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Which functional groups of the molybdopterin ligand should be considered when modeling the active sites of the molybdenum and tungsten cofactors? - a DFT study

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Abstract

A DFT study about the influence of the various functional groups of the molybdopterin ligand on electronic and geometric properties of active site models for the molybdenum and tungsten cofactors has been undertaken. We used analogous molybdenum and tungsten complexes with increasingly accurate representation of the molybdopterin ligands and compared bond lengths, angles, charge distribution, composition of the binding orbitals, as well as the redox potentials in relation to each other. Based on our findings, we suggest to use ligand systems including the pyrane and the pyrazine rings, besides the dithiolene function, in order to obtain sufficiently reliable computational, but also synthetic, models for the molybdenum and tungsten cofactors, whereas the second ring of the pterin might be neglected for efficiency reasons.

Keywords

molybdenum, tungsten, molybdopterin, DFT calculations

Introduction

Enzymes depending on molybdenum and tungsten cofactors are ubiquitous and indispensable [1,2].

They usually catalyze oxygen-transfer reactions from the substrate to water, or vice versa, in the form of two-electron redox reactions: $R + H_2O \rightarrow RO + 2 H^+ + 2 e^-$. These reactions are part of the carbon, nitrogen and sulfur metabolism.

One common feature of these proteins is the unusual molybdopterin ligand (also referred to as pyranopterindithiolate [1], pterindithiolene [3] or pterin-ene-dithiolate [4]), one or two of which is bound to the metal at the active site (Scheme 1), depending on the enzyme family [5,6]. This ligand is coordinated to the metal by a dithiolene function. The molybdopterin ligand is usually modeled in bioinorganic studies of the molybdenum and tungsten cofactors by using any dithiolene ligand with two substituents on the ene-function. Dithiolenes are *non-innocent* ligands that take actively part in redox reactions at the metal, sometimes even changing the oxidation state of the metal, which has been shown in great detail for a number of ligands (not only dithiolenes) by the Wieghardt group [7-17]. For example, the redox potential of $[MoO(S_2C_2(CN)_2)_2]^{1-/2-}$ is 1 V higher than that of $[MoO(S_2C_2Me_2)_2]^{1-/2-}$ [18,19]. Such a participation in redox processes is accompanied by structural changes of the dithiolene ligand. For instance, the C=C bond length is increased if the metal is oxidized, because electron density is pushed towards the metal, while the C-S bond is shortened. Consequently, the way the molybdopterin ligand is modeled can be expected to have a strong impact on the result of both experimental and theoretical studies, for the reactivity as well as for the structure.

In theoretical studies, the ligand is typically modeled with rather simple systems: ethenedithiol (edt, $S_2C_2H_2^{2-}$) [20], maleonitril (mnt, $S_2C_2(CN)_2^{2-}$) [21-23], 1,2-dimethyl-dithiolene ($S_2C_2Me_2^{2-}$) [21, 24] or benzenedithiol (bdt, $S_2C_6H_4^{2-}$) [22,24a,25]. Functional groups of molybdopterin, besides the dithiolene function that binds to the metal, were ignored, probably to reduce the computational load. Notable exceptions to this are the study of McNamara et al., in which a simplified form of molybdopterin without the pyrane ring was used [26], and the study of Joshi et al. about the folding angle and electronic effects, in which the full molybdopterin ligand (without the phosphate group) was used [27].

In this paper, we present a systematic theoretical study (DFT calculations) of various and

increasingly accurate models of the molybdopterin ligand. The earliest group of synthetic models for the molybdenum and tungsten dependent oxidoreductases that is still used today is based on a metal (Mo or W) coordinated by two dithiolene ligands and one oxo ligand in the oxidation states (OS) +4 and +5 or with two oxo ligands in the oxidation state +6 respectively [28-50]. For this type of models, quite a substantial amount of experimental data is available. Therefore we focus on this group of compounds, although there are now more accurate models of the proteins known [51-56]. Thus, we study models of the form $[MO(dithiolene)_2]^{n-}$ ($M = Mo, W$; $n = 0, 1, 2$). In oxidation state +6 of the metal, a second oxo ligand is usually present in the synthetic models [40-44,47-50]. To simplify the calculations and the comparisons, we abstained from including this second oxo ligand and kept the same coordination number and ligand set throughout all three oxidation states. The aim of our study is to ascertain which parts of molybdopterin need to be included in the calculations, in order to obtain accurate structures, energies, reactivities, and reduction potentials of the models.

Methods

All calculations were performed with the Gaussian 03 (revision C.02) software package [57]. All structures were fully optimized without any restrictions and the minima were verified by analytical frequency calculations.

Geometry optimizations, population analysis of molecular orbitals and partial-charge distribution (with the NPA and NBO methods [58]) were carried out at the DFT level using the B3LYP method (Becke's three-parameter-hybrid functional [59], combined with the correlation functional of Lee, Yang and Parr [60]; unrestricted formalism for the open-shell systems). The geometry parameters (Table S1) and the coordinates of the fully optimized structures can be found in the Supporting Material (Table S4).

The LANL2DZ [61] basis set, including the Los Alamos relativistic effective core potentials of Hay and Wadt [62], was used for Mo and W, and the 6-311G(d,p) basis, including polarization functions [63] for a better description of the S and O atoms, was used for the remaining atoms.

Solvation energies were estimated by single-point energy calculations using the IEF-PCM

model in Gaussian-03 [64]. The calculations used water as solvent ($\epsilon = 78.39$ and probe radius = 1.385 Å) and the default UA0 radii. Reduction potentials were calculated from these energies using a solvation energy for the electron of 4.28 eV [65].

The stereochemistry of the mpt and prz ligands (Scheme 2) were the same as that found in the enzymes. In particular, we used the structures of DMSO reductase [66] and aldehyde oxidoreductase [67]. The quality and accuracy of the DFT calculations were estimated by comparison with experimental structural data. Quite a number of X-ray structures of enzyme model complexes of the general composition $[\text{MO}(\text{dithiolene})_2]^{n-}$ with $n = 1$ or 2 , and $M = \text{Mo}$ or W have been published [26-44] and are therefore available for evaluation of the quality of our computations, all showing the same general geometry as our computed compounds. In particular, X-ray structures of compounds with the ethenedithiol ligand ($[\text{MoO}(\text{edt})_2]^{1/2-}$) [45] and the pyranedithiolene ligand ($[\text{MoO}(\text{pdt})_2]^{2-}$) [46] are known, i.e. the exact models that are used in this study. The latter allows a comparison of the largest quantity of structural parameters. The computed structure of this compound in the oxidation state +4 is almost identical with the experimental data obtained by crystallography. The only larger difference is that the calculated Mo–S bond lengths are ~ 0.1 Å too long (2.47 Å vs. 2.37 Å). This has frequently been observed before in theoretical studies [68]. With respect to the overall geometry no differences were found.

Results

Investigated complexes

The investigated complexes consist of a metal (either molybdenum or tungsten) with two identical equatorial dithiolene ligands and one apical oxo ligand in a (distorted) square pyramidal coordination geometry. The emphasis of this study lies on the dithiolene ligands. Four different ligands as increasingly accurate models for the natural molybdopterin ligand were investigated, as is shown in Scheme 2. For each of the four ligands, we studied the metal in each of its three biologically relevant oxidation states, +4, +5 and +6. We therefore introduce the systematic

numbering depicted in Scheme 2.

When the metal is in the oxidation state +6, synthetic models usually have a second oxo ligand [40-44,47-50]. However, to simplify the calculations and to evaluate the interaction of the dithiolene with the metal center, we have abstained from including this second oxo ligand and kept the same coordination number and ligand set throughout all three oxidation states. Thereby, we may understand even subtle influences of the different functional groups of molybdopterin on electronic and geometric properties of the central metals.

Structural Analysis

One interesting structural feature is the folding angle, which was introduced into the discussion about dithiolene ligands by Lauher and Hoffmann [69]. It defines the angle between the M–S–S plane and the S–C=C–S plane, as shown in Scheme 3. Upon oxidation, one of the dithiolene ligands bends towards the metal and the apical oxygen, while the other bends slightly away from them. This is illustrated in Figure 1 for the molybdenum compounds with the pdt ligand. This behavior is a consequence of the changing π -electron density distribution in response to the change of oxidation state of the metal. To be more precise: the „dithiolate folding effect“ [70] depends on the occupation of the d -orbitals of the metal. In high oxidation states ($+5/d^1$ and $+6/d^0$), the need for a flow of electron density towards the metal to stabilize these high oxidation states is greater. A folding of the dithiolene ligand towards the metal causes a much better π -overlap of the metal d -orbitals with the sulfur p -orbitals and therefore provides a better electron-transfer pathway resulting in a stabilization of the compound. In Figure 2, the folding angle values are depicted for all compounds.

The folding angles of the tungsten compounds are larger than those of the molybdenum compounds. Tungsten therefore is able to achieve a better π -overlap with the coordinated sulfur atoms than molybdenum. The differences of the folding angles between the four ligand systems is more pronounced for the molybdenum complexes than for the tungsten complexes. Interestingly, the largest differences were found for the ligand that bends away from the metal.

In the +4 oxidation state, the folding angle is larger for the compounds with the smaller and less accurate molybdopterin models edt (**1**) and pdt (**2**), while the compounds with the prz ligand (**3**) are in good agreement with the complexes of the most complete molybdopterin model (mpt, **4**). In the +5 oxidation state, the folding angles are larger for the smaller models compared to the molybdopterin complexes (**4**), while in oxidation state +6 the folding angle of the prz (**3**) compounds is smaller and that of the edt (**1**) and pdt (**2**) compounds is again larger.

Naturally, besides the folding angle, the bond lengths of the most prominent connections are of interest. In all cases, a decrease of the metal–sulfur bond lengths and an increase of the C=C double bond lengths are observed (see Figure 3) in response to the oxidation of the compounds from the oxidation state +4 to +6. This is in accordance with a recent study by Lim et al. of planar nickel bisdithiolene [71]. The higher charge of the metal and its decreased size upon oxidation are responsible for the decreased metal–sulfur bond lengths. Moreover, the lack of electrons close to the metal center after removal of two electrons when going from oxidation state +4 to +6 causes the C=C double bond to support the complex by donating π -electron density towards the center. This results in an increase of the C=C double bond length.

It is notable that the M–S bond lengths are shorter for W than for Mo, owing to the higher charge of the nucleus, relativistic effects and stronger contractions. The decrease of the metal–sulfur bond lengths (~ 0.044 Å for W and 0.052 Å for Mo) and the increase of the C=C double bond (~ 0.022 Å for W and 0.026 Å for Mo) is also less pronounced for tungsten than for molybdenum. This is caused by the fact that the W–S bonds are already comparatively short in oxidation state +4 and that the stronger ligand folding, resulting in a stronger π -overlap between tungsten and sulfur, provides more electron density directly from the sulfur atoms and therefore less electron density is needed from the C=C double bond.

The four Mo–S bonds of each compound are not identical as is shown in detail in Table 1. In all cases, the decrease of the M–S bond lengths is stronger for the ligand that bends towards the metal center than for the ligand that bends away. This is caused by the fact that the ligand bending towards the metal shares more π -electron density with the metal due to the better π -overlap of the

metal *d*-orbitals with the sulfur *p*-orbitals.

Table 1: M–S Bond Lengths (Å) for all compounds.

	1a^{IV}	1a^V	1a^{VI}	1b^{IV}	1b^V	1b^{VI}
M-S(2)	2.482	2.454	2.435	2.460	2.445	2.423
M-S(3)	2.482	2.454	2.435	2.460	2.445	2.423
M-S(4)	2.482	2.440	2.409	2.460	2.436	2.397
M-S(5)	2.482	2.439	2.409	2.460	2.436	2.397
	2a^{IV}	2a^V	2a^{VI}	2b^{IV}	2b^V	2b^{VI}
M-S(2)	2.474	2.449	2.403	2.453	2.440	2.392
M-S(3)	2.469	2.447	2.402	2.448	2.438	2.393
M-S(4)	2.473	2.435	2.430	2.452	2.432	2.418
M-S(5)	2.471	2.432	2.427	2.451	2.430	2.416
	3a^{IV}	3a^V	3a^{VI}	3b^{IV}	3b^V	3b^{VI}
M-S(2)	2.473	2.450	2.440	2.452	2.441	2.424
M-S(3)	2.469	2.444	2.432	2.449	2.437	2.414
M-S(4)	2.473	2.435	2.413	2.452	2.432	2.397
M-S(5)	2.469	2.434	2.410	2.449	2.432	2.401
	4a^{IV}	4a^V	4a^{VI}	4b^{IV}	4b^V	4b^{VI}
M-S(2)	2.471	2.450	2.438	2.451	2.441	2.421
M-S(3)	2.468	2.444	2.431	2.447	2.436	2.415
M-S(4)	2.471	2.436	2.414	2.451	2.433	2.399
M-S(5)	2.468	2.435	2.417	2.447	2.431	2.399

The four M–S bonds are most similar for complexes in oxidation state +4. The variation is smallest for the smallest ligand (edt; **1**) and largest for the pdt (**2**) ligand. In this oxidation state, the differences occur between the sulfur atoms of the same dithiolene ligand, while the M–S bond lengths of the sulfur atoms in *trans* position to each other are equal (edt **1**, prz **3**, mpt **4**) or almost equal (pdt **2**) (a *trans* trend).

In the +5 and +6 oxidation states, however, the M–S bond lengths of the sulfur atoms of the same dithiolene ligand are more or less identical (a *cis* trend), while there is a difference for the sulfur atoms in *trans* position to each other. This *cis* trend is caused by the ligand folding. The ligand that bends away from the metal and the ligand that bends towards the metal are different with

respect to the possible overlap between metal *d*-orbitals and sulfur *p*-orbitals. The much better overlap between the metal and the ligand that bends towards the metal results in much shorter M–S distances for this ligand. The difference between the two ligands of each compound with respect to the M–S bonds is most evident in oxidation state +6: The differences are ~0.01 Å for the +5 oxidation state and ~0.03 Å for the +6 oxidation state. The differences are most pronounced for the smallest (edt) ligand. For molybdenum, the average M–S bond lengths vary between 2.41 Å and 2.48 Å, whereas they show a slightly smaller range of 2.41 Å and 2.46 Å for tungsten (Figure 3).

