Bonding of organometallic fragments to polyoxometallates

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Abstract

The chemistry of polyoxometallates has become a subject of great interest, since these compounds have been considered suitable models for understanding heterogeneous catalytic processes, while being very similar to organometallic complexes more widely known for their role in homogeneous processes. In order to develop a reliable model for the study of the interaction between polyoxometallates and organometallic fragments, a theoretical study based on extended Hückel calculations was done on the simple M_6O_x derivatives, for which many experimental data are available. The charges, the relative energies of possible isomers, and the nature of the frontier orbitals are consistent with the known behavior of the organometallic adducts on which the model was based. A different isomerization pathway between the three isomers of cis-$Nb_2M_4O_{19}(RhCp)^{2-}$ is suggested, based on the migration of the organometallic fragment over the surface of the polyoxometallate.

Key words: Niobium; Rhodium; Molybdenum; Titanium; Polyoxometallate; Extended Hückel calculations

1. Introduction

Great interest has developed around the chemistry of polyoxometallates during recent years [1]. One reason is that the structural characteristics of these compounds make them suitable models for studying heterogeneous catalytic processes using much simpler systems from the experimental point of view than, for instance, a metal oxide. Indeed, the attachment of organometallic fragments to these species is thought to lead to interesting analogies with organometallic complexes adsorbed on surfaces and their reactions. Klemperer and coworkers have synthesized a relatively large number of derivatives containing both an organometallic fragment and a M_6O_x [1a, 2–6] or M_5O_y [7–9] anion and studied their chemistry and structure. Some theoretical calculations have been made, but only the polyoxometallates have been addressed [10–13]. In this work, the specific aim is to understand how some organometallic fragments bind to the small polyoxometallates containing only five or six metal atoms and to find out what will be the frontier orbitals of the resulting species, in order to understand their reactivity patterns. Extended Hückel molecular orbital calculations have been used [14].

2. The isolated polyoxoanions

The basic element in this study will be the $M_6O_{19}^{2-}$ anion and its structure, known from X-ray studies of salts of both the tungsten and the molybdenum derivatives [15], is given in **a**.

Modifications of this anionic fragment, either by replacing some of the metal atoms or by removing a MO group, have also been found in association with organometallic groups. Models of two relevant ones, cis-$Nb_2W_4O_{19}^{4-}$ and $Mo_5O_{18}^{3-}$, are shown in **b** and **c**, respectively.

There is an important difference between the two structures in **b** and **c**. While to the outside the hexametallic species only offers oxygen atoms, the $Mo_5O_{18}^{3-}$ ion exhibits a kind of cavity or lacuna and the central oxygen atom can also be approached. These lacunae will be more characteristic of larger polyoxometallates such as the Keggin type anions, $XMo_{12}O_{40}^{y-}$ where X can belong to several types of atoms (Si, B, P, Ge) and a metal atom from the bulk becomes available to coordination [16].

The $Mo_6O_{19}^{2-}$ anion was modelled after the X-ray structure with three types of Mo–O bonds: terminal, bridging and central (to the central oxygen atom) and

