecule and B corresponds to sur-

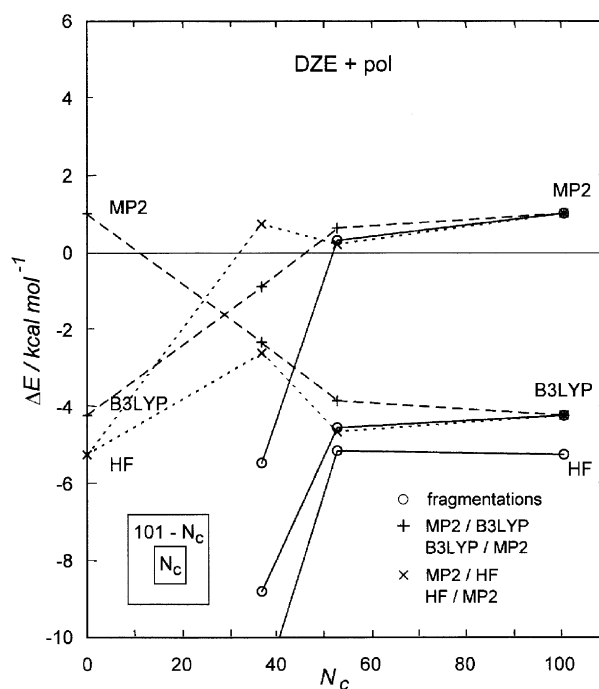


Figure 2. Energy differences [kcal mol^{-1}] between the *meso* and *d,l* configurations in all-electron 6-31G* calculations.

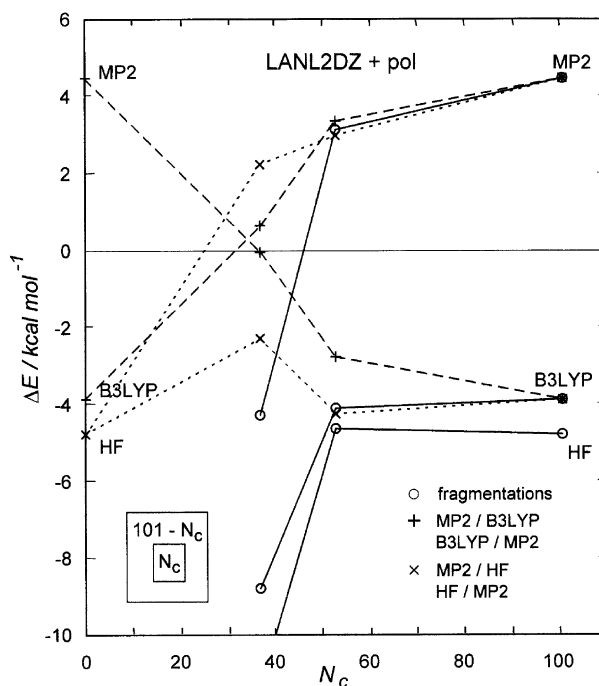


Figure 3. Energy differences [kcal mol^{-1}] between the *meso* and *d,l* configurations in pseudopotential LanL2DZ calculations.

rounding atoms and bonds. According to the QM/MM philosophy, part A must be treated with a performing quantum mechanics (QM) method, and part B with either a molecular mechanics (MM) or a QM-less performing method. We chose the second case but then we met a problem: among the methods used throughout this paper, that is, MP2 and

B3LYP, which performs best? Therefore, in principle, we have two cases to consider: A(MP2)B(B3LYP) and A(B3LYP)B(MP2). On the other hand we also considered the two more classical partitions: A(MP2)B(HF) and A(B3LYP)B(HF). We simply write method 1/method 2 where method 1 is used in the A part and method 2 in the B part. The energy is written as Equation (1).

$$E = E_A(\text{method 1}) + E_{(A+B)}(\text{method 2}) - E_A(\text{method 2}) \quad (1)$$

Note that, as expected, the change from pure to cartesian d and f functions in the basis sets is of no importance for the results. For example, in the F2 case, the error in the HF energy difference is only 1.9%, while at the MP2 level it is 1.5%, that is, indistinguishable in the figures. Similar errors were found for populations of oxygen atoms (see below). This saving was of crucial importance in the study of F1 and F0 molecules.