The smallest models (with edt) show the most pronounced differences to the mpt (4) compounds with respect to the M–S and C=C bond lengths (Figure 3). The M–S bonds are longer and the C=C double bonds are shorter due to the fact that there is no possibility of a distribution of π -electron density to additional atoms of the ligand. The pdt compounds (2) mimic the behavior of the mpt compounds (4) quite well in oxidation states +4 and +5. However, in oxidation state +6, the difference to the mpt complexes is almost as large as that of the edt compounds (1). Accordingly, the most pronounced geometrical difference between the different ligand systems is found in the oxidation state +6 of the tungsten series.

The dependence of the M–S bond lengths on a change in the oxidation state of the metal for the mpt (4) compounds is best reproduced by the prz (3) compounds. The same applies for the C=C double bond, for which the prz compounds reproduce not only the trends, but also the absolute values of the mpt ligand.

Electronic structure and bond analysis

In this section, we study various aspects of the electronic structure, e.g. the charges obtained by natural population analysis (NPA), the binding orbitals (natural bond analysis, NBO) and the redox-active orbitals (the highest occupied molecular orbitals, HOMO, and the lowest unoccupied molecular orbitals, LUMO). The NPA charges for the metal, the apical oxo ligand, the two sulfur atoms of each of the two dithiolene ligands and the doubly bonded carbon atoms of the two ligands are shown for the molybdenum compounds in Figure 4. The quite similar graphs for the analogous

tungsten compounds can be found in the supplementary material, Figure S1. The charge on the tungsten atom is $\sim 0.02 e$ higher than that on the molybdenum atom in all complexes. Again this is the result of the higher charge of its nucleus.

When the compounds are oxidized from oxidation state +4 to +5, the charge on the metal increases as expected. But the oxidation to +6 causes the charge to decrease slightly, as a consequence of a quite effective electron density distribution from the ligands towards the metal. This behavior was found throughout all investigated complexes. For example, the Mo charge is 0.55 for **1a^{iv}**, 0.67 for **1a^v** and 0.57 for **1a^{vi}** with the edt ligand. In all investigated complexes, formally about 3.5, 4.5 and 5.5 electrons are transferred from the ligands onto the metal in oxidation states +4, 5, and 6, respectively.

The negative charges on the directly coordinated ligand atoms decrease regularly during the two oxidations. In fact, the charge on the four sulfur atoms becomes even positive in oxidation state +6. The total charge transfer from the four sulfur atoms onto the metal is therefore large. For the MoO(edt)₂ complexes, the charge on the apical oxo ligand is -0.60 for **1a^{iv}**, -0.54 for **1a^v** and -0.46 for **1a^{vi}**, and for the sulfur atoms of the ligand that bends away from the metal, the values are -0.24 for **1a^{iv}**, -0.10 for **1a^v** and +0.11 for **1a^{vi}**. The charges on the sulfur atoms in trans position to each other, belonging to different ligands, are of course not equal upon oxidation. The ligand that achieves a better π -overlap with the metal by bending towards it in the oxidation states +5 and +6 donates more electron density onto the metal than the other ligand. Therefore, the increase in charge is larger for the sulfur atoms of this ligand than for the sulfur atoms of the opposite ligand. This corresponds to the M–S bond lengths with the *trans*-trend in oxidation state +4 and the *cis*-trend in oxidation states +5 and +6.

The results with the edt ligand are quite different compared to the three other ligand systems, especially for the carbon atoms. On the other hand, all data of the pdt (**2**), prz (**3**) and mpt ligands (**4**) are very similar, not only with respect to the trends, but also with respect to the absolute values. This is because the charge can be distributed throughout a much larger molecule for the latter three ligands, whereas in edt it has to stay at the carbon atoms of the double bond.

For the three other ligands, the charge on the oxygen atom in the pyrane ring is more or less identical (not shown in Figure 4). The same is true for the nitrogen atoms of the pyrazine ring for prz (**3**) and mpt (**4**). Since the values of the relevant atoms for the three ligand systems with the pyrane ring are more or less equal, the influence of the pterin functional group on the NPA charges is rather insignificant. In conclusion, the small edt ligand system is clearly not a proper model of the molybdopterin ligand.

To analyze the bond situation at the metal in more detail, a natural bond analysis (NBO) of the natural localized molecular orbitals (NLMOs) [72] was carried out. In Table 2, the most important parameters (the metal–sulfur bonds) are collected. A larger data overview can be found in the supplementary material (Table S2). It should be noted that the electronic structure is strongly delocalized, so that ~2% of the electrons are cannot be assigned to certain Lewis structure. Therefore, the assignment is somewhat ambiguous, especially for the S atoms, for which the default analysis indicates that a lone-pair can be converted to a π bond for one or two of the S ligands in the oxidized +VI state. However, a nearly equally good assignment with two lone-pairs on all S atoms can always be obtained and this is shown in Table 2 to simplify the comparison.

Table 2: Selected NBO Parameters for **1a/b** and **4a/b** (iv-vi). %Mo/W and %S are the contributions of the atoms to the bond M–S.

Bond	Bond-type	% Mo	% S	Occupancy	Bond	Bond-type	%W	%S	Occupancy
1a^{iv}					1b^{iv}				
Mo-S(2)	σ	20	77	1.81	W-S(2)	σ	20	77	1.83
Mo-S(3)	σ	20	77	1.81	W-S(3)	σ	20	77	1.83
Mo-S(4)	σ	20	77	1.81	W-S(4)	σ	20	77	1.83
Mo-S(5)	σ	20	77	1.81	W-S(5)	σ	20	77	1.83
1a^v					1b^v				
Mo-S(2)	σ	23	74	1.78	W-S(2)	σ	22	75	1.82
Mo-S(3)	σ	23	73	1.78	W-S(3)	σ	22	75	1.82
Mo-S(4)	σ	26	71	1.79	W-S(4)	σ	25	73	1.81
Mo-S(5)	σ	26	72	1.80	W-S(5)	σ	25	73	1.81
1a^{vi}					1b^{vi}				

Mo-S(2)	σ	20	80	1.81	W-S(2)	σ	20	80	1.82
Mo-S(3)	σ	20	80	1.81	W-S(3)	σ	20	80	1.82
Mo-S(4)	σ	24	76	1.81	W-S(4)	σ	21	79	1.81
Mo-S(5)	σ	24	76	1.81	W-S(5)	σ	21	79	1.81
Bond	Bond-type	%Mo	%S	Occupancy	Bond	Bond-type	%W	%S	Occupancy
4a^{iv}					4b^{iv}				
Mo-S(2)	σ	20	77	1.80	W-S(2)	σ	20	77	1.82
Mo-S(3)	σ	20	77	1.81	W-S(3)	σ	20	77	1.82
Mo-S(4)	σ	20	77	1.80	W-S(4)	σ	20	77	1.82
Mo-S(5)	σ	20	77	1.81	W-S(5)	σ	20	77	1.82
4a^v					4b^v				
Mo-S(2)	σ	23	73	1.78	W-S(2)	σ	22	74	1.80
Mo-S(3)	σ	23	73	1.78	W-S(3)	σ	22	75	1.80
Mo-S(4)	σ	26	72	1.79	W-S(4)	σ	24	73	1.80
Mo-S(5)	σ	26	72	1.79	W-S(5)	σ	24	73	1.80
4a^{vi}					4b^{vi}				
Mo-S(2)	σ	21	79	1.83	W-S(2)	σ	23	77	1.83
Mo-S(3)	σ	18	82	1.81	W-S(3)	σ	21	79	1.81
Mo-S(4)	σ	27	73	1.84	W-S(4)	σ	21	79	1.83
Mo-S(5)	σ	22	78	1.81	W-S(5)	σ	19	81	1.81

The Lewis structures based on this analysis for all investigated compounds show a metal–oxygen triple bond. The metal-oxygen triple bond is not uncommon for complexes of this kind [73]. It consists of the usual σ - and π - bonds for a metal oxygen double bond, plus another π -bond provided by the oxygen through one of its „free“ electron pairs.

The four sulfur atoms of the two dithiolene ligands are bound by σ -bonds. The contribution of the metal to these σ -bonds is for all complexes in all oxidation states in the range of 15–27%, while the sulfur atoms contribute between 71% and 85%. The values for the metal–oxygen bond are in the same range (70–80% for oxygen and 20–30% for the metal). The metal is therefore surrounded by five atoms bound in a strongly polarized manner. The polarization decreases slightly in the course of oxidation. For instance, the contribution of the metal increases for the mpt

compound (**4a**) from 20% in oxidation state +4 to 23–26% in oxidation state +5 and stays in this range in oxidation state +6 (18–27%), while the contributions of the sulfur atoms decrease accordingly (77% for +4, but 72–73% for +5 and 73–82% for +6). This behavior was found for all other complexes as well, although the numbers are slightly different. In general, the contribution of tungsten is marginally smaller (~0.5%) than that of molybdenum and the contributions of the respective sulfur atoms therefore larger by this same amount. Another difference between the two metals is the degree of metal *s*-orbital participation, which is slightly larger for tungsten (and the metal *d*-orbital participation is therefore slightly smaller). This is again related to the larger relativistic effects of tungsten.

In general, the prz (**3**) ligand gives results that are most similar to that of the mpt ligand (**4**), with a mean absolute difference in the M and S contributions of the M–S bonds of only 0.2% and a maximum difference of less than 1%. For the edt (**1**) and pdt (**2**) ligands, the differences are appreciably higher, on average 0.7 and 1.4 % units. The differences are largest for the oxidized (+VI) complexes. In particular, for the oxidized pdt model (**2a^{VI}**), the Mo contribution is only 15–16 %, whereas it is 18–27% for the corresponding mpt model (**4a^{VI}**). This shows that the molybdopterin model has a quite strong influence of the electronic structure of the complex.

The redox behavior of the investigated molecules is to a large extent determined by the redox-active molecular orbitals, i.e. the HOMO (highest occupied molecular orbital) in oxidation state +4, the SOMO (singly occupied molecular orbital) in oxidation state +5 and the LUMO (lowest unoccupied molecular orbital) in oxidation state +6. These orbitals would be involved in the reaction with a potential redox partner. The shape of the redox-active orbitals is shown in Figure 5 and their composition in terms of metal and ligand participation is described in Table 3. In all cases, the metal $d_{x^2-y^2}$ orbital is involved (i.e. the orbital perpendicular to the oxo ligand and directed between the four M–S bonds). For the sulfur atoms, it is in most cases the p_z orbital (directed out of the S–C=C–S plane) that is involved in the redox-active molecular orbital, but in some cases, it is instead the p_y orbital (located in the S–C=C–S plane). This depends on the amount of metal participation and it is only observed for the oxidation state +4 (i.e. for the HOMO): If the metal

participation is high (>60%), the S p_y orbitals are used. Without the bending of the ligand, which only occurs in oxidation states +5 and +6, and with the need for the transfer of electron density onto the metal, the orbital overlap is only sufficient for the in-plane p_y orbital. This is especially important for tungsten, with its higher nuclear charge. Therefore, the sulfur p_y orbitals are used for all tungsten compounds in oxidation state +4. For molybdenum, they are used only if the ligand contains also electron withdrawing groups i.e. the pyrazine ring or the pterin group. For the smaller ligands, the orbital overlap between metal orbital and sulfur p_z orbital in oxidation state +4 is sufficient. However, for the new geometry upon ligand folding in oxidation states +5 and +6, only the out-of-plane p_z orbital provides a sufficient orbital overlap and is therefore used for all metal–sulfur bonds. Further participants in the frontier orbitals are the carbon atoms of the C=C double bond (p_z orbitals) and to a low degree (2%) the apical oxygen (p_y orbital).

From Figure 5 and Table 3, it can be seen that this leads to a major difference in the HOMO for the reduced Mo complex between the edt and pdt ligands on one hand and the more accurate prz and mpt ligands, on the other hand. In the former complexes, there is only a small contribution of Mo (6–40 %), whereas it is 63–73 % in the latter two complexes. For the other five complexes, the difference is opposite, i.e. the smaller models have a larger contribution from the metal, but the edt and pdt ligands still have a larger difference to the mpt ligand (by 19 and 13 % units on average), compared to the prz ligand (8 % units difference on average). For the S contribution, the difference is smaller, but the trends are the same.

Table 3: Orbital contributions in % of the metal and the S atoms for the HOMO in oxidation state +4, the SOMO in oxidation state +5 and the LUMO in oxidation state +6.

	1a^{iv}	1a^v	1a^{vi}	1b^{iv}	1b^v	1b^{vi}
Mo/W (4/5d _{x2-y2})	6	31	52	75	36	60
S (3p _z)	46	42	36	10 (p _y)	41	32
	2a^{iv}	2a^v	2a^{vi}	2b^{iv}	2b^v	2b^{vi}
Mo/W (4/5d _{x2-y2})	40	32	51	74	39	58
S (3p _z)	38	40	35	10 (p _y)	39	31
	3a^{iv}	3a^v	3a^{vi}	3b^{iv}	3b^v	3b^{vi}

Mo/W (4/5d _{x2-y2})	73	34	44	70	35	52
S (3p _z)	11 (p _y)	39	33	9 (p _y)	38	31
	4a^{iv}	4a^v	4a^{vi}	4b^{iv}	4b^v	4b^{vi}
Mo/W (4/5d _{x2-y2})	63	26	39	61	29	45
S (3p _z)	10 (p _y)	40	32	8 (p _y)	39	31

The size of the energetic gap in oxidation state +6 between the LUMO (former HOMO/SOMO) and the new HOMO (former HOMO-1) depends on the molybdopterin ligand model as well. For instance, it is 1.90 eV (Mo) and 2.23 eV (W) for the edt compounds (**1**) and slightly smaller for the pdt compounds (**2**), 1.74 eV (Mo) and 2.07 eV (W). However, for the other two ligands, prz (**3**) and mpt (**4**), it is significantly smaller and very similar to each other (0.63 and 0.65 eV (Mo) and 0.60 and 0.73 eV (W) for prz and mpt, respectively). Again, the prz ligand (**3**) is a sufficient model for the mpt ligand (**4**), whereas the smaller ligands (**1**, **2**) show considerable deviations.