a

b   c
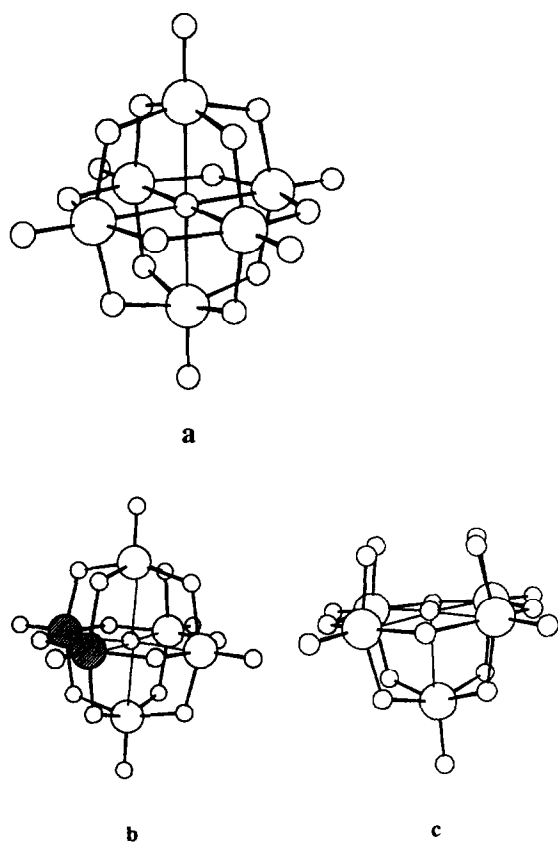
symmetry as high as possible (further details in the appendix). When two molybdenum atoms were replaced by two niobium atoms, the respective M–O distances were kept constant. In order to have some insight into the results of the extended Hückel calcula-

tions, given their qualitative nature, as many parameters as possible were compared with those reported in a recent *ab initio* study [13]. It should be added that the addition of an organometallic fragment (MCp, Cp $= \eta^5\text{-}C_5H_5$), to the $M_6O_{19}^{2-}$ anion will considerably increase the size of the system under study. Unfortunately, not many things can be compared, since optimizing the geometry was not attempted with extended Hückel calculations and the *ab initio* ones aimed at studying the protonation. The best parameters to compare are therefore the net charges at the atoms. For the $Nb_2W_4O_{19}^{4-}$ anion, charges at the metals were respectively $+2.24$ and $+2.54$ for Nb and W, while those of the oxygens oscillate between -1.04 and -1.06 (bridging oxygens), reach -0.77 for the terminal ones and are the most negative for the central one [13].

The results from the semiempirical calculations are shown graphically in Fig. 1. For the same $Nb_2W_4O_{19}^{4-}$ anion, the oxygen charges range from -0.99 to -1.03 and those on the metals from 1.79 (Nb) to 2.85 (Mo).

In spite of the qualitative nature of extended Hückel calculations, the agreement between charges is very good for those on the oxygens and moderate for those on the metals. It should be added, though, that different basis sets used in *ab initio* calculations can lead to greater differences for charges of metals in high formal oxidation states than those found here between two different methods.

Another comparison can be made between the relative energies of the $Nb_2W_4O_{19}^{4-}$ isomers. The *trans* isomer was calculated at an energy 1 kcal/mol higher than the *cis* [13], while the extended Hückel results lead to a *cis* isomer more stable by 0.02 eV (4–5 kcal/mol) which again is in surprisingly good agreement.
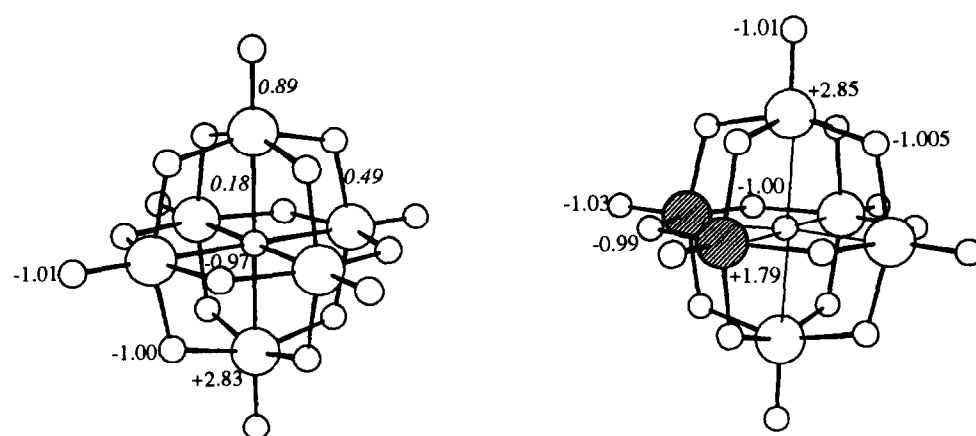

Fig. 1. Charges for the atoms in $M_6O_{19}^{2-}$ (left) and $Nb_2W_4O_{19}^{4-}$ (right) and Mo–O overlap populations for the three different bonds (left, italic).

