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Metallodendrimers for catalytic epoxidation – theoretical insights into structure of Mo(VI) complexes of poly(propylene imine) dendrimers

V. Trifonova[1], K. Vassilev[2], A. Ahmedova[3]*

[1] *Department of Analytical and Inorganic Chemistry, University "Prof. Assen Zlatarov", 1, Prof. Yakimov str., 8010 Burgas, Bulgaria*
[2] *Department of Biotechnology, University "Prof. Assen Zlatarov", 1, Prof. Yakimov str., 8010 Burgas, Bulgaria*
[3] *Faculty of Chemistry and Pharmacy, University of Sofia, 1, J. Bourchier av., 1164 Sofia, Bulgaria*

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

The present theoretical study is focused on detailed structural description of Mo(VI) complex of a second generation poly(propylene imine) dendrimer DAB-G_2-PPI-$(NH_2)_8$ that has previously been synthesized and evaluated as catalyst for alkenes epoxidation with organic hydroperoxides. In order to verify the suggested geometry with five-coordinate metal centers, which is rare case for Mo(VI), we performed structural description of possible complexes by quantum chemical (DFT) calculations. This was achieved through modeling and geometry optimization of the MoO_2^{2+} complex with the smallest triamine fragment of the dendrimer. Different compositions of model complexes were taken into account and numerous combinations of DFT functionals (B3LYP, B2LYP, O3LYP, M05 and M06) and basis sets were used for optimizations. The M06/6-31G(d,p)-(LanL2DZ; Mo) calculations gave the best agreement with available crystallographic data for similar cis-dioxo Mo(VI) complexes. Therefore, this method was used to optimize the structure of the tetrameric Mo(VI) complex of DAB-G_2-PPI-$(NH_2)_8$. The results pointed out that M06/6-31G(d,p) optimized structure of the five-coordinate cis-dioxo Mo(VI) complex with the tridentate dendrimer fragments is possible and confirms the feasibility of the experimentally suggested coordination mode of DAB-G_2-PPI-$(NH_2)_8$. Calculations on a complex with additionally coordinated water molecule indicated that the five-coordinate Mo(VI) complexes of PPI dendrimer preserve the potential to coordinate one O-donor solvent molecule. These structural characteristics can explain the ability of the Mo-centers of the modeled metallodendrimer to coordinate also hydroperoxides, used as oxygen sources for the catalytic epoxidation of alkenes, and thus, ensure the realization of a crucial catalytic step in the olefin epoxidation reactions.

Key words: DFT calculations; cis-dioxo Mo(VI) complexes; PPI dendrimers; alkene epoxidation

INTRODUCTION

The metal-catalyzed, partial and selective oxidation of alkenes has been of practical importance for more than 50 years due to the broad variety of possible transformations of the formed epoxides [1]. The most selective catalytic reactions for epoxidation of alkenes are those that employ alkyl hydroperoxides and metal complexes of d^0 transition metal ions in their highest oxidation state, e.g. Mo(VI), W(VI), Ti(IV), V(V) [2]. The mechanistic aspects of these catalytic processes have been thoroughly studied and indicated that the cis-dioxomolybdenum(VI) complexes are the catalyst of choice for highly selective epoxidation of cycloalkenes with *tert*-butyl hydroperoxide (TBHP, *t*-BuOOH) [3]. This could be explained with the high Lewis acidity of the Mo(VI) ion and its ability to withdraw electron density from the peroxide oxygens, which makes them more susceptible to nucleophilic attack by olefins. Despite the significant progress that has been achieved in this field [4-6], there is still intense research attempting to improve the catalyst stability, the rate and yield of substrate conversion under mild conditions preserving the high selectivity, and their implementation as recyclable (heterogeneous) catalysts [7-13]. In our research dedicated to the use of various metal complexes for catalytic applications [14-16] we have demonstrated the high potential of metallodendrimers in this field [13] which was later employed by other authors [17,18]. In view of future implementation of chelating fragments from dendritic macromolecules for formation of polymeric metal complexes as highly efficient catalysts, we focus the current theoretical study on detailed structural description of the Mo(VI) complex of second generation (G_2) dendrimer based on poly(propylene imine), PPI. The complexes of

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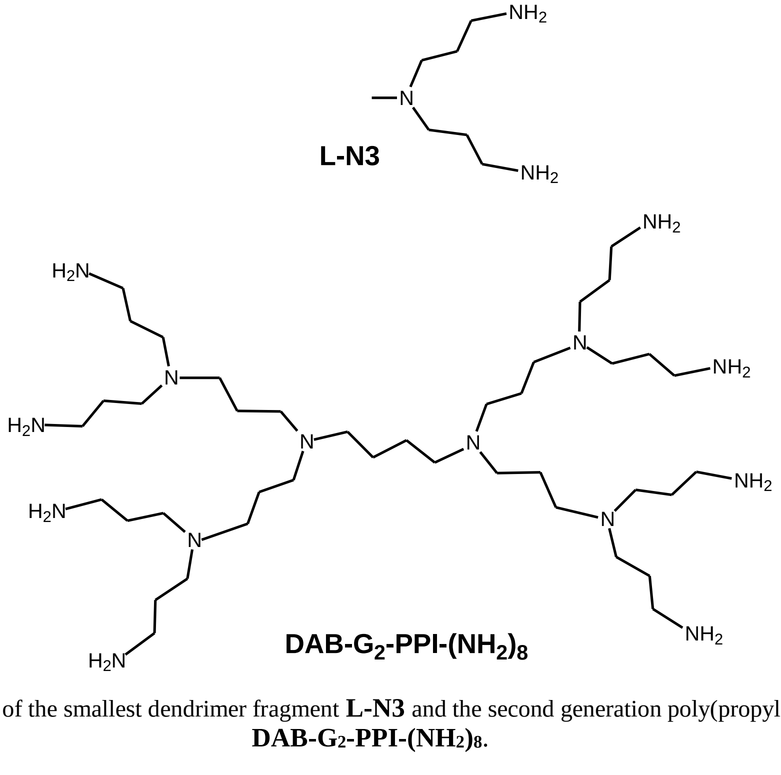
* To whom all correspondence should be sent:
E-mail: *Ahmedova@chem.uni-sofia.bg*