The smaller gap between HOMO and LUMO for the complexes with the larger ligands means that they are easier to reduce than the smaller models. The reduction would be the relevant catalytic step for those enzymes that are oxidases and the regeneration step for those that are reductases. It is therefore an important part of the enzymatic catalysis. These findings again indicate that the way the molybdopterin ligand is modeled has an important influence on the results.

This is nicely illustrated in Table 4, which shows the calculated redox potentials of the transition between oxidation states +4 and +5 which are those, that are experimentally available and directly relevant for the enzymatic reactions in nature. The transition between oxidation states +5 and +6 (Table S4) can usually not be observed since the complexes and enzymes in oxidation state +6 contain a second oxo ligand. The $M^{IV} \leftrightarrow M^V$ potentials calculated in water are negative and in the range from -0.10 to -0.14 V for the molybdenum compounds and more negative for tungsten (-0.33 to -0.38 V). Experimental redox potentials in acetonitrile have been measured for $[MoO(edt)_2]^{2-/1-}$ [45] and $[MoO(pdt)_2]^{2-/1-}$ [46], -0.61 and -0.56 V. This is a reasonable, considering the difference in solvents (the calculated potentials in diethylether are -1.38 and -1.35 V, respectively, Table S4). In particular, the sign and size of the difference between the two ligands is accurately reproduced. For

both metals, the mpt give the most negative values, which differ by $\sim 0.04\text{--}0.05$ V from pdt and prz, and by $\sim 0.02\text{--}0.03$ V from edt. In case of the redox potentials, the influence of the four different ligand systems on the complex properties is not very pronounced (up to 0.13 V), even though there are examples in the literature where different substituents on the dithiolene cause differences in redox potential as large as 1 V [18,19].

Table 4: Redox Potentials (E_0 vs. NHE in V, in aqueous solution) of the relevant oxidation states

	Mo ^{IV} /Mo ^V	W ^{IV} /W ^V
[MO(edt) ₂] ²⁻	-0.11	-0.36
[MO(pdt) ₂] ²⁻	-0.10	-0.33
[MO(prz) ₂] ²⁻	-0.10	-0.34
[MO(mpt) ₂] ²⁻	-0.14	-0.38

Conclusion

In this paper, we have studied how the model used for the molybdopterin ligand affects the properties of the active site. Our results show that there are quite extensive differences between the properties obtained with different models, especially with the smaller edt and pdt models. For the M–S bond lengths, the average difference between the edt and mpt ligands is 0.012 Å, whereas the difference is only 0.002 and 0.001 Å for the pdt and prz ligands, respectively. For the C=C bond lengths, the average differences (compared to mpt) are 0.004, 0.001, and 0.002 Å for the edt, pdt and prz models, respectively. However, for the folding angles, all three ligand models give similar average differences of 0.8, 1.5, and 1.4°, respectively. The NPA charges differ in the order edt > pdt > prz with 0.034, 0.018 and 0.016 for the metals, 0.020, 0.017 and 0.013 for oxygen, 0.019, 0.012 and 0.006 for the carbon and 0.022, 0.003 and 0.002 for the sulfur atoms, showing the greatest differences for the edt compounds and the smallest for the prz compounds. The natural bond orbital analysis shows largest differences for the edt and pdt ligands, especially for the oxidized state, with differences in the composition of the M–S orbitals of up to 11 % units. Some redox-active orbitals also show extensive differences between the various ligand models, but in this

case, the largest differences are found for the HOMO in the reduced state (Figure 4), for which the edt and pdt HOMO orbitals are strongly different from that with mpt for the Mo complexes. For the HOMO–LUMO gap, the edt and pdt ligand models give a larger difference to the mpt model (0.04 a.u.) compared to the prz ligand (0.02 a.u.). Finally, for redox potentials, the differences are rather small and similar for all the three simplified models, ~ 0.05 V on average. This shows that great care is needed in the selection of the model of the molybdopterin ligand both in theoretical and experimental investigations, if properties should be obtained that are really relevant to the native metal site in the proteins.

Another important observation is that the changes of the bond lengths and folding angles when the oxidation state of the metal is changed are always smallest for the mpt (**4**) compounds. This could be of significance for the catalytic performance of the active sites of the enzymes for instance resulting in a lower reorganization energy. This ligand also gives smaller differences between molybdenum and tungsten, indicating that the normally observed quite large differences between these two metals may be less significant in the enzymes.

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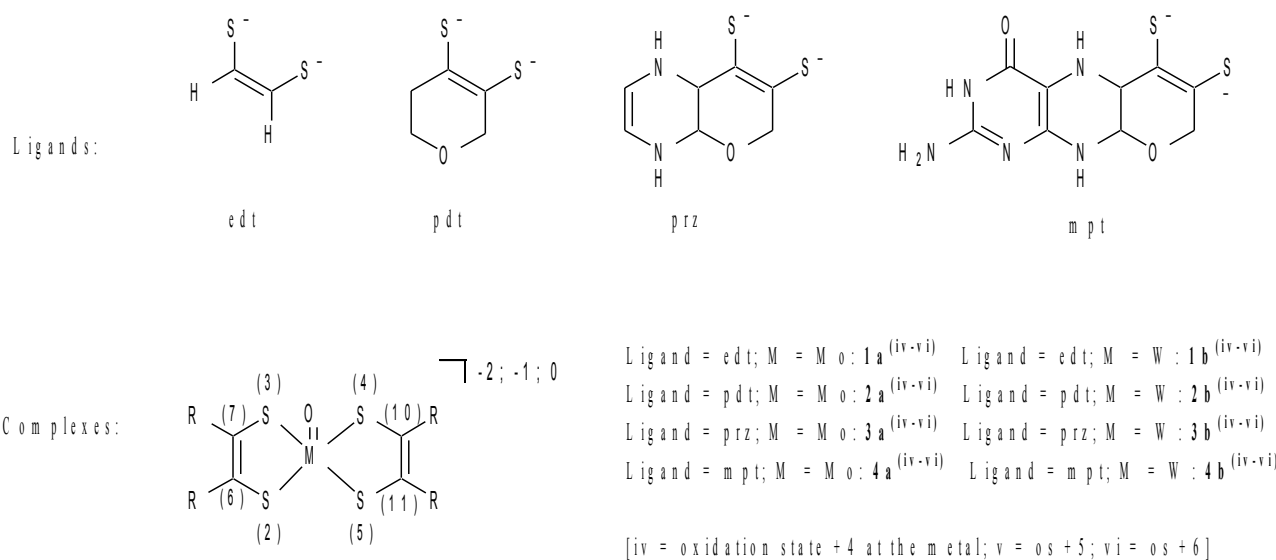
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Figures

Scheme 1: The general structure of the active sites of the molybdenum and tungsten enzymes.

Additional ligands not shown here may be oxo, sulfido, hydroxide and/or water.



Scheme 2: The investigated ligand systems and resulting complexes with numbering scheme of the compounds and the relevant atoms.

Scheme 3: Definition of the folding angle

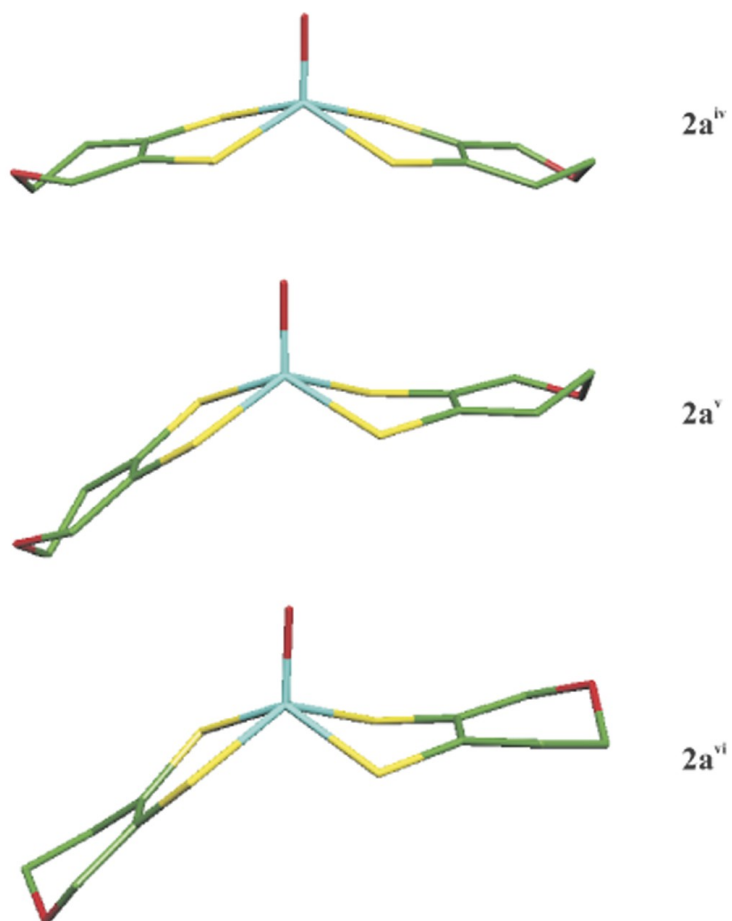
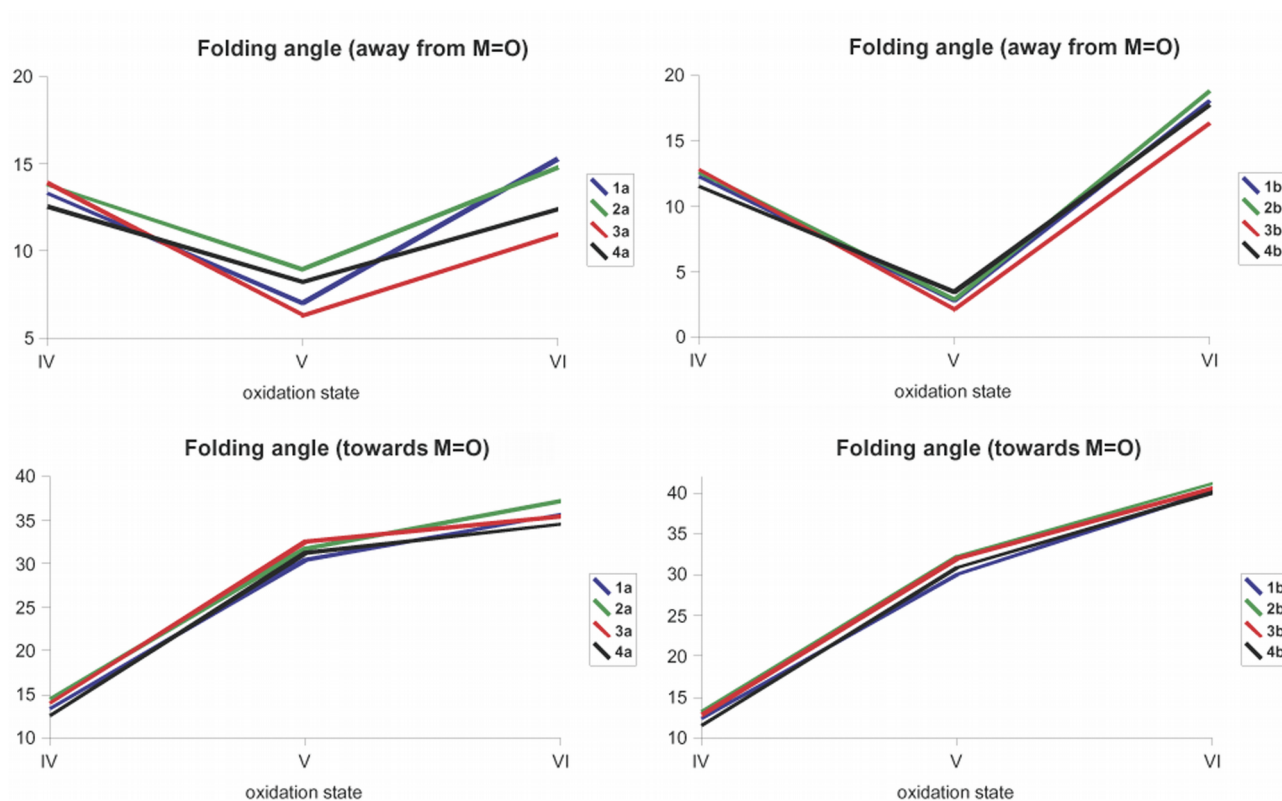


Figure 1: Bending of both ligands upon oxidation of the molybdenum pdt compounds **2a**

Figure 2: The folding angles (towards M=O: left; away from it: right) in all oxidation states for all



Mo (top) and W (bottom) compounds.