The overlap populations written on the left drawing of Fig. 1 are not very meaningful in themselves, as a different bond length was used for each type of Mo–O bond. As expected, the short Mo–O_t bond has the strongest overlap population, the longest Mo–O_{cent} bond the weakest, while Mo–O_b bonds exhibit intermediate values. They may be useful later when observing any changes caused by formation of organometallic adducts.

3. The $Mo_5O_{18}Ti(\eta^5\text{-}C_5H_5)^{3-}$ anion: electronic structure and reactivity

This new compound can be formally conceived as originating from $M_6O_{19}{}^{2-}$ when one MoO^{4+} group is replaced by TiCp (Cp = η^5-C_5H_5). As a matter of fact, it is synthesized from Cp_2TiCl_2 and $Mo_2O_7^{2-}$, while for the tungsten analogue $WO_4{}^{2-}$ is used as source of the metal [8], in a self assembling process.

The first consequence of the introduction of the TiCp$^+$ fragment is the separation of the bridging oxygen atoms into three groups, those bridging Ti and Mo and those bridging Mo–Mo along the equator or a meridian, as drawn in **d**. Their charges become therefore different, the oxygens near titanium becoming more negatively charged.

d
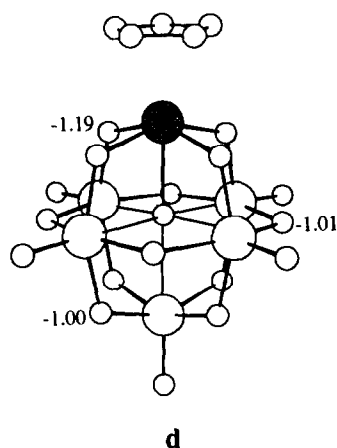
Klemperer and coworkers studied the mono- and diprotonation of the tungsten trianion [9]. Although the hydrogen atoms could not be located when the structures of the protonated species were determined using X-ray techniques, the presence of considerably lengthened M–O bonds revealed the protonation site, which always happened to be at an oxygen bridging titanium and molybdenum, as suggested by the calculated charges. Up to two of the four possible positions could therefore be protonated, the structure of the products depending on the nature of the counter-ion

and other factors which may influence the formation of a hydrogen bond network.

Another experimental result to be tested with this model concerns the reactivity of $Mo_5O_{18}Ti(\eta^5\text{-}C_5H_5)^{3-}$ towards other electrophiles. Reaction with MoO_2Cl^+ and $Mn(CO)_3{}^+$ led to the formation of new adducts. The structure of the first one is schematized in **e**.

e
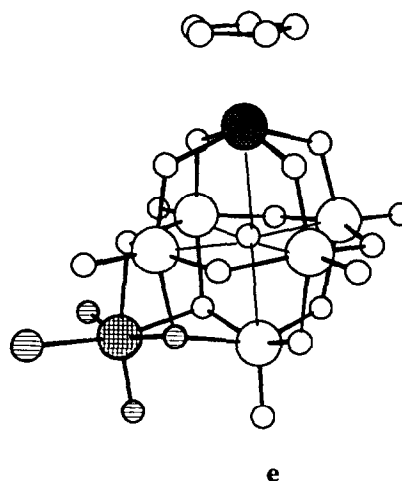
In order to understand the reactivity towards electrophilic and nucleophilic reagents, the frontier orbitals of the trianion were examined. The HOMO and LUMO are shown in Fig. 2.