In the framework of the ONIOM procedure,^[13–15] in which part A is the F_n ($n=0–3$) fragment parts and part B the complementary parts, we must first consider which is the convergence of the procedure in function of n , both for an all-electron and for a pseudopotential calculation (Figures 2 and 3). The energy difference ΔE between the *meso* and *d,l* configurations is plotted versus N_c , the number of atoms in the central parts. On the right of the figures, $N_c=101$ corresponds to the entire molecules (F0) treated at the MP2, B3LYP, and HF levels. Then, moving to the left, the fragmentations F1 ($N_c=53$) and F2 ($N_c=37$) are considered. Finally, on the left we still have the energies corresponding to the entire molecules, but of the complementary parts ($101-N_c$) in the framework of the hybrid-methods procedure. The points corresponding to fragments F3 ($N_c=25$) are not drawn, since the corresponding clusters no longer have singlet spin symmetry in their ground state (cf. Table 2); in addition, they cannot be considered as good representations of the entire molecules, and this may also imply numerical inconsistencies. For example, consider the case MP2/B3LYP in all-electron calculations (+ in Figure 2), for which the lowest spin states were chosen. In the case of the *d,l* configuration, we found the triplet state (T) to be the most stable in UHF and MP2 calculations, while the quintet state (Q) is the most stable at the B3LYP level. However, triplet and quintet states are close in energy at all levels of theory, well below the singlet state (S). This is not the case in MP2 calculations, where the singlet state is slightly lower than the quintet state, but we may foresee an artefact due to too high an HF value. In the case of the *meso* configuration we obtained quintet states energies well below singlet-state energies at the HF and B3LYP levels of theory, but only slightly lower at the MP2 level. However, we were unable to obtain a satisfactory convergence for the triplet state. Owing to the fact that triplet and quintet energies are almost equal in the *d,l* configuration, we disregarded the problem and considered only quintet states for these clusters. These energetic orders are summarized in Table 3, in which the energy increases from left to right for each level of theory. This scheme is also valid for pseudopotential LanL2DZ results. Now, returning to Figure 2, we might suppose that the point

Table 3. Energetic order of singlet (S), triplet (T), and quintet (Q) states of the F3 fragments from various theoretical methods.

MP2	HF	B3LYP
<i>d,l</i> : T \cong S \cong Q	<i>d,l</i> : T \cong Q < S	<i>d,l</i> : Q \cong T < S
<i>meso</i> : Q \cong S	<i>meso</i> : Q < S	<i>meso</i> : Q < S

F3 ($N_c=25$) should lie close to the line joining points F2 ($N_c=37$) and $N_c=0$, that is, F3 might have a value around -1.25 kcal mol⁻¹. A similar value is obtained for the energy difference ΔE : S//S (-1.58 kcal mol⁻¹). In the last notation the spin state at the left of the double slash is that for both configurations of the A part (i.e., treated by MP2 in this example), and that on the right is for both configurations of the A part, but treated with the method used for the B part (i.e., B3LYP in this example). Within the ONIOM procedure, part of the energy of each configuration is given by a calculation concerning the entire molecule treated with the method used for the B part. In our case the ground states of the entire molecules are always singlet states; therefore, it was not worth mentioning in the above notation. Furthermore, we thought it was not reasonable to mix different spin states between *d,l* and *meso* configurations, even in MP2 calculations, where the different spin states appear similar. This value could be considered as a good result if F3 is regarded as a simulation of the entire molecule F0, which is a singlet in its ground state. However, numerically this is not a logical result since in B3LYP calculations the singlet state is somewhat higher in energy than quintet or triplet states for both *d,l* and *meso* configurations. This could only be explained by some error compensations between singlet spin states at the two levels of theory. If we consider F3 on its own, the best combination should be in principle Q//Q. Its value (-4.68 kcal mol⁻¹) lies slightly below the complementary B3LYP value on the left of the figure, which is not very satisfactory. In a LanL2DZ pseudopotential calculation, these points lie respectively at $+7.66$ kcal mol⁻¹ (S//S) and -3.54 kcal mol⁻¹ (Q//Q). The S//S combination is completely out of range (Figure 3), since an acceptable value should be around 0.0 kcal mol⁻¹. The Q//Q value is comparable to that obtained from the all-electron calculation. The same erratic behavior occurs when considering other combinations of the above-mentioned quantum methods. Therefore, it is clearly not reasonable to consider the F3 fragmentation in the framework of the ONIOM procedure.