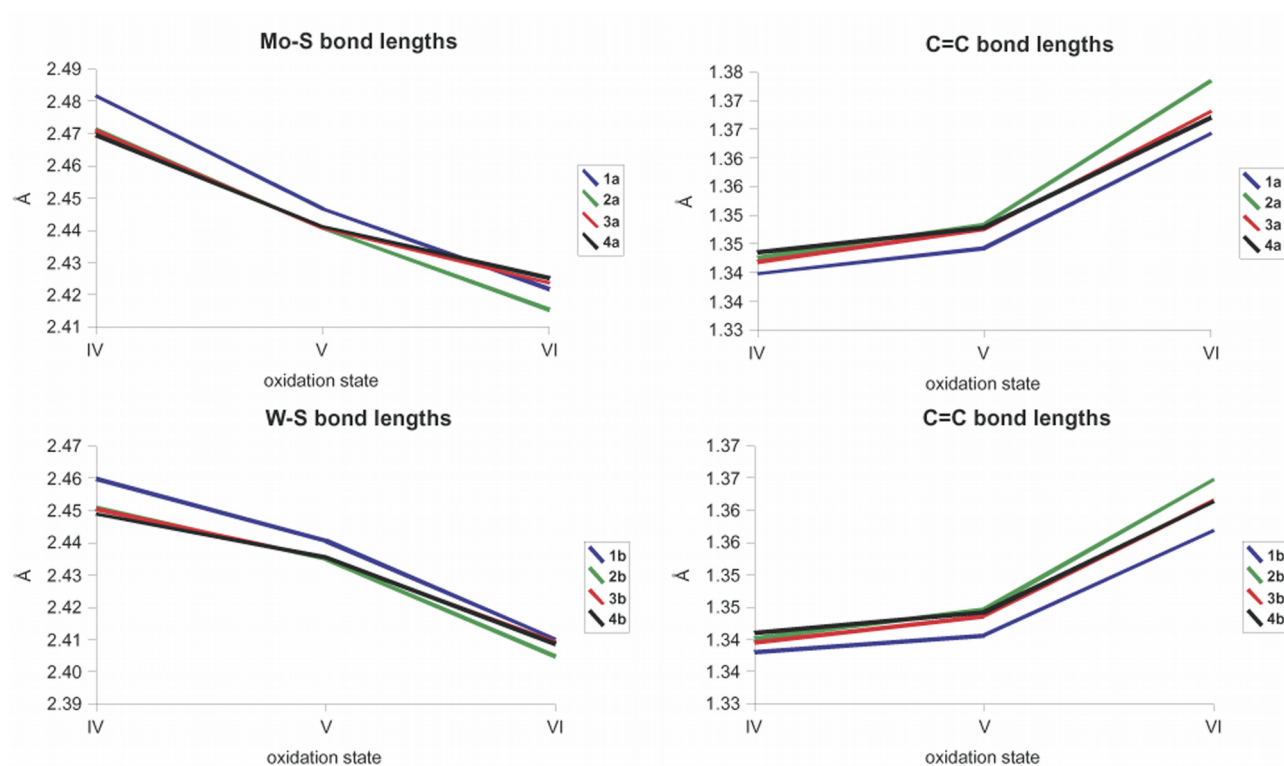


Figure 3: Dependence of the metal–sulfur and C=C bond lengths on oxidation states for the molybdenum (top) and tungsten (bottom) complexes.

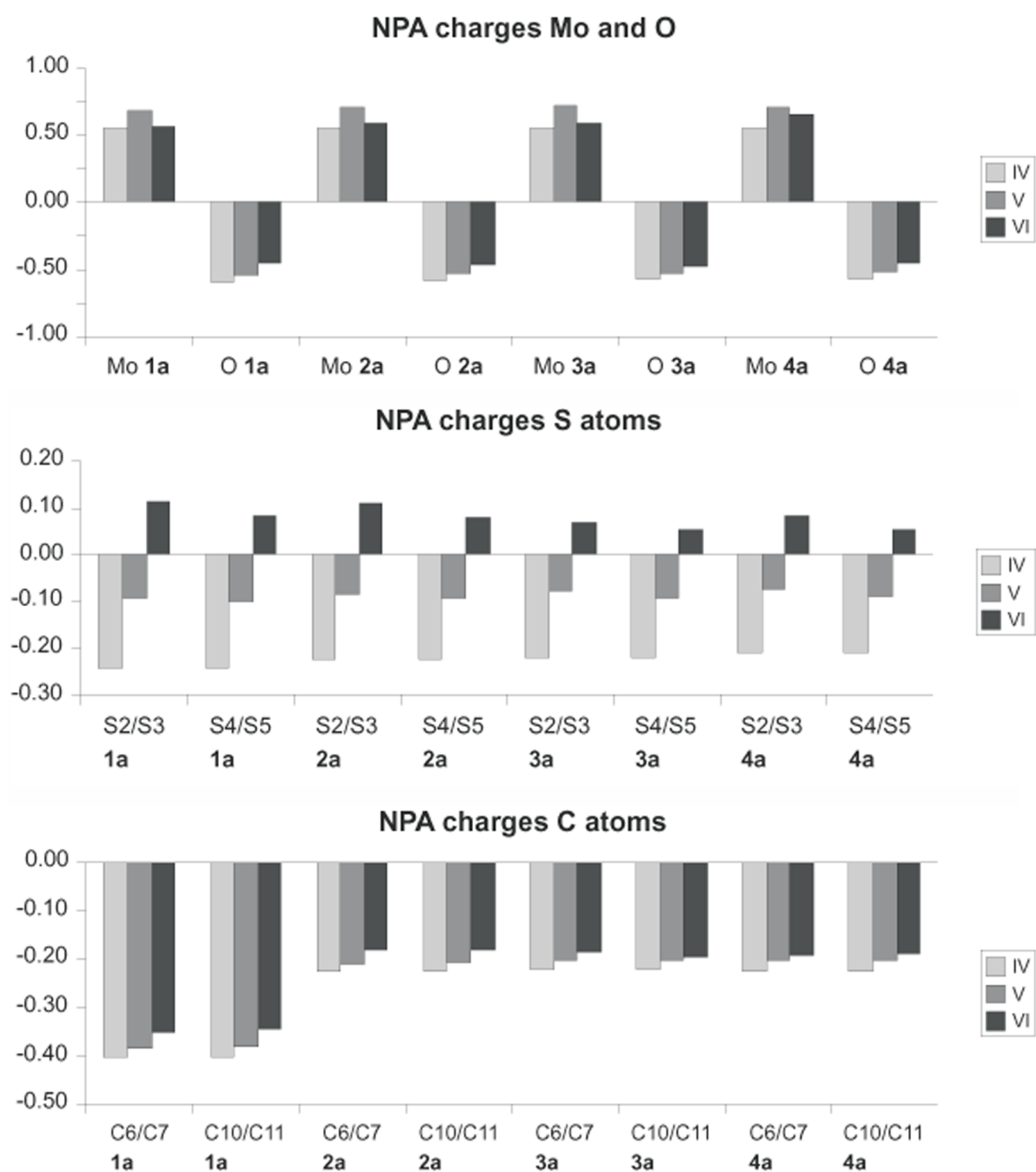


Figure 4: The NPA charges on Mo and the apical oxo ligand, as well as the average charge on the two sulfur atoms and the two ethene carbon atoms of each ligand.

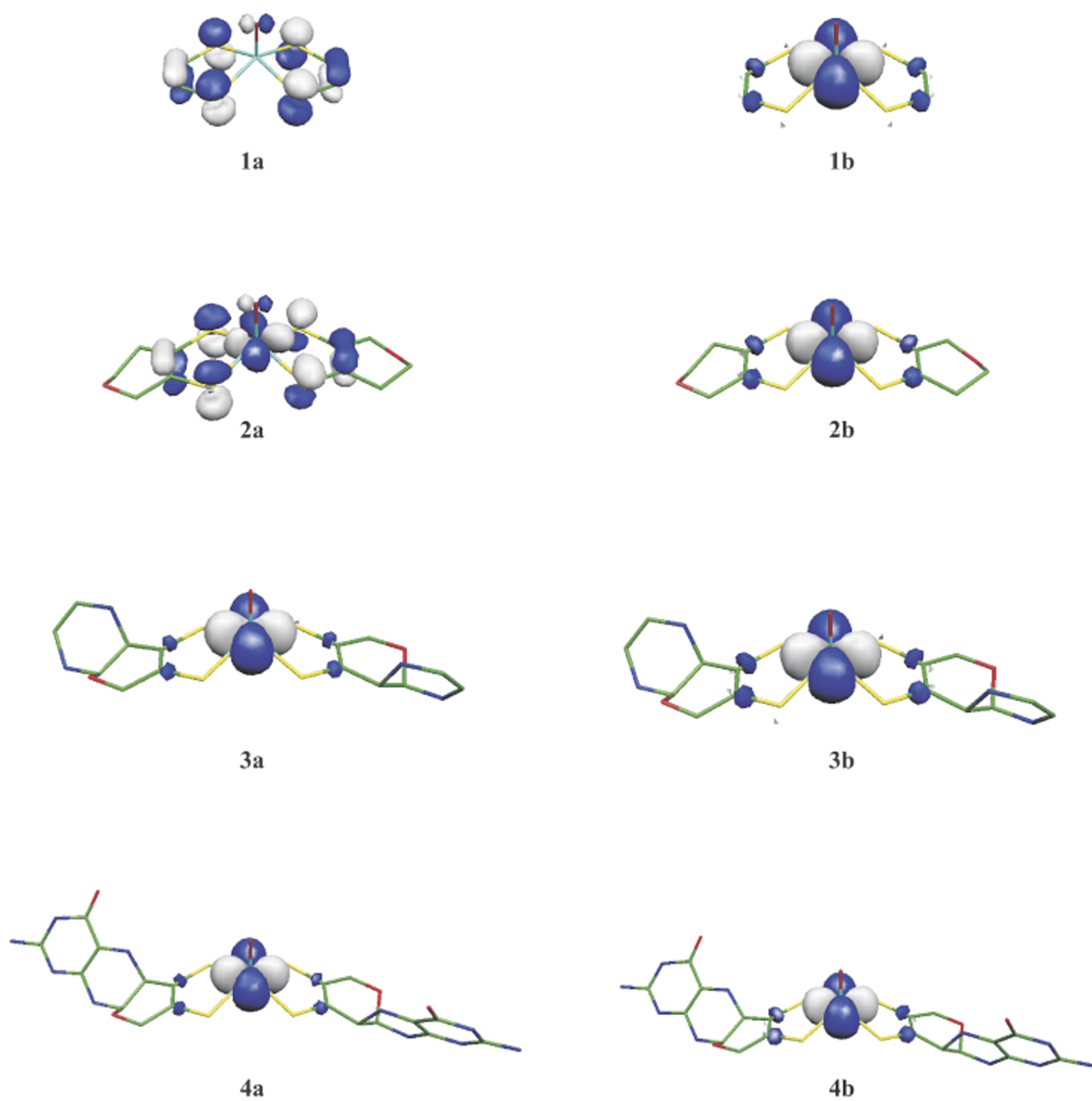


Figure 5: The highest occupied orbitals of all complexes in oxidation state IV

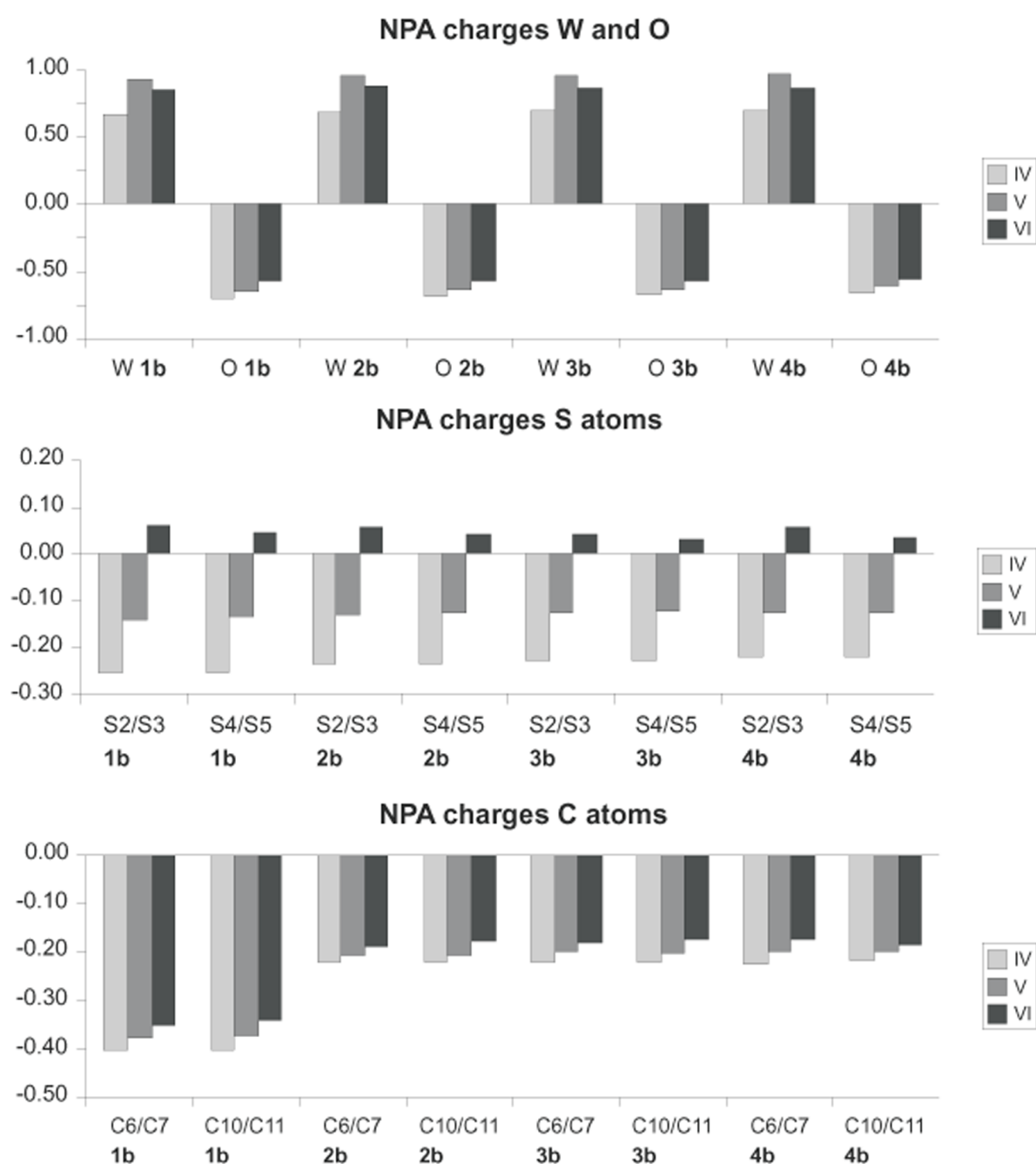


Figure S1: The NPA charges on the relevant atoms for all tungsten complexes.