As can easily be seen from Fig. 2, three groups of atoms contribute to the HOMO: the carbons of the cyclopentadienyl ligand, the titanium atom and two of the oxygens adjacent to this metal. Attack by electrophiles should take place at one of these atoms, if the reaction were orbitally controlled. The nature of the adducts suggests instead a charge controlled reaction and the electrophile reagents should coordinate at the same position as the proton. It does not happen that way, certainly for steric reasons: the incoming groups
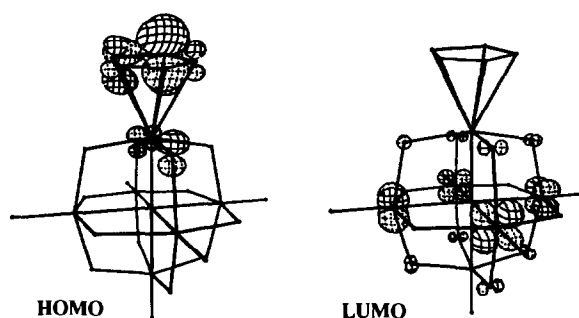

HOMO   LUMO

Fig. 2. The HOMO and the LUMO of the trianion $Mo_5O_{18}Ti(\eta^5\text{-}C_5H_5)^{3-}$ in a tridimensional representation.

(both MoO_2Cl^+ and $Mn(CO)_3^+$) are much bulkier than H^+. Steric repulsions are likely to be very important between the cyclopentadienyl group, namely its hydrogens, and oxygens in MoO_2Cl^+ or $Mn(CO)_3^+$. These groups will therefore turn to the second mostly negatively charged type of atoms, the oxygens bridging two molybdenum atoms along a meridian and they coordinate to two of them. For geometrical reasons, the third oxygen atom to add to the electrophile reagent has to be equatorial.

Calculations were done for those two possible geometries in the case of the MoO_2Cl^+ adduct. The experimental coordination site was indeed found to be more stable by ca. 1 eV.

To our knowledge reactions with nucleophiles have not been attempted or, at least, no stable product was isolated. This is not too surprising considering, to start, the three minus overall charge. Supposing, in spite of this, that such reactions might occur and were orbitally controlled, the nature of the LUMO suggests attack at one of the equatorial molybdenum atoms (24% contribution from each of the four to this molecular orbital). These metal atoms also carry the more positive charges and a charge controlled process would lead to the same result. The molybdenum atoms are, however, embedded in a cage formed by negatively charged oxygens and carbons and there is no easy access to them. Such reactions are thus not likely to take place, for all these reasons.

## 4. Electronic structure and reactions of cis-Nb_2-$M_4O_{19}^{4-}$

The chemistry based on this cis-disubstituted anion is much richer than that of $Mo_5O_{18}Ti(\eta^5\text{-}C_5H_5)^{3-}$. It was chosen, rather than $M_6O_{19}^{2-}$ ($M = Mo$ or W), for its greater nucleophilic character which made it more reactive [5]. The -4 global charge is reflected, as seen earlier (Fig. 1), in a more negative charge in some of the outer oxygen atoms, and reaction with positively charged fragments should therefore be easier.

Adducts of cis-$Nb_2M_4O_{19}^{4-}$ were prepared by Klemperer and coworkers with several organometallic fragments, namely $M(CO)_3^+$ with $M = Re$, Mn [2,4], $Rh(\eta^5\text{-}C_5Me_5)^{2+}$ [4], $Ru(p\text{-}CH_3C_6H_4CH(CH_3)_2)^{2+}$ [6], and the determination of their structure was attempted using X-ray diffraction methods. The difficulties encountered with disorder (impossibility of distinguishing between Nb and W) led to detailed ^{17}O NMR studies, on the basis of which structures were assigned. Three different isomers are possible and their existence and interconversion were discussed.

In order to study this system theoretically, the $Rh(\eta^5\text{-}C_5Me_5)^{2+}$ derivative was chosen and the

organometallic moiety modelled by the simpler RhCp fragment. The frontier orbitals of RhCp [17], characteristic of a kind of half-octahedron, immediately suggest its coordination to a tridentate site of the polyoxoanion, while interatomic distances favour the bridging oxygen atoms, relative to the terminal ones. To use these, a large, unfavourable distortion would have to take place in the skeleton of the cis-$Nb_2M_4O_{19}^{4-}$ anion.