Now let us consider all-electron calculations on the isolated F3 fragment cluster with addition of hydrogen atoms to saturate the dangling bonds. We obtain an aberrant range from $+3.13$ kcal mol⁻¹ (singlet) to -2.14 kcal mol⁻¹ (quintet) for MP2 calculations, since the energy difference for the F2 cluster is -5.45 kcal mol⁻¹. For B3LYP calculations we obtain $+0.50$ (singlet) and -1.68 kcal mol⁻¹ (quintet); these values are not in agreement with the energy difference for the F2 clusters (-8.79 kcal mol⁻¹), although at the (meaningless) limit $N_c \rightarrow 0$, we might have $\Delta E \rightarrow 0$. To conclude, this fragmentation is probably unrealistic, since five-atom rings linked to molybdenum centers are broken. On the other hand, these energy differences are so small that the methods used in this paper to treat high-spin ground states or excited

singlet states are deficient. Therefore, it was wiser to avoid all these points in the figures.

Let us now comment on the results shown in Figure 2 and Figure 3. The first result that should be underlined is that, both in the fragmentation and ONIOM processes, F1 differences in energies are close to F0 in all methods. Clearly this means that, although *t*Bu groups (and more generally Y groups) have a real chemical role in the complex, they are not of prime importance in the calculation of the electronic structures. Independent of the methods used these results apply to all-electron calculations and pseudopotential calculations as well. The F2 isolated fragments are far from the F0 entire molecule. This was not the case for atomization energies. In ONIOM calculations this is less clear. Sometimes the sign of the F0 energy difference is constant for the MP2/HF calculations (all-electron and pseudopotential) and for the MP2/B3LYP pseudopotential calculation, while it is changed in MP2/B3LYP all-electron calculations. On the other hand, in B3LYP/HF results these points lie far from the hypothetical line joining B3LYP and HF points. In this fragmentation an important electronic change is made, since the four aromatic systems are broken, but the main electronic characteristics of the complex have probably not yet deteriorated enough, since we still are not far from F0 results. These F2 results clearly emphasize the advantage of using hybrid methods instead of pure fragmentations. The F3 cases were discussed previously.

Now let us compare the methods. For the entire molecules we have a disparity between HF and B3LYP on one hand and MP2 calculations on the other. Indeed, the *meso* configuration has the lowest energy in the first two cases, whereas with MP2 the *d,l* configurations are lowest in energy. Since the B3LYP energy difference of the entire molecules is close to the HF value, this means that the B3LYP treatment of correlation is equivalent in *d,l* and *meso* configurations and that correlation effects almost cancel out in the difference. This is not the case for MP2 calculations. The two configurations, although close in energy, have quite different structures. Indeed, in the *d,l* configuration, the bent Mo-O-Mo central sequence of bonds infers stronger interactions between bipyridyl rings and also between these rings and other parts of the molecules.^[1] Correlation effects might differ substantially between the two configurations and therefore MP2 results appear more realistic than B3LYP results. This disparity is increased in LanL2DZ calculations, but the general shapes of the curves are the same. Therefore, it is clear that the physics of the problem is conserved and not changed by the replacement of core electrons by pseudopotentials (plus adequate valence basis sets) for sulfur and molybdenum atoms. This corroborates our assumption that the reduced basis used for molybdenum atoms did not introduce a spurious effect.

We cannot obtain further information from the direct comparison of the MP2/B3LYP and B3LYP/MP2 curves. Indeed, in the ONIOM formalism these two curves are symmetrical with respect to the line $\Delta E = [F0(MP2) + F0(B3LYP)]/2$. However, it is worth comparing these two approximations with MP2/HF and B3LYP/HF. In Figures 2 and 3, the MP2/B3LYP curves lie close to the MP2/HF ones.

This may be explained by the proximity of the target B3LYP and HF ($N_c=0$) points (left of the figures). Both curves decrease regularly from right to left. More unexpected are the positions of the F2 points in the B3LYP/HF curves (vide supra). Contrary to the MP2/HF curves, the F2 fragment brings an apparent erratic point to these curves. Without being a definite proof, this result corroborates our previous conclusion that the MP2 method appears more appropriate than the B3LYP method for calculating the energy difference between the *d,l* and *meso* configurations.

Electronic Populations

The main point to consider is whether a difference is observed between *meso* and *d,l* configurations which could be relevant to discussing reactivity. Determination of electronic population is more time- and memory-consuming than a simple energy calculation. At the limits of the computer used, we were able to obtain results for the entire molecule only for the *meso* configuration, thanks to its symmetry. Therefore, it is of prime importance to first consider the variation of these populations as a function of the size of the fragment. Although the best population analysis is obtained with MP2 calculations, we also include in our discussion the results obtained with the other methods used in this paper, that is, HF and B3LYP. We also discuss the differences introduced by the use of pseudopotentials and different definitions of charges. Moreover, since our goal is to obtain a description of the electronic population around oxygen and neighboring non-H atoms it is not necessary to introduce polarization functions on hydrogen atoms.