Table S1: Geometry parameters

[Å/°]	1a(iv)	1a(v)	1a(vi)	1b(iv)	1b(v)	1b(vi)
M(1)-S(2)	2.4818	2.4538	2.4348	2.4598	2.4451	2.4228
M(1)-S(3)	2.4817	2.4536	2.4348	2.4597	2.4450	2.4230
M(1)-S(4)	2.4818	2.4396	2.4087	2.4598	2.4363	2.3971
M(1)-S(5)	2.4817	2.4394	2.4086	2.4598	2.4363	2.3971
C(6)=C(7)	1.3398	1.3437	1.3631	1.3379	1.3389	1.3540
C(10)=C(11)	1.3398	1.3449	1.3655	1.3379	1.3423	1.3599
M(1)-[S(2)-S(3)]	13.33	7.04	15.29	12.29	2.77	18.03
M(1)-[S(4)-S(5)]	13.29	30.42	35.63	12.30	30.03	40.17
	2a(iv)	2a(v)	2a(vi)	2b(iv)	2b(v)	2b(vi)
M(1)-S(2)	2.4735	2.4489	2.4025	2.4528	2.4398	2.3918
M(1)-S(3)	2.4687	2.4466	2.4023	2.4483	2.4375	2.3926
M(1)-S(4)	2.4727	2.4351	2.4297	2.4516	2.4320	2.4179
M(1)-S(5)	2.4710	2.4320	2.4266	2.4506	2.4298	2.4161
C(6)=C(7)	1.3426	1.3481	1.3754	1.3401	1.3425	1.3684
C(10)=C(11)	1.3426	1.3489	1.3716	1.3401	1.3467	1.3614
M(1)-[S(2)-S(3)]	13.81	8.96	37.17	12.64	2.88	41.14
M(1)-[S(4)-S(5)]	14.38	31.72	14.80	13.12	32.21	18.82
	3a(iv)	3a(v)	3a(vi)	3b(iv)	3b(v)	3b(vi)
M(1)-S(2)	2.4728	2.4495	2.4396	2.4524	2.4408	2.4237
M(1)-S(3)	2.4690	2.4440	2.4319	2.4485	2.4365	2.4143
M(1)-S(4)	2.4728	2.4350	2.4132	2.4524	2.4321	2.3968
M(1)-S(5)	2.4690	2.4343	2.4100	2.4486	2.4316	2.4008
C(6)=C(7)	1.3419	1.3466	1.3671	1.3394	1.3417	1.3588
C(10)=C(11)	1.3419	1.3486	1.3693	1.3394	1.3455	1.3642
M(1)-[S(2)-S(3)]	13.93	6.32	10.94	12.78	2.09	16.30
M(1)-[S(4)-S(5)]	13.93	32.52	35.39	12.79	31.96	40.48
	4a(iv)	4a(v)	4a(vi)	4b(iv)	4b(v)	4b(vi)
M(1)-S(2)	2.4710	2.4504	2.4378	2.4506	2.4412	2.4211
M(1)-S(3)	2.4680	2.4439	2.4314	2.4474	2.4359	2.4153

Table S2: NBO Parameters [MO(edt)₂]^{z-}, M = Mo, W, z = -2, -1, 0

A-B		Occ.	% A	Hybridization			% B	Hybridization		
1a(iv)				s	p	d		s	p	d
Mo-S(2)	σ	1.81	20.4	13.5	0.6	85.9	76.8	20.0	79.9	0.1
Mo-S(3)	σ	1.81	20.4	13.5	0.5	86.0	76.8	19.9	80.0	0.1
Mo-S(4)	σ	1.81	20.4	13.5	0.6	85.9	76.8	20.0	79.9	0.1
Mo-S(5)	σ	1.81	20.4	13.5	0.5	86.0	76.8	19.9	80.0	0.1
1a(v)										
Mo-S(2)	σ	1.78	22.8	11.9	1.0	87.1	73.5	16.3	83.6	0.1
Mo-S(3)	σ	1.78	23.2	11.0	0.9	88.1	73.3	16.2	83.6	0.1
Mo-S(4)	σ	1.79	26.1	12.6	0.7	86.7	71.4	16.2	83.7	0.2
Mo-S(5)	σ	1.8	25.7	14.1	0.8	85.1	71.6	16.3	83.6	0.2
1a(vi)										
Mo-S(2)	σ	1.81	19.7	25.4	28.5	46.1	80.3	15.0	84.9	0.2
Mo-S(3)	σ	1.81	19.7	25.4	28.5	46.1	80.3	15.0	84.9	0.2
Mo-S(4)	σ	1.81	23.6	16.0	27.5	56.5	76.4	14.2	85.6	0.2
Mo-S(5)	σ	1.81	23.6	16.0	27.5	56.5	76.4	14.2	85.6	0.2
1b(iv)										
A-B				s	p	d		s	p	d
W-S(2)	σ	1.83	20.3	18.8	0.8	80.4	77.2	23.9	76.0	0.1
W-S(3)	σ	1.82	20.4	18.6	0.7	80.7	77.2	23.8	76.1	0.1
W-S(4)	σ	1.83	20.3	18.8	0.8	80.4	77.2	23.9	76.0	0.1
W-S(5)	σ	1.83	20.4	18.6	0.7	80.7	77.2	23.8	76.1	0.1
1b(v)										
W-S(2)	σ	1.82	22.3	17.8	1.3	80.9	74.5	19.8	80.1	0.1
W-S(3)	σ	1.82	22.3	17.8	1.3	80.8	74.5	19.8	80.1	0.1
W-S(4)	σ	1.81	24.7	19.4	1.1	79.5	72.7	18.8	81.0	0.2
W-S(5)	σ	1.81	24.7	19.3	1.1	79.6	72.7	18.8	81.0	0.2
1b(vi)										
W-S(2)	σ	1.82	19.9	22.3	33.0	44.8	80.1	17.4	82.4	0.2
W-S(3)	σ	1.82	19.9	22.3	33.0	44.8	80.1	17.4	83.4	0.2
W-S(4)	σ	1.82	21.3	19.0	34.0	47.0	78.7	16.5	83.3	0.2
W-S(5)	σ	1.81	21.3	19.0	34.0	47.0	78.7	16.5	83.3	0.2

NBO Parameters [MO(pdt)₂]^{z-}, M = Mo, W, z = -2, -1, 0

A-B		Occ.	% A	Hybridization			% B	Hybridization		
2a(iv)				s	p	d		s	p	d
Mo-S(2)	σ	1.81	20.6	13.5	0.4	86.1	76.5	19.9	80.0	0.1
Mo-S(3)	σ	1.81	20.1	12.8	0.5	86.8	76.8	19.9	80.0	0.1
Mo-S(4)	σ	1.80	19.8	12.8	0.5	86.8	76.9	19.9	80.0	0.1
Mo-S(5)	σ	1.81	20.9	13.6	0.4	86.0	76.4	19.9	80.1	0.1
2a(v)										
Mo-S(2)	σ	1.78	22.7	11.2	0.8	88.1	73.5	16.2	83.7	0.1
Mo-S(3)	σ	1.78	23.5	10.8	0.8	88.4	72.9	16.1	83.7	0.1
Mo-S(4)	σ	1.79	25.6	13.0	0.6	86.5	71.5	16.2	83.7	0.2
Mo-S(5)	σ	1.79	26.3	12.8	0.7	86.6	71.1	16.2	83.6	0.2
2a(vi)										
Mo-S(2)	σ	1.81	15.4	21.8	31.4	46.3	84.6	18.3	81.6	0.1
Mo-S(3)	σ	1.81	16.0	21.2	31.1	47.7	84.0	18.8	81.0	0.1
Mo-S(4)	σ	1.81	15.9	20.7	30.7	48.7	84.1	18.5	81.4	0.1
Mo-S(5)	σ	1.81	15.5	21.5	32.4	46.1	84.5	18.6	81.3	0.1
2b(iv)										
W-S(2)	σ	1.82	20.3	18.9	0.6	80.5	77.2	23.8	76.1	0.1
W-S(3)	σ	1.82	20.0	18.1	0.6	81.2	77.2	23.7	76.2	0.1
W-S(4)	σ	1.82	19.5	18.4	0.7	81.0	77.5	23.9	76.0	0.1
W-S(5)	σ	1.82	20.8	18.8	0.6	80.6	76.8	23.7	76.2	0.1
2b(v)										
W-S(2)	σ	1.80	22.3	16.3	1.0	82.6	74.6	20.1	79.7	0.1
W-S(3)	σ	1.80	22.0	17.4	1.2	81.4	74.7	20.1	79.7	0.1
W-S(4)	σ	1.80	24.1	18.9	0.9	80.2	73.1	19.1	80.7	0.2
W-S(5)	σ	1.81	24.1	19.9	1.0	79.1	73.1	19.1	80.8	0.2
2b(vi)										
W-S(2)	σ	1.80	20.4	19.0	34.6	46.4	79.6	16.6	83.1	0.2
W-S(3)	σ	1.81	21.1	19.5	33.9	46.6	79.0	16.8	83.0	0.2
W-S(4)	σ	1.82	19.5	22.1	32.2	45.7	80.5	17.6	82.2	0.2
W-S(5)	σ	1.81	19.5	21.9	33.0	45.1	80.5	17.8	82.1	0.2

A-B		Occ.	% A	Hybridization			% B	Hybridization		
				s	p	d		s	p	d
3a(iv)										
Mo-S(2)	σ	1.80	20.2	13.4	0.5	86.2	76.7	19.7	80.2	0.1
Mo-S(3)	σ	1.81	20.2	12.9	0.4	86.6	76.9	19.9	80.0	0.1
Mo-S(4)	σ	1.80	20.2	13.4	0.5	86.2	76.7	19.7	80.2	0.1
Mo-S(5)	σ	1.81	20.2	12.9	0.4	86.6	76.9	19.9	80.0	0.1
3a(v)										
Mo-S(2)	σ	1.78	22.7	11.2	0.8	88.1	73.9	17.0	82.9	0.1
Mo-S(3)	σ	1.79	22.5	11.0	0.7	88.3	74.2	17.1	82.8	0.1
Mo-S(4)	σ	1.79	24.9	13.2	0.6	86.2	72.2	16.6	83.3	0.2
Mo-S(5)	σ	1.79	25.0	12.9	0.6	86.5	72.3	16.6	83.3	0.1
3a(vi)										
Mo-S(2)	σ	1.83	21.3	29.4	18.1	52.5	78.8	16.9	82.9	0.2
Mo-S(3)	σ	1.81	18.6	25.1	28.7	46.1	81.5	17.1	82.8	0.2
Mo-S(4)	σ	1.86	26.8	13.5	16.9	69.5	73.2	16.2	83.7	0.2
Mo-S(5)	σ	1.81	22.4	16.8	28.5	54.8	77.7	16.1	83.7	0.2
3b(iv)										
W-S(2)	σ	1.82	19.9	18.9	0.6	80.5	77.3	23.7	76.2	0.1
W-S(3)	σ	1.82	19.9	18.4	0.6	81.0	77.5	24.0	75.9	0.1
W-S(4)	σ	1.82	19.8	18.8	0.6	80.6	77.3	23.7	76.2	0.1
W-S(5)	σ	1.82	19.9	18.4	0.6	81.0	77.5	24.0	75.9	0.1
3b(v)										
W-S(2)	σ	1.80	22.2	17.3	1.1	81.6	74.5	20.1	79.8	0.1
W-S(3)	σ	1.80	22.0	17.3	1.0	81.7	74.7	20.2	79.6	0.1
W-S(4)	σ	1.80	24.1	19.1	0.9	80.0	73.0	18.9	80.9	0.2
W-S(5)	σ	1.81	24.1	18.9	0.9	80.2	73.2	19.1	80.7	0.2
3b(vi)										
W-S(2)	σ	1.82	22.8	16.2	26.2	57.6	77.2	17.9	81.9	0.2
W-S(3)	σ	1.81	20.3	20.1	34.9	45.1	79.7	18.0	81.8	0.2
W-S(4)	σ	1.83	20.7	25.7	25.7	48.5	79.3	19.0	80.8	0.2
W-S(5)	σ	1.81	19.0	21.5	33.2	45.3	81.0	19.3	80.5	0.2

NBO Parameters [MO(mpt)₂]^z, M = Mo, W, z = -2, -1, 0

4a(iv)				s	p	d		s	p	d
Mo-S(2)	σ	1.80	20.16	13.34	0.48	86.18	76.72	19.76	80.15	0.10
Mo-S(3)	σ	1.81	20.34	12.88	0.46	86.88	76.79	19.78	80.13	0.09
Mo-S(4)	σ	1.80	20.16	13.34	0.48	86.18	76.72	19.75	80.15	0.10
Mo-S(5)	σ	1.81	20.34	12.88	0.46	86.66	76.79	19.78	80.13	0.09
4a(v)										
Mo-S(2)	σ	1.78	23.24	11.01	0.81	88.19	73.25	16.24	83.64	0.13
Mo-S(3)	σ	1.78	23.18	10.85	0.75	88.40	73.35	16.16	83.73	0.12
Mo-S(4)	σ	1.79	25.56	13.09	0.63	86.28	71.51	16.12	83.73	0.15
Mo-S(5)	σ	1.79	25.68	12.77	0.61	86.62	71.55	16.08	83.77	0.15
4a(vi)										
Mo-S(2)	σ	1.83	20.96	29.74	17.69	52.57	79.04	15.64	84.20	0.16
Mo-S(3)	σ	1.81	18.48	25.09	28.86	46.05	81.52	15.74	84.10	0.16
Mo-S(4)	σ	1.84	26.68	13.12	16.68	70.20	73.32	14.80	85.00	0.20
Mo-S(5)	σ	1.81	22.07	16.64	28.31	55.06	77.93	14.83	84.97	0.20
4b(iv)										
W-S(2)	σ	1.82	19.78	18.81	0.65	80.55	77.42	23.76	76.13	0.11
W-S(3)	σ	1.82	19.92	18.37	0.64	81	77.47	23.93	75.97	0.11
W-S(4)	σ	1.82	19.78	18.81	0.65	80.55	77.42	23.76	76.13	0.11
W-S(5)	σ	1.82	19.92	18.37	0.64	81	77.47	23.93	75.96	0.11
4b(v)										
W-S(2)	σ	1.80	22.16	17.46	1.13	81.42	74.44	19.87	79.99	0.14
W-S(3)	σ	1.80	22.08	17.35	1.10	81.55	74.61	19.97	79.89	0.14
W-S(4)	σ	1.80	24.08	19.16	0.94	79.90	73.01	18.81	81.02	0.17
W-S(5)	σ	1.81	24.22	18.89	0.92	80.19	73.05	19.00	80.83	0.16
4b(vi)										
W-S(2)	σ	1.82	22.76	15.85	26.44	57.71	77.24	16.65	83.12	0.23
W-S(3)	σ	1.81	20.92	18.96	33.96	47.08	79.08	16.71	83.06	0.24
W-S(4)	σ	1.83	20.57	25.86	25.95	48.19	79.43	17.82	81.99	0.19
W-S(5)	σ	1.81	19.17	22.47	33.06	44.47	80.83	17.81	82.00	0.19