There are three different types of bridging oxygen atoms, depending on their binding to two niobiums, two molybdenums, or one niobium and one molybdenum. The three types of isomers which can be formed are schematically shown below in f, g and h.

f

g

h
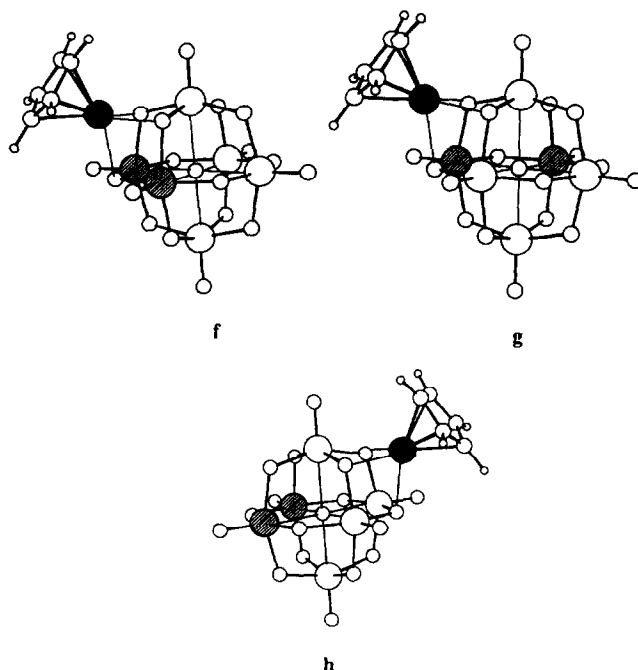
Both isomers f and h contain a mirror plane, while g has no symmetry elements. On the other hand, g is twice as likely to occur as either f or h, on statistical grounds. Though the energies do not differ significantly, the calculations indicate h to be the most stable isomer. g comes next, with an energy of 0.05 eV higher and then f at an energy another 0.05 eV higher. These energies are compatible with the existence of more than one isomer in solution. Indeed, as observed in the ^{17}O NMR spectra, two isomers appear to be initially formed from the reaction mixture. They most probably consist, as discussed in the original paper [4], of f and g, which have in common the fact the rhodium atom is coordinated to at least one niobium-oxygen.

The explanation given in ref. 4 for the formation of exactly these two isomers is consistent with an initial
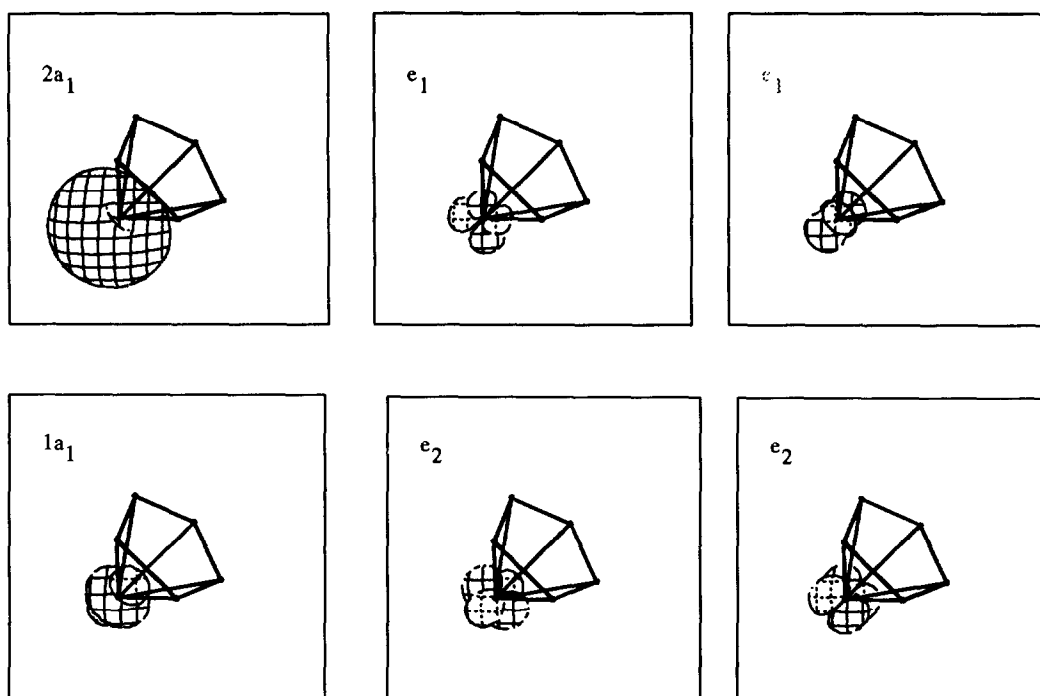
Fig. 3. The frontier orbitals of a d^6 RhCp fragment.