Table 4 lists atomic populations for some atoms in the different fragment molecules of the *meso* configuration and from different definitions of charges at the MP2/6-31G* level. The different atoms chosen are the two kinds of oxygen (central μ -oxo and terminal doubly bonded oxo), molybdenum, nitrogen, carbon, and sulfur, as well as the sum for the entire NCS group. We show the results for the Mulliken (M) analysis, the two arising from a fitting to the calculated electrostatic potential: the Besler, Merz, Kollman and Singh (MKS) definition,^[9] the Breneman and Wiberg (ChelpG) method^[10] and, where available, those obtained from a natural population analysis (NPA).^[8] A first important conclusion is that, for all definitions of charges, there are practically no differences between the results for the entire molecule (F0) and for the fragment F1 and very small differences for F2. This is important, because the population analysis for the fragment molecule F1 is much easier to obtain than that for F0 and a fortiori for F2. Therefore, the *meso* and the *d,l* configurations can be compared more easily between the F1 or F2 fragments instead of the F0 entire molecules. Some additional remarks must be made: 1) For F3, the charges obtained in the quintet state are in general more coherent with those of other fragments than in the singlet state, which is not too surprising, since the quintet state (the ground state) is probably better described than the singlet state at the MP2 level. 2) The Mulliken charges roughly lie in magnitude between the natural charges and

Table 4. Atomic charge distribution [$10^{-2} e^{-}$] of selected atoms in the *meso* configuration for various fragmentations and different charge definitions in all-electron MP2/6-31G* calculations. Mulliken analysis (M); natural orbitals (NPA); from an adjustment to the electrostatic potential according to Breneman and Wiberg (CHelpG) or Besler, Merz, Kollman and Singh (MKS). Q: quintet state; S: singlet state. *F_n* fragmentations are defined in text.

Charge definition	<i>F_n</i>	–O–	Mo	=O	N _{sp}	C _{sp}	S	NCS
M	F0	–73	+137	–35	–42	+7	–27	–62
	F1	–73	+137	–35	–42	+6	–25	–61
	F2	–74	+137	–34	–43	+7	–24	–60
	F3(Q)	–76	+140	–33	–45	+7	–21	–59
	F3(S)	–71	+135	–34	–38	+7	–8	–38
CHelpG	F0	–49	+80	–30	–31	+17	–37	–51
	F1	–51	+81	–30	–32	+17	–37	–52
	F2	–54	+85	–30	–35	+19	–35	–52
	F3(Q)	–54	+108	–34	–37	+21	–33	–49
	F3(S)	–50	+111	–35	–32	+22	–20	–30
MKS	F0	–45	+58	–27	–13	–3	–31	–46
	F1	–48	+62	–27	–16	–1	–30	–47
	F2	–40	+65	–27	–16	–1	–29	–45
	F3(Q)	–37	+101	–34	–19	+2	–27	–44
	F3(S)	–36	+102	–35	–17	+5	–15	–26
NPA	F2	–77	+141	–31	–62	+12	–16	–67
	F3(Q)	–79	+140	–30	–62	+11	–14	–64
	F3(S)	–72	+138	–31	–52	+9	+1	–42

those obtained from the electrostatic potential. 3) The charge on the doubly bonded oxygen atoms is insensitive to both the fragmentation and the definition of charges. 4) The charge on the central oxygen atom is roughly twice the charge on the doubly bonded oxygen atoms. 5) The charge on the entire NCS group also appears quite insensitive. We can conclude that around the molybdenum atoms the electronic density is correctly described by all the definitions we considered and that F1 (or even F2) can be used instead of F0.

The *meso* and *d,l* configurations are compared in Table 5 for F2 fragments. With the definitions of charges as described above, we show the results for MP2/6-31G* calculations (part a) and LanL2DZ pseudopotential calculations (part b). Clearly, in all cases, no significant difference is observed between the atomic populations of the two configurations. A negative charge is present on the carbon atom of the NCS group according to Mulliken population analysis in a

LanL2DZ calculation. The same type of anomaly was obtained in the test calculation on HCN, but for other definitions of charges the electronic atomic populations are very similar, regardless of whether pseudopotentials are used or not. Therefore, as for HCN, this is not a basis-set effect. Then, from Tables 4 and 5, a general conclusion is that any difference between atomic populations of the two configurations is not a reason for favoring one or the other as a preferred candidate in the oxidation process.