Table S3: Eigenvalues and energetic gaps of the redox-active orbital (all values are in atomic units)

	3a(iv)	3a(v)		3a(vi)
HOMO-1(115)	0,055	-0,087	HOMO(115)	-0,182
HOMO (116)	0,055	-0,076	LUMO(116)	-0,159
LUMO (117)	0,195	0,054	LUMO+1(117)	-0,075
Δ 117-116	0,140	0,130	Δ 116-115	0,023
	4a(iv)	4a(v)		4a(vi)
HOMO-1(157)	0,046	-0,096	HOMO(157)	-0,179
HOMO (158)	0,048	-0,081	LUMO(158)	-0,155
LUMO (159)	0,129	0,047	LUMO+1(159)	-0,070
Δ 159-158	0,082	0,128	Δ 158-157	0,024
	1b(iv)	1b(v)		1b(vi)
HOMO-1(57)	0,087	-0,093	HOMO(57)	-0,240
HOMO (58)	0,104	-0,062	LUMO(58)	-0,158
LUMO (59)	0,250	0,081	LUMO+1(59)	-0,076
Δ 59-58	0,146	0,143	Δ 58-57	0,082
	2b(iv)	2b(v)		2b(vi)
HOMO-1(87)	0,068	-0,097	HOMO(87)	-0,230
HOMO (88)	0,084	-0,068	LUMO(88)	-0,154
LUMO (89)	0,223	0,078	LUMO+1(89)	-0,069
Δ 89-88	0,139	0,146	Δ 88-87	0,076
	3b(iv)	3b(v)		3b(vi)
HOMO-1(115)	0,053	-0,085	HOMO(115)	-0,177
HOMO (116)	0,072	-0,077	LUMO(116)	-0,155
LUMO (117)	0,197	0,068	LUMO+1(117)	-0,069
Δ 117-116	0,125	0,146	Δ 116-115	0,0222
	4b(iv)	4b(v)		4b(vi)
HOMO-1(157)	0,047	-0,095	HOMO(157)	-0,179
HOMO (158)	0,066	-0,079	LUMO(158)	-0,152
LUMO (159)	0,128	0,059	LUMO+1(159)	-0,067
Δ 159-158	0,062	0,138	Δ 158-157	0,0268

Table S4. Calculated redox potentials in water and diethylether.

	Diethylether				Water			
	Mo ^{IV/V}	Mo ^{V/VI}	W ^{IV/V}	W ^{V/VI}	Mo ^{IV/V}	Mo ^{V/VI}	W ^{IV/V}	W ^{V/VI}
[MO(edt) ₂] ²⁻	-1.38	0.24	-1.64	0.10	-0.11	0.65	-0.36	0.52
[MO(pdt) ₂] ²⁻	-1.35	0.20	-1.59	0.07	-0.10	0.61	-0.33	0.49
[MO(prz) ₂] ²⁻	-1.28	0.13	-1.53	0.10	-0.10	0.47	-0.34	0.47
[MO(mpt) ₂] ²⁻	-1.31	0.24	-1.56	0.18	-0.14	0.60	-0.38	0.56

Table S5: Coordinates of the fully optimized geometries

1a^{iv} [MoO(edt)₂]²⁻

Mo	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.481789
S	2.461767	0.000000	0.313700
S	0.401439	1.373760	-2.027530
S	-2.059342	1.377542	0.141852
C	1.686234	-0.343614	2.928407
C	2.691709	-0.343592	2.042929
C	-2.144330	2.216505	-1.423420
C	-1.139300	2.214952	-2.309405
O	-0.458445	-1.569325	-0.518879
H	-1.216595	2.768443	-3.245062
H	-3.062006	2.771200	-1.618245
H	1.871784	-0.526884	3.986599
H	3.717991	-0.526835	2.360640

1a^v [MoO(edt)₂]¹⁻

Mo	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.453776
S	2.435705	0.000000	0.296146
S	0.473267	1.422426	-1.924675
S	-1.965867	1.424584	0.237706
C	1.682663	0.180195	2.912892
C	2.688473	0.180183	2.021934
C	-2.165066	1.960335	-1.430693
C	-1.158659	1.959409	-2.322866
O	-0.529808	-1.510299	-0.596980
H	-1.301450	2.344034	-3.328715
H	-3.146165	2.345687	-1.693353
H	1.871577	0.276123	3.977887
H	3.722906	0.276078	2.337928

1a^{vi} [MoO(edt)₂]

Mo	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.434785
S	2.412640	0.000000	0.327775
S	0.577416	1.461212	-1.825657
S	-1.886695	1.461321	0.326322
C	1.614679	0.374055	2.885015
C	2.641384	0.374057	1.988369
C	-2.064177	1.959748	-1.325760
C	-1.035708	1.959701	-2.223955
O	-0.629552	-1.401799	-0.720785
H	-1.191894	2.331801	-3.231521
H	-3.041527	2.331888	-1.616175
H	1.794694	0.536210	3.942232
H	3.664742	0.536206	2.309076

1b^{iv} [WO(edt)₂]²⁻

W	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.459808
S	2.440108	0.000000	0.310144
S	0.377597	1.333027	-2.032517
S	-2.061476	1.336666	0.118296
C	1.691230	-0.320952	2.931898
C	2.695207	-0.320652	2.047533
C	-2.169017	2.178479	-1.452094
C	-1.165439	2.177151	-2.336913
O	-0.449589	-1.587053	-0.508719
H	-1.236093	2.718822	-3.279141
H	-3.094248	2.721201	-1.640718
H	1.867055	-0.491298	3.993154
H	3.725908	-0.490856	2.355531

1b^v [WO(edt)₂]¹⁻

W	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.445050
S	2.429114	0.000000	0.278152
S	0.426876	1.372042	-1.967457
S	-2.002129	1.373542	0.200516
C	1.698467	0.071451	2.909792
C	2.697598	0.071423	2.018493
C	-2.223470	1.862253	-1.484688
C	-1.222064	1.861629	-2.378497
O	-0.504716	-1.539663	-0.565039
H	-1.373534	2.208018	-3.396247
H	-3.217352	2.209155	-1.750386
H	1.887360	0.109849	3.977872
H	3.737335	0.109678	2.327416

1b^{vi} [WO(edt)₂]

W	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.422830
S	2.402157	0.000000	0.317314
S	0.514690	1.383429	-1.888688
S	-1.940325	1.382904	0.262646
C	1.610946	0.453853	2.864761
C	2.629118	0.453792	1.972283
C	-2.168716	1.682768	-1.442663
C	-1.145976	1.683000	-2.338937
O	-0.592227	-1.448990	-0.675752
H	-1.328225	1.912177	-3.383432
H	-3.180318	1.911721	-1.760407
H	1.777746	0.655637	3.916580
H	3.650009	0.655600	2.275484

2a^{iv} [MoO(pdt)₂]²⁻

Mo	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.473460

S	2.447642	0.000000	0.321611
S	0.403296	1.372950	-2.016618
S	-2.042706	1.383622	0.136861
C	1.683431	-0.365851	2.932721
C	2.696530	-0.352033	2.051833
C	1.910119	-0.638365	4.399377
C	4.113664	-0.602054	2.513495
H	1.239636	-1.430060	4.749455
H	1.678258	0.267577	4.989910
C	4.229514	-0.371153	4.017546
H	4.428558	-1.628111	2.271016
H	4.801978	0.069982	1.983588
H	5.191938	-0.723069	4.409805
H	4.144897	0.708158	4.232089
O	3.233931	-1.089138	4.731190
C	-2.156456	2.205318	-1.441829
C	-1.140824	2.210136	-2.319962
C	-3.437715	2.944606	-1.752945
C	-1.232235	2.941297	-3.636203
C	-3.546606	3.213234	-3.251609
H	-4.303082	2.354195	-1.423416
H	-3.480033	3.896130	-1.201676
H	-1.244193	2.217464	-4.472270
H	-0.354063	3.580122	-3.776185
H	-4.362764	3.910025	-3.480057
H	-3.745227	2.265853	-3.781988
O	-0.458062	-1.565542	-0.522100
O	-2.366105	3.815510	-3.760614

2a^v [MoO(pdt)₂]¹⁻

Mo	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.448933
S	2.427298	0.000000	0.306624
S	0.473141	1.420789	-1.920193
S	-1.942098	1.445517	0.231072
C	1.680681	0.223797	2.921335
C	2.694178	0.239360	2.032507
C	1.925930	0.407859	4.403890
C	4.121394	0.437595	2.492989
H	1.397095	-0.362167	4.971401
H	1.530238	1.386367	4.724962
C	4.141042	1.031770	3.899882
H	4.655246	-0.521304	2.485145
H	4.651171	1.103072	1.802583
H	5.142322	0.989888	4.336593
H	3.822270	2.085631	3.864452
O	3.296863	0.297416	4.775093
C	-2.177282	1.953666	-1.451762
C	-1.162343	1.953831	-2.340313
C	-3.545152	2.463508	-1.845707
C	-1.351121	2.453013	-3.754979
C	-3.672594	2.518042	-3.367175
H	-4.324643	1.813328	-1.433045

H	-3.706173	3.462806	-1.420626
H	-1.310866	1.602562	-4.456753
H	-0.539945	3.136008	-4.021288
H	-4.558206	3.081108	-3.673401
H	-3.755729	1.496371	-3.770836
O	-0.533293	-1.509212	-0.594380
O	-2.560206	3.181539	-3.950831

2a^{vi} [MoO(pdt)₂]

Mo	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.402519
S	2.392210	0.000000	0.219654
S	0.481308	1.512653	-1.839483
S	-1.864404	1.523363	0.302490
C	1.477040	-0.899275	2.634868
C	2.504182	-0.883644	1.720357
C	1.624903	-1.635200	3.953835
C	3.803273	-1.590850	2.024847
H	0.755427	-2.273185	4.122130
H	1.654288	-0.891328	4.767917
C	3.931136	-1.851093	3.525377
H	3.829426	-2.543150	1.483348
H	4.644820	-0.992493	1.661046
H	4.755928	-2.531946	3.738053
H	4.109610	-0.908883	4.064296
O	2.754913	-2.482953	4.011001
O	-0.440381	-1.568224	-0.479763
C	-0.509121	2.903718	-1.590602
C	-1.531427	2.909695	-0.676201
C	-0.286722	4.086666	-2.517907
C	-2.452734	4.101553	-0.562333
O	-0.996656	5.242827	-2.121801
H	0.768721	4.363401	-2.526626
H	-0.564050	3.790960	-3.543000
C	-2.357630	4.963831	-1.822086
H	-2.163888	4.697584	0.310449
H	-3.481670	3.767145	-0.398383
H	-2.843963	5.928522	-1.674762
H	-2.839045	4.456722	-2.670964

2b^{iv} [WO(pdt)₂]²⁻

W	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.452815
S	2.428222	0.000000	0.313172
S	0.375304	1.328270	-2.026174
S	-2.049660	1.338116	0.116894
C	1.691123	-0.338461	2.933514
C	2.700739	-0.326052	2.052450
C	1.918730	-0.586973	4.401811
C	4.120949	-0.552161	2.510856
H	1.261026	-1.384526	4.763386
H	1.673069	0.322784	4.980816

C	4.236221	-0.295794	4.011505
H	4.447188	-1.578312	2.284241
H	4.801186	0.119213	1.969227
H	5.202912	-0.630499	4.408349
H	4.140063	0.785969	4.207854
O	3.250098	-1.012891	4.739703
O	-0.448670	-1.584209	-0.510119
C	-1.172645	2.168598	-2.345321
C	-2.183930	2.164358	-1.465997
C	-1.267298	2.889528	-3.664309
C	-3.469921	2.892860	-1.774047
O	-2.407877	3.755731	-3.792431
H	-0.394270	3.534515	-3.809724
H	-1.274999	2.161114	-4.496465
C	-3.584150	3.151677	-3.274705
H	-3.516336	3.847580	-1.228630
H	-4.331399	2.299645	-1.438440
H	-4.403634	3.843740	-3.505671
H	-3.780653	2.199853	-3.797674

2b^v [WO(pdt)₂]¹⁻

W	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.439804
S	2.420667	0.000000	0.285908
S	0.427365	1.373777	-1.960774
S	-1.984543	1.388096	0.196620
C	1.701580	0.067358	2.920506
C	2.708043	0.082792	2.032183
C	1.956703	0.123758	4.410316
C	4.146057	0.157984	2.490721
H	1.385417	-0.655617	4.921395
H	1.619636	1.096098	4.808852
C	4.207532	0.644346	3.937622
H	4.621536	-0.827599	2.406296
H	4.712686	0.840777	1.847408
H	5.204763	0.505245	4.363443
H	3.959109	1.716784	3.981432
O	3.319481	-0.095330	4.763945
O	-0.509971	-1.535657	-0.569158
C	-1.231277	1.833254	-2.396502
C	-2.242785	1.826981	-1.507443
C	-1.439236	2.268007	-3.828884
C	-3.631877	2.259541	-1.916537
O	-2.678302	2.935624	-4.050394
H	-0.658656	2.975346	-4.122119
H	-1.361023	1.393784	-4.497343
C	-3.761663	2.248920	-3.438897
H	-3.838354	3.265938	-1.529639
H	-4.380636	1.590390	-1.478041
H	-4.670214	2.761596	-3.765516
H	-3.801679	1.209615	-3.801773