second- (G_2) and forth- (G_4) generation poly(propylene imine) dendrimers with various metal ions have previously been synthesized and experimentally tested for their catalytic activity for epoxidation of alkenes with different organic hydroperoxides [13]. The highest activity showed the Mo(VI) complex with the G_4 PPI dendrimer having 32 amino end-groups, DAB-G_4-PPI-$(NH_2)_{32}$, and using the TBHP. The structure of the Mo(VI) complexes have been proposed based on FT-IR spectroscopy and titration data only. However, the suggested five-coordinate metal centers is rare case for Mo(VI), especially with N-donor ligands, and needed further confirmation. Therefore, we subjected the structural description on quantum chemical (DFT) calculations of various possible geometries of the metal centers in order to verify the most probable structure of the formed metallodendrimers. For that purpose we modeled the coordination of the MoO_2^{2+} ion with the smallest tridentate fragment of the dendrimer, namely bis(propyleneamine)-methylamine (denoted as **L-N3**, Fig.1), and taking into account different compositions and coordination modes. The best computational method was selected out of numerous combinations of DFT functionals (B3LYP, B2LYP, O3LYP, M05 and M06) with different basis sets (6-31G(d,p), 6-311G, 6-311G(d,p), D95 and D95V for all non-metals and LanL2DZ for Mo) based on the agreement of the calculated results with available crystallographic data on similar structures. The closest agreement with experimental bond lengths for cis-dioxo Mo(VI) complexes was obtained with the M06/6-31G(d,p)-(LanL2DZ; Mo) method, which was used further on to optimize the structure of various complexes with different compositions as well as the tetrameric cis-dioxo Mo(VI) complex of the second generation poly(propylene imine) dendrimer **DAB-G_2-PPI-$(NH_2)_8$**. (Fig. 1). Thereby, we could confirm the feasibility of the five-coordinate cis-dioxo Mo(VI) centers with the tridentate alkylamine ligands and provide additional details on the geometry and electronic structures of the modeled complexes and the corresponding spectroscopic (IR) characteristics.

COMPUTATIONAL DETAILS

All quantum chemical calculations were performed using the Gaussian 09 suite of programs [19]. Various DFT methods were applied for geometry optimizations including hybrid functionals that combine the Becke exchange [20] and LYP correlation functionals [21, 22], such as B3LYP and B2LYP, or the O3LYP functional [23, 24], as well as the pure functionals of Truhlar and Zhao, M06 [25] and M05 [26]. All listed functionals were combined with the split-valence basis set of double-zeta quality including polarization functions 6-31G(d,p) [27,28] for all light elements.



L-N3

DAB-G_2-PPI-$(NH_2)_8$

Fig. 1. Chemical formula of the smallest dendrimer fragment **L-N3** and the second generation poly(propylene imine) dendrimer **DAB-G_2-PPI-$(NH_2)_8$**.

To test the basis sets performance, the B3LYP functional was combined with the 6-31G(d,p), 6-311G and 6-311G(d,p) basis sets, and the Dunning/Huzinaga full or valence double-zeta basis sets D95 and D95V [29]. In all cases the molybdenum orbitals were calculated using the LanL2DZ basis set including the Los Alamos effective core potentials (ECP) [30]. The geometry optimizations, employing all described DFT methods, were performed on the MoO_2^{2+} unit coordinated to the smallest tridentate fragment of the dendrimer, **L-N3**, with the composition $[MoO_2(L\text{-}N3)]^{2+}$. All geometry optimizations were followed by calculation of the vibrational frequencies and intensities at the same level of theory and proved that local minima have been attained. Based on critical evaluation of the calculated geometrical parameters through comparison with available experimental data, the best performing DFT method has been selected and employed in the additional calculations of complexes with different structure and compositions. The M06/6-31G(d,p)-(LanL2DZ; Mo) method was used to calculate complexes of the following compositions $[MoO_2(L\text{-}N3)]^{2+}$, $[MoO_2(L\text{-}N3)Cl]^{+}$, $MoO_2(L\text{-}N3)Cl_2$ and $[(MoO_2)_4(DAB\text{-}G_2)]^{8+}$, where DAB-$G_2$ is a short-hand notation for the **DAB-G_2-PPI-$(NH_2)_8$** dendrimer. Due to better convergence with the B3LYP functional that was obtained in the case of water coordinated Mo(VI) complexes, it was used to calculate the structures with compositions $[MoO_2(L\text{-}N3)(H_2O)]^{2+}$, using the 6-31G(d,p) or 6-311G(d,p) basis sets for all non-metals.

RESULTS AND DISCUSSION

Currently, we modeled and optimized all probable structures of cis-dioxo Mo(VI) complexes of a poly(propylene imine) dendrimer using the smallest dendritic fragment **L-N3** to form complexes with different compositions and charge. The aim was to evaluate the feasibility of the spectroscopically suggested five