Conclusion

One purpose of this work was to consider which electronic simplifications could be used to treat in an easier manner the entire molecules (101 atoms) in order to gain information on the oxidation reaction.

Table 5. Atomic charge distribution [$10^{-2} e^{-}$] of selected atoms in the *meso* and *d,l* configurations (F2 fragmentation) from all-electron (6-31G*) and LanL2DZ pseudopotential MP2 calculations and different charge definitions (see Table 4 caption). For all but the central O atom, *d,l* results are mean values.

Charge definition	Config.	–O–	Mo	=O	N _{sp}	C _{sp}	S	NCS
a) DZE + polarization								
M	<i>meso</i>	–74	+137	–34	–43	+7	–24	–60
	<i>d,l</i>	–74	+138	–34	–43	+5	–24	–62
CHelpG	<i>meso</i>	–54	+85	–30	–35	+19	–35	–52
	<i>d,l</i>	–60	+101	–31	–39	+21	–36	–54
MKS	<i>meso</i>	–40	+65	–27	–16	–1	–29	–45
	<i>d,l</i>	–45	+78	–29	–7	–8	–28	–44
NPA	<i>meso</i>	–77	+141	–31	–62	+12	–16	–67
	<i>d,l</i>	–78	+141	–30	–64	+13	–17	–68
b) LanL2DZ + polarization								
M	<i>meso</i>	–65	+101	–20	–11	–33	–16	–61
	<i>d,l</i>	–63	+99	–19	–11	–36	–15	–63
CHelpG	<i>meso</i>	–62	+99	–37	–35	+20	–37	–52
	<i>d,l</i>	–72	+123	–39	–41	+23	–38	–56
MKS	<i>meso</i>	–43	+76	–35	–14	–2	–29	–45
	<i>d,l</i>	–58	+102	–38	–9	–8	–29	–46
NPA	<i>meso</i>	–80	+144	–36	–60	+13	–16	–62
	<i>d,l</i>	–81	+143	–36	–61	+15	–16	–63

An important simplification is achieved by replacing the *t*Bu groups by hydrogen atoms, or by the corresponding partitions in the framework of the hybrid methods (F1). Indeed, only 53 atoms must now be treated, either as a new molecule or at the high level in the ONIOM procedure. We have shown that all the calculated energies, configurational energy differences, and electronic atomic populations are similar to those corresponding to the entire molecules, at all the levels of theory considered, with or without pseudopotentials. Breaking the pyridyl rings (F2) leads to acceptable values for ONIOM calculations; however, energy differences for fragment molecules are then in contradiction with F0 results. Nevertheless, the population analyses are still correct. The fragmentation F3, which retains only nitrogen atoms from the bipyridyl moiety, is much less acceptable. The B3LYP calculations give an opposite sign, in comparison to MP2 calculations, for the energy difference between the *meso* and *d,l* configurations. They are close to the HF results. We finally were inclined to use the MP2 solution, which finds that the *d,l* configurations are slightly lower in energy than the *meso* configuration.

This difference was not clearly emphasized by atomization energies, for which in both B3LYP and MP2 calculations, the fragmentations F2 and F1 give good representations of F0. Pseudopotential LanL2DZ results also lie in the same range of values. As predicted, the energies of *d,l* and *meso* configurations are very similar. It is noteworthy that fragment energies and the difference $\Delta E[(\textit{meso})-(\textit{d,l})]$ behave differently. Indeed MP2 and B3LYP have similar values of the former, while B3LYP and HF give similar values for the latter.

From MP2/6-31G* calculations, we can draw two main conclusions on atomic electronic populations. The central oxygen atom is twice as negatively charged as the terminal oxygen atoms. These values are quite insensitive to both the size of the fragment and the type of charge definition (except for the unreasonable F3 fragmentation). Apart from the less confident Mulliken populations, the trend is that this atom is more highly charged in the *d,l* than in the *meso* configurations. The population of the NCS group is also insensitive to the fragmentation process, but differences appear between the different definitions of charges. In particular the MKS definition gives results clearly different from the three others. In absolute values, the charges on the C and N atoms are much lower than those obtained from other definitions, and the C charges are even slightly negative instead of slightly positive. In pseudopotential LanL2DZ calculations, apart from the Mulliken partition, the results of all three other definitions of charges are quite comparable to those of all-electron calculations. Therefore, we can conclude that, even without inclusion of polarization functions in basis sets of first-row atoms, the replacement of core electrons by LanL2DZ pseudopotentials could be advantageously used if necessary in the study of such very large systems.

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