2b^{vi} [WO(pdt)₂]

W	0.000000	0.000000	0.000000
S	0.000000	0.000000	2.391827
S	2.383688	0.000000	0.206587
S	0.422641	1.433534	-1.900666
S	-1.913984	1.453349	0.248708
C	1.440859	-0.987991	2.578288
C	2.462790	-0.970784	1.668457
C	1.539402	-1.812050	3.847430
C	3.726339	-1.755360	1.925197
H	0.642070	-2.422652	3.963465
H	1.588776	-1.125192	4.709384
C	3.837157	-2.105387	3.409036
H	3.711069	-2.673910	1.328269
H	4.596030	-1.175172	1.599699
H	4.629274	-2.834099	3.583927
H	4.057042	-1.203378	3.998893
O	2.632294	-2.709120	3.859557
O	-0.418186	-1.590954	-0.450919
C	-0.557909	2.846446	-1.638247
C	-1.571323	2.855223	-0.729255
C	-0.321472	4.027272	-2.562550
C	-2.495108	4.044006	-0.612742
O	-1.036363	5.183532	-2.174500
H	0.733811	4.305446	-2.555811
H	-0.583831	3.733091	-3.592217
C	-2.397434	4.904411	-1.873713
H	-2.214368	4.639965	0.262521
H	-3.524797	3.706902	-0.457054
H	-2.883277	5.869865	-1.729396
H	-2.878675	4.394911	-2.721213

3a^{iv} [MoO(prz)₂]²⁻

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.778232
C	1.131153	0.000000	-0.721992
S	2.749723	0.058254	0.025926
O	-1.331245	0.157269	-2.081166
C	1.046706	1.439302	-4.151840
C	0.179913	0.634243	-4.786993
Mo	2.333565	0.510832	2.417149
O	2.448221	2.199632	2.665172
C	-1.355755	-0.046328	-0.659800
H	-1.847181	-1.012123	-0.439546
H	-1.999059	0.743050	-0.261349
C	1.087569	-0.049068	-2.228190
H	1.853280	-0.756488	-2.587942
C	-0.276955	-0.569035	-2.703665
H	-0.358557	-1.626689	-2.404001
N	1.321940	1.283638	-2.804141
H	2.142614	1.733918	-2.427823
N	-0.416993	-0.489995	-4.144433
H	-1.396904	-0.592149	-4.384400

S	4.566158	-0.465589	2.837653
C	4.531619	-0.974503	4.541155
C	3.396597	-1.031487	5.254779
C	5.856253	-1.386659	5.133630
S	1.814801	-0.548034	4.586399
C	3.404037	-1.514884	6.682789
O	5.831287	-1.596987	6.554007
H	6.219774	-2.305171	4.636683
H	6.605951	-0.608616	4.965340
H	2.544628	-2.187882	6.839838
C	4.678286	-2.324924	6.962964
N	3.336890	-0.383980	7.620500
H	4.625055	-3.253667	6.371616
N	4.799533	-2.680780	8.363085
C	3.604066	-0.658370	8.950766
H	2.590465	0.259602	7.404807
C	4.344232	-1.718813	9.311986
H	5.752468	-2.976035	8.544696
H	3.222295	0.035671	9.691624
H	4.571256	-1.934193	10.348240
H	1.531254	2.259468	-4.670350
H	-0.053435	0.756450	-5.836928

3a^v [MoO(prz)₂]¹⁻

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.758234
C	1.134766	0.000000	-0.725071
S	2.731266	0.032234	0.022671
O	-1.317371	0.273412	-2.056641
C	1.030033	1.614615	-4.075854
C	0.161159	0.840106	-4.737899
Mo	2.350069	-0.166023	2.428605
O	2.845525	1.254784	3.232257
C	-1.360188	-0.010064	-0.662047
H	-1.840061	-0.989522	-0.493275
H	-2.002378	0.752211	-0.215112
C	1.093740	0.029306	-2.236860
H	1.845916	-0.670057	-2.634215
C	-0.284676	-0.455997	-2.722313
H	-0.387794	-1.520400	-2.459740
N	1.323131	1.391513	-2.729344
H	2.184553	1.792339	-2.389062
N	-0.413974	-0.315317	-4.145866
H	-1.367149	-0.486548	-4.439504
S	4.248319	-1.690055	2.371859
C	4.186141	-2.326098	4.021928
C	3.043953	-2.355212	4.738288
C	5.469507	-2.918949	4.557948
S	1.515058	-1.715789	4.109943
C	3.004584	-2.983245	6.111806
O	5.408488	-3.284724	5.932929
H	5.743949	-3.795673	3.944791
H	6.282405	-2.194407	4.475305

H	2.080219	-3.576275	6.206120
C	4.191010	-3.952220	6.269147
N	3.084266	-1.955143	7.151970
H	4.048305	-4.790123	5.569048
N	4.263583	-4.472919	7.606283
C	3.343615	-2.406970	8.445954
H	2.378856	-1.239863	7.056677
C	3.953985	-3.578475	8.666076
H	5.129634	-4.977307	7.747623
H	3.071304	-1.749566	9.261475
H	4.187019	-3.927040	9.662362
H	1.499676	2.467827	-4.548000
H	-0.097358	1.020297	-5.771918

3a^{vi} [MoO(prz)₂]

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.729407
C	1.159266	0.000000	-0.724589
S	2.716739	-0.010058	0.033259
O	-1.275166	0.377286	-2.055243
C	0.987826	1.919351	-3.875744
C	0.140841	1.190454	-4.620710
Mo	2.316020	-0.359459	2.406347
O	2.962288	0.847733	3.411718
C	-1.348105	0.007618	-0.689789
H	-1.798752	-0.993748	-0.589393
H	-2.016575	0.721406	-0.205453
C	1.132175	0.120801	-2.237021
H	1.889618	-0.544772	-2.678056
C	-0.251137	-0.320126	-2.767537
H	-0.370385	-1.399984	-2.600608
N	1.346665	1.515638	-2.594407
H	2.160475	1.944638	-2.181792
N	-0.353859	-0.047699	-4.167099
H	-1.247273	-0.315358	-4.555897
S	4.043124	-2.026995	2.161961
C	3.911484	-2.771598	3.735884
C	2.745395	-2.762112	4.453617
C	5.123218	-3.532166	4.234951
S	1.295452	-1.973300	3.876782
C	2.645540	-3.476489	5.780878
O	5.023345	-3.911787	5.594783
H	5.268545	-4.418700	3.593976
H	6.017935	-2.913770	4.148547
H	1.686127	-4.005213	5.838952
C	3.769299	-4.533144	5.897591
N	2.717893	-2.494206	6.864757
H	3.589258	-5.345349	5.179800
N	3.790165	-5.073867	7.221588
C	3.245714	-2.902655	8.087882
H	2.942448	-1.552648	6.572837
C	3.728520	-4.141295	8.274640
H	4.494341	-5.788815	7.342447

H	3.211418	-2.178841	8.890813
H	4.052465	-4.487911	9.245036
H	1.377202	2.867120	-4.218517
H	-0.172235	1.504205	-5.605136

3b^{iv} [WO(prz)₂]²⁻

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.785762
C	1.135735	0.000000	-0.710061
S	2.746750	0.051754	0.070528
O	-1.311907	0.166062	-2.089711
C	1.083776	1.463765	-4.128044
C	0.223664	0.662363	-4.776814
W	2.316110	0.463273	2.445494
O	2.440930	2.160625	2.707351
C	-1.349310	-0.039900	-0.668199
H	-1.846802	-1.004036	-0.454327
H	-1.993688	0.751314	-0.274518
C	1.109896	-0.039345	-2.215118
H	1.878898	-0.744361	-2.573290
C	-0.250999	-0.556215	-2.706482
H	-0.335035	-1.615803	-2.414526
N	1.348273	1.297070	-2.779828
H	2.159291	1.751828	-2.388834
N	-0.377277	-0.467604	-4.147909
H	-1.354597	-0.569618	-4.398162
S	4.526940	-0.502776	2.885254
C	4.487768	-1.037808	4.588479
C	3.348301	-1.088219	5.290665
C	5.802462	-1.468434	5.184184
S	1.778927	-0.575275	4.596875
C	3.334994	-1.579898	6.713864
O	5.763495	-1.694664	6.602576
H	6.161684	-2.384931	4.680406
H	6.561806	-0.696211	5.031556
H	2.465427	-2.242357	6.861170
C	4.596895	-2.409134	6.997802
N	3.277585	-0.454350	7.658096
H	4.535093	-3.333208	6.400063
N	4.702670	-2.775399	8.396436
C	3.533323	-0.738799	8.988181
H	2.548677	0.207630	7.439214
C	4.255575	-1.812025	9.348011
H	5.649624	-3.086237	8.583106
H	3.157455	-0.043010	9.730282
H	4.472708	-2.036427	10.384383
H	1.571410	2.288738	-4.635733
H	-0.000496	0.792185	-5.827751

3b^v [WO(prz)₂]¹⁻

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.774602

C	1.139264	0.000000	-0.715858
S	2.741537	0.047993	0.052168
O	-1.310786	0.066981	-2.081580
C	0.991186	1.355973	-4.176738
C	0.168314	0.491824	-4.784774
W	2.169452	1.008763	2.211446
O	1.999185	2.698767	1.983218
C	-1.353877	-0.080987	-0.666021
H	-1.829521	-1.041763	-0.400014
H	-2.002309	0.717767	-0.299440
C	1.110449	-0.080361	-2.223324
H	1.899502	-0.772744	-2.559792
C	-0.239171	-0.665933	-2.678881
H	-0.297178	-1.710200	-2.334490
N	1.280476	1.247649	-2.816479
H	2.106693	1.726218	-2.490190
N	-0.359083	-0.642023	-4.110056
H	-1.301553	-0.876150	-4.395139
S	4.477412	0.498638	2.820376
C	4.430300	0.004877	4.516464
C	3.293294	-0.028105	5.228005
C	5.755004	-0.403531	5.119583
S	1.731546	0.454236	4.543216
C	3.291045	-0.450440	6.678974
O	5.715369	-0.545033	6.535838
H	6.091223	-1.347870	4.657294
H	6.514871	0.353170	4.910619
H	2.428493	-1.110098	6.864016
C	4.562588	-1.267097	6.974056
N	3.259434	0.722519	7.558949
H	4.507083	-2.208384	6.405407
N	4.670350	-1.575665	8.372592
C	3.539452	0.486347	8.905851
H	2.483611	1.338512	7.366622
C	4.258665	-0.575087	9.292252
H	5.577309	-1.970668	8.585750
H	3.189866	1.221584	9.619088
H	4.507715	-0.754219	10.328777
H	1.424347	2.193422	-4.708138
H	-0.086649	0.580116	-5.831460

3b^{vi} [WO(prz)₂]

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.756764
C	1.157012	0.000000	-0.722788
S	2.738446	0.045614	0.040272
O	-1.290258	0.085479	-2.082684
C	0.926079	1.472130	-4.109152
C	0.116083	0.614685	-4.743824
W	2.059353	1.194009	2.036212
O	1.724475	2.791913	1.543179
C	-1.348225	-0.097360	-0.682229
H	-1.791000	-1.077954	-0.434678

H	-2.018084	0.672639	-0.295807
C	1.128881	-0.067659	-2.234899
H	1.918644	-0.753963	-2.579789
C	-0.225600	-0.646044	-2.701567
H	-0.289942	-1.697767	-2.387429
N	1.286458	1.274667	-2.774392
H	2.103597	1.766063	-2.445345
N	-0.333482	-0.573891	-4.123850
H	-1.227161	-0.906200	-4.459575
S	4.368784	0.850768	2.686610
C	4.303382	0.164544	4.285294
C	3.157127	0.157676	5.014926
C	5.594826	-0.390643	4.847474
S	1.676478	0.836403	4.392938
C	3.146238	-0.328347	6.451788
O	5.553312	-0.580602	6.248520
H	5.820476	-1.341890	4.337082
H	6.419140	0.296415	4.646297
H	2.239221	-0.925624	6.632421
C	4.364104	-1.251731	6.682333
N	3.245892	0.818804	7.348468
H	4.237195	-2.164031	6.081409
N	4.464729	-1.607028	8.059575
C	3.587182	0.540798	8.677964
H	2.512060	1.500126	7.220991
C	4.212746	-0.594708	9.012140
H	5.270437	-2.183680	8.257547
H	3.372125	1.308978	9.406945
H	4.515273	-0.806817	10.026785
H	1.286555	2.374027	-4.582577
H	-0.199826	0.771685	-5.764278

4a^{iv} [MoO(mpt)₂]²⁻

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.775839
C	1.131575	0.000000	-0.724308
S	2.748941	0.039306	0.022854
O	-1.344746	0.039817	-2.080718
C	1.006409	1.269528	-4.238923
C	0.114974	0.388320	-4.832919
C	0.226365	1.398568	-6.871556
C	1.570583	2.321937	-5.033649
O	2.360810	3.192887	-4.677424
Mo	2.342557	0.446678	2.422865
O	2.498341	2.123627	2.711278
C	-1.358909	-0.074321	-0.645988
H	-1.854642	-1.020629	-0.364980
H	-1.996262	0.742594	-0.297254
C	1.085076	-0.113013	-2.226994
H	1.860661	-0.826988	-2.549359
C	-0.274695	-0.683835	-2.660959
H	-0.322947	-1.733377	-2.332666
N	-0.170718	1.566030	-8.210858