attachment of rhodium to one of the terminal niobium-oxygens. These carry the highest negative charges, as pointed out earlier, which would favour coordination of a $RhCp^{2+}$ cation. The energies of the possible η^1 isomers of cis-$Nb_2M_4O_{19}(RhCp)^{2-}$ where rhodium binds terminal oxygens are, however, the same, at the available level of calculations, but 0.6–0.7 eV less stable than the final products, and, interestingly, slightly more stable (0.02–0.03 eV) than those where rhodium is binding bridging oxygens. The low stability is related to the fact that the rhodium atom does not achieve an 18 electron configuration in the lower coordination number sites.

Another point of interest concerns the formation of the third isomer, h, which was not present in the initial mixture. It forms at low temperatures in the presence of an excess of the rhodium containing reagent, $\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2$, or at higher temperatures in its absence. The first mechanism was thought to involve the coordination of a second $Rh(\eta^5\text{-}C_5Me_5)$ fragment at a different site, followed by loss of one of them.

As some points were not completely clear from the experimental work, specially the higher temperature process, another isomerization pathway was theoretically probed, involving other intermediates. These can become important if the organometallic fragment migrates on the "surface" of the polyoxometallate. It is certainly impossible to study such a complicated process, but it is possible to build intermediates along such a pathway, by imagining several coordination modes of

the RhCp fragment. As the organometallic fragment moves from one O_3 face to another, it has to cross the edge they share and an η^2 isomer may result. The energy of η^2 isomers depends very much on the pairs of oxygen atoms chosen and the most stable species are similar to the one depicted in i.

i
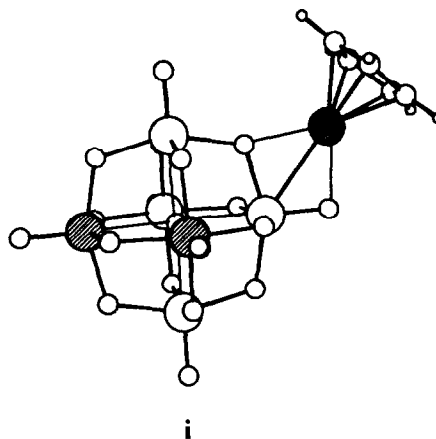
The special feature of such a geometry is that, although apparently Rh is coordinated to two oxygen atoms, the characteristics of the underlying polyoxometallate lead to a very short Rh–Mo distance of 2.82 Å. This is very much in the range of metal–metal bonding distances and calculations give a Mo–Rh over-
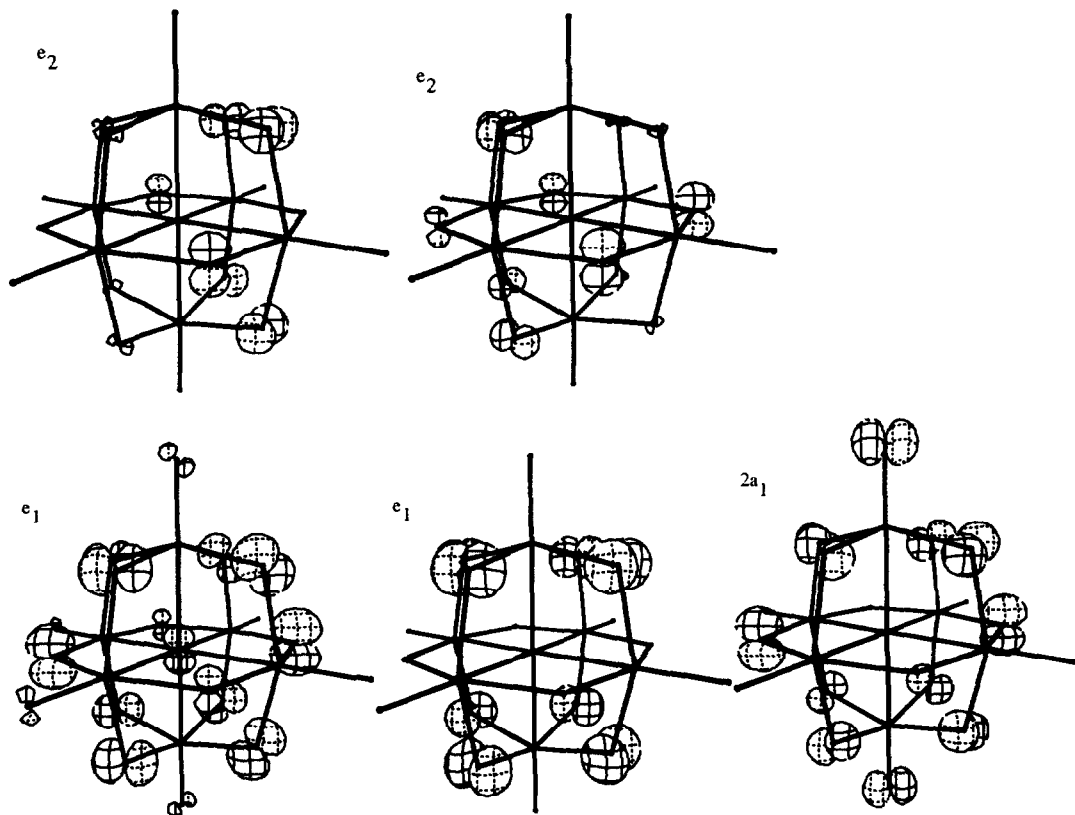
Fig. 4. The five orbitals of $Nb_2M_4O_{19}^{2-}$ overlapping more significantly with RhCp.

lap population of 0.06, indicative of a bond between the two metal atoms. With this third bond, the rhodium atoms lose some of the electronic unsaturated character typical of the η^2 sites. The energy of this species is of the same order of magnitude of that of the stable isomers **f, g, h** (comparable to that of **f**) and interconversion between them should be easy.

Another way of going from one O_3 face to another is through an O vertex. As seen earlier, the energies of η^1 isomers are higher than those of the η^2 (by ca. 0.5 eV) and this type of intermediate is less likely to occur.

The electronic structure of the RhCp adduct was also addressed. The interaction between this organometallic fragment and the polyoxometallate was studied for the **h** isomer (C_s symmetry). The frontier orbitals of d^6 RhCp are shown in Fig. 3, labelled as in ref. 17, for simplicity. The three low energy ones, (e_2, $1a_1$) are filled for this electron count and derive from the t_{2g} set of an octahedral complex (the MCp fragment is analogous to a half octahedron). The three unoccupied, high energy orbitals are e_1 (from the octahedral e_g set) and an sp hybrid ($2a_1$).