H	0.615592	1.655903	-8.845835
H	-0.742235	0.773725	-8.477596
N	1.103618	2.312809	-6.375923
H	1.408141	3.099347	-6.932161
N	1.279312	1.184104	-2.889009
H	2.053656	1.737495	-2.548775
N	-0.409784	-0.655841	-4.096807
H	-1.260782	-1.046512	-4.474201
N	-0.263342	0.438553	-6.153097
S	4.546321	-0.600706	2.812937
C	4.491673	-1.189027	4.487601
C	3.356617	-1.226497	5.205463
C	5.794815	-1.715059	5.030342
S	1.796162	-0.653140	4.563663
C	3.335876	-1.837342	6.583665
O	5.757159	-2.082099	6.421580
H	6.121619	-2.587335	4.436585
H	6.578488	-0.956782	4.952501
H	2.435502	-2.466783	6.674996
C	4.557546	-2.753244	6.761951
N	3.356606	-0.820251	7.643665
H	4.427290	-3.625419	6.103172
N	4.651212	-3.227170	8.121110
C	3.598710	-1.237169	8.936571
H	2.704625	-0.056311	7.529979
C	4.299361	-2.409826	9.177356
H	5.406544	-3.866397	8.321389
C	3.207769	-0.424549	10.052036
N	4.639747	-2.868355	10.427317
O	2.597475	0.641714	10.028966
N	3.624025	-0.961257	11.300443
C	4.307854	-2.129387	11.437959
H	3.448172	-0.362399	12.094938
N	4.687066	-2.489020	12.744216
H	3.910359	-2.475418	13.396981
H	5.099092	-3.413655	12.715684

4a^v [MoO(mpt)₂]¹⁻

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.757168
C	1.134287	0.000000	-0.727629
S	2.732731	0.030047	0.014686
O	-1.327236	0.240498	-2.056090
C	1.107750	1.494604	-4.145406
C	0.186731	0.703057	-4.802088
C	0.430984	1.793270	-6.783262
C	1.776120	2.533666	-4.866600
O	2.617282	3.316928	-4.437666
Mo	2.349464	-0.228949	2.414423
O	2.871467	1.157498	3.255986
C	-1.362444	-0.019748	-0.654850
H	-1.843938	-0.994648	-0.468829
H	-2.002072	0.751533	-0.220657

C	1.092609	-0.002783	-2.239543
H	1.833789	-0.727293	-2.614496
C	-0.294131	-0.484525	-2.710390
H	-0.392615	-1.551581	-2.459794
N	0.078686	2.047645	-8.107139
H	-0.497019	1.299170	-8.468575
H	0.856608	2.253710	-8.720630
N	1.357046	2.618415	-6.221606
H	1.742554	3.399493	-6.734373
N	1.329161	1.337048	-2.778219
H	2.166674	1.794632	-2.441571
N	-0.424656	-0.334375	-4.128690
H	-1.251490	-0.710179	-4.567127
N	-0.148623	0.835858	-6.125119
S	4.223765	-1.781531	2.316622
C	4.138643	-2.496926	3.932420
C	2.994244	-2.530739	4.644217
C	5.402562	-3.158066	4.429885
S	1.486939	-1.818247	4.044366
C	2.917146	-3.264182	5.962618
O	5.321773	-3.620929	5.776465
H	5.662626	-3.995388	3.759100
H	6.233729	-2.450436	4.408575
H	1.982977	-3.850918	5.980977
C	4.086327	-4.264386	6.058293
N	2.994432	-2.342831	7.095469
H	3.919827	-5.061282	5.317685
N	4.139129	-4.855835	7.361889
C	3.138103	-2.928391	8.351889
H	2.338617	-1.572524	7.069108
C	3.766166	-4.150205	8.487949
H	4.807834	-5.595207	7.514960
C	2.702150	-2.232810	9.524038
N	4.016978	-4.765881	9.687538
O	2.126217	-1.151384	9.578554
N	3.019803	-2.925815	10.723333
C	3.653951	-4.129987	10.759679
H	2.809086	-2.418641	11.571849
N	3.954231	-4.648106	12.018077
H	4.288858	-5.598735	11.936535
H	3.208623	-4.569221	12.697728

4a^{vi} [MoO(mpt)₂]

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.729780
C	1.158916	0.000000	-0.725386
S	2.716755	-0.008914	0.029666
O	-1.283090	0.359093	-2.056892
C	1.044637	1.835940	-3.937094
C	0.154637	1.094401	-4.685529
C	0.265485	2.494530	-6.472912
C	1.620566	3.021201	-4.497131
O	2.425365	3.769092	-3.957233

Mo	2.310586	-0.403268	2.394266
O	2.966103	0.774786	3.423549
C	-1.350254	0.010249	-0.685012
H	-1.811792	-0.984012	-0.567381
H	-2.008994	0.739157	-0.210068
C	1.130619	0.106040	-2.239125
H	1.881168	-0.576645	-2.669029
C	-0.257325	-0.337777	-2.759145
H	-0.372115	-1.417843	-2.591853
N	-0.146829	2.914337	-7.719481
H	-0.680503	2.210224	-8.208093
H	0.536444	3.382379	-8.296879
N	1.157375	3.284947	-5.809806
H	1.484422	4.155355	-6.207789
N	1.342242	1.491045	-2.620133
H	2.164307	1.948109	-2.246615
N	-0.368040	-0.072592	-4.157919
H	-1.182279	-0.430353	-4.635946
N	-0.232841	1.406785	-5.955384
S	4.025963	-2.077871	2.111353
C	3.880660	-2.885797	3.652992
C	2.712885	-2.893836	4.363683
C	5.080089	-3.682790	4.117352
S	1.275566	-2.059998	3.817624
C	2.583232	-3.684617	5.646964
O	4.965058	-4.145574	5.452551
H	5.231612	-4.529763	3.427378
H	5.979172	-3.065901	4.084348
H	1.623262	-4.220985	5.641423
C	3.704406	-4.746747	5.732648
N	2.664161	-2.783585	6.782284
H	3.500726	-5.540448	5.002334
N	3.741107	-5.324667	7.045066
C	3.229694	-3.188613	7.970614
H	2.492722	-1.796256	6.661623
C	3.761694	-4.454854	8.125826
H	4.359668	-6.116862	7.157660
C	3.298749	-2.257793	9.062252
N	4.288678	-4.930086	9.286507
O	2.926705	-1.093211	9.049179
N	3.880247	-2.822082	10.221774
C	4.337273	-4.105709	10.296595
H	4.007887	-2.175431	10.989108
N	4.919785	-4.501166	11.479811
H	5.103547	-5.493273	11.512135
H	4.534968	-4.125937	12.334306

4b^{iv} [WO(mpt)₂]²⁻

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.783436
C	1.136152	0.000000	-0.712282
S	2.746123	0.033243	0.067834
O	-1.325807	0.040593	-2.089722

C	1.042409	1.281116	-4.222020
C	0.157890	0.400101	-4.826526
C	0.284470	1.417697	-6.860659
C	1.610897	2.337595	-5.008219
O	2.396116	3.208949	-4.642048
W	2.323528	0.403006	2.449957
O	2.487035	2.088884	2.749436
C	-1.352599	-0.070702	-0.654150
H	-1.854264	-1.014764	-0.376082
H	-1.990919	0.748958	-0.313051
C	1.107255	-0.107989	-2.213921
H	1.886760	-0.819950	-2.532117
C	-0.248547	-0.679758	-2.661603
H	-0.297710	-1.730242	-2.336690
N	-0.101609	1.588948	-8.202652
H	0.689760	1.683239	-8.830650
H	-0.668911	0.796264	-8.477120
N	1.155300	2.332252	-6.354349
H	1.462826	3.121377	-6.905244
N	1.304621	1.191197	-2.870442
H	2.070480	1.749648	-2.519871
N	-0.370799	-0.647854	-4.098533
H	-1.217760	-1.038772	-4.484671
N	-0.209130	0.454064	-6.149728
S	4.507926	-0.628714	2.861612
C	4.448891	-1.237421	4.536913
C	3.309695	-1.268819	5.243618
C	5.742217	-1.777864	5.082496
S	1.760834	-0.671932	4.575445
C	3.268237	-1.886220	6.616394
O	5.689128	-2.160301	6.469902
H	6.068108	-2.646200	4.482472
H	6.533027	-1.025237	5.020702
H	2.359627	-2.505508	6.698094
C	4.478183	-2.818417	6.796906
N	3.294780	-0.876587	7.683069
H	4.341472	-3.684489	6.131524
N	4.556605	-3.302242	8.153553
C	3.524250	-1.303923	8.974711
H	2.658406	-0.099744	7.569713
C	4.208623	-2.486734	9.212585
H	5.302636	-3.952004	8.354821
C	3.136832	-0.493023	10.092646
N	4.535277	-2.957023	10.461826
O	2.540359	0.581084	10.072068
N	3.538694	-1.042259	11.340250
C	4.206634	-2.219898	11.474887
H	3.365537	-0.445954	12.137254
N	4.573248	-2.592090	12.781176
H	3.792990	-2.572056	13.429505
H	4.973480	-3.521787	12.749682

4b^v [WO(mpt)₂]¹⁻

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.765830
C	1.130361	0.000000	-0.724549
S	2.736720	0.032284	0.022250
O	-1.328509	0.206885	-2.056216
C	1.109200	1.432708	-4.169548
C	0.189574	0.627681	-4.811857
C	0.437783	1.677386	-6.814459
C	1.779072	2.456666	-4.910649
O	2.619612	3.248427	-4.496173
W	2.349364	-0.073708	2.424826
O	2.778543	1.419497	3.143761
C	-1.363012	-0.029487	-0.650458
H	-1.846971	-0.999943	-0.447076
H	-2.001207	0.750780	-0.230067
C	1.093358	-0.026881	-2.234833
H	1.837119	-0.756325	-2.595938
C	-0.290988	-0.522674	-2.698494
H	-0.383657	-1.586065	-2.430604
N	0.088077	1.904966	-8.144022
H	-0.487840	1.149693	-8.490718
H	0.867575	2.096719	-8.760193
N	1.362323	2.514129	-6.267685
H	1.748445	3.284903	-6.795358
N	1.327166	1.302868	-2.799083
H	2.160696	1.771663	-2.468314
N	-0.422619	-0.395974	-4.118940
H	-1.247294	-0.782783	-4.551712
N	-0.142711	0.733185	-6.138261
S	4.331113	-1.484082	2.483532
C	4.283504	-2.048729	4.164233
C	3.140397	-2.095444	4.872805
C	5.588699	-2.560419	4.724830
S	1.589019	-1.547681	4.202698
C	3.102783	-2.700711	6.255442
O	5.528956	-2.897758	6.109070
H	5.919070	-3.435259	4.138077
H	6.363340	-1.795810	4.638309
H	2.213857	-3.350426	6.328099
C	4.340461	-3.599564	6.448902
N	3.102728	-1.673196	7.295494
H	4.238749	-4.473463	5.787662
N	4.424037	-4.057961	7.803041
C	3.270389	-2.127719	8.602347
H	2.396685	-0.955516	7.192874
C	3.984151	-3.281975	8.855878
H	5.139145	-4.732391	8.028480
C	2.767581	-1.361853	9.701554
N	4.261329	-3.764967	10.109250
O	2.113415	-0.325707	9.651231
N	3.117858	-1.916193	10.962241
C	3.837314	-3.061803	11.115033
H	2.858117	-1.350340	11.758457
N	4.155908	-3.438624	12.418195

H	4.559906	-4.365431	12.428058
H	3.397168	-3.351928	13.082141

4b^{vi} [WO(mpt)₂]

C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.756681
C	1.155979	0.000000	-0.723823
S	2.738112	0.056576	0.040403
O	-1.283427	0.113147	-2.079926
C	0.831421	1.553696	-4.024984
C	-0.023111	0.704913	-4.694771
C	-0.304274	2.122817	-6.448096
C	1.112275	2.847696	-4.578780
O	1.789961	3.730018	-4.072690
O	1.706206	2.786888	1.547348
C	-1.348494	-0.090211	-0.680736
H	-1.795782	-1.072056	-0.450168
H	-2.017960	0.677121	-0.289086
C	1.135679	-0.097501	-2.231315
H	1.891848	-0.828845	-2.549135
C	-0.237063	-0.634906	-2.702401
H	-0.328067	-1.692832	-2.423022
N	-0.774686	2.424481	-7.707602
H	-0.991929	3.391307	-7.900539
H	-1.479832	1.775268	-8.024686
N	0.492900	3.045782	-5.837874
H	0.728263	3.918865	-6.290998
N	1.426386	1.203218	-2.818699
H	1.622122	1.973326	-2.193705
N	-0.342974	-0.521138	-4.123650
H	-1.151420	-0.959117	-4.544176
N	-0.588844	0.971849	-5.905712
S	4.372153	0.877888	2.688972
C	4.306650	0.150276	4.269653
C	3.159347	0.119052	4.997141
C	5.602440	-0.405023	4.820790
S	1.679036	0.815873	4.395314
C	3.140207	-0.420711	6.414155
O	5.562777	-0.616368	6.219673
H	5.837418	-1.346471	4.296958
H	6.421047	0.292031	4.632626
H	2.253513	-1.063057	6.544112
C	4.386390	-1.311500	6.634176
N	3.182840	0.682659	7.364174
H	4.281022	-2.221706	6.025664
N	4.496809	-1.680921	8.004489
C	3.391953	0.311067	8.700246
H	2.443570	1.368751	7.266065
C	4.095912	-0.828914	9.015282
H	5.176797	-2.380527	8.260061
C	2.899153	1.147702	9.749309
N	4.424868	-1.209488	10.285203
O	2.223691	2.162024	9.624434

N	3.264322	0.679277	11.036696
C	3.999158	-0.448807	11.253335
H	2.878185	1.209043	11.806767
N	4.237409	-0.804342	12.565510
H	4.399579	-0.051231	13.218484
H	4.906150	-1.556972	12.643205
W	2.061071	1.194227	2.040640