The empty fragment orbitals interact with combinations of oxygen lone pairs having appropriate symmetry and forming three σ bonds. On the other hand, the

filled orbitals of RhCp can backdonate electrons to empty orbitals of the polyoxometallate. Owing to the nodal characteristics of $1a_1$ (no overlap results) only two backdonation components from e_2 are observed. The five orbitals of $Nb_2M_4O_{19}^{2-}$ which exhibit the more significant overlap with RhCp orbitals are represented in Fig. 4 (the label refers to the symmetry of the RhCp orbital with which they combine). Many others mix, because the overall symmetry is only C_s.

This example shows that the polyoxometallate can bind effectively an organometallic fragment.
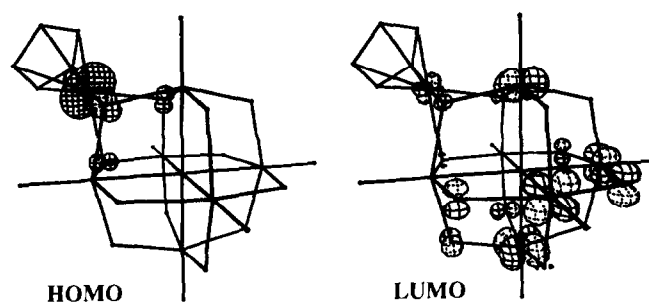

Fig. 5. The HOMO and the LUMO of the $Nb_2M_4O_{19}(RhCp)^{2-}$ polyoxometallate.

The frontier orbitals of $Nb_2M_4O_{19}(RhCp)^{2-}$ are represented in Fig. 5. The LUMO is very similar to that of $Mo_5O_{18}Ti(\eta^5\text{-}C_5H_5)^{3-}$, being strongly localized in the metal atoms; also, the negative charge of the species does not favour reactions with nucleophiles.

The HOMO is more interesting as it is concentrated on the rhodium atom and reactions at the metal should therefore be possible using the appropriate reagents. Migration to an edge (low energy intermediate) could happen simultaneously, providing some electronic unsaturation.

5. Final comments

In the previous sections some of the electronic characteristics of polyoxometallates containing a hexametallic frame were studied and related to their known behaviour. The results of the extended Hückel calculations were compared, when possible, with those of more sophisticated *ab initio* calculations. Both charges and relative energies of isomers for the parent $Nb_2M_4O_{19}{}^{4-}$ ions gave comparable results. This ion can coordinate strongly organometallic fragments. More recently, the $M_6O_{19}{}^{2-}$ species has been found to behave as a heterogeneous catalyst in the polymerization of norbornene [18].

The results obtained thus far indicate that the extended Hückel method can be useful in helping to understand how more complicated polyoxometallate ions will react with organometallic fragments and their role in catalytic processes.

Acknowledgments

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Appendix

All calculations were of the extended Hückel type [14] with modified H_{ij}'s [19]. Standard parameters were used for O, C and H, while those for the metals were respectively: Mo (ζ, H_{ii}/eV) 5s 1.96, -9.66; 5p 1.90 -6.36; 4d 4.54, -12.30, ζ_2 1.901, C_1 0.5899, C_2 0.5899; Nb (ζ, H_{ii}/eV) 5s 1.89, -10.10; 5p 1.852 -6.86; 4d 4.08, -12.10, ζ_2 1.637, C_1 0.6404, C_2 0.5812; Rh (ζ, H_{ii}/eV) 5s 2.135, -8.09; 5p 2.099 -4.57; 4d 4.29, -12.50, ζ_2 1.97, C_1 0.5471, C_2 0.6417.

In the basic $M_6O_{19}{}^{2-}$ polyoxometallate, the following distances were used (Å): Mo–O_c 2.32; Mo–O_t 1.66; Mo–O_b 1.95, and octahedral symmetry was considered. When niobium or titanium replaced one or more molybdenum atoms, the skeleton was not changed. Idealized models were created for all the other studied molecules from the experimentally determined structures which were mentioned in the text.

Three dimensional drawings of molecular orbitals were made using the program CACAO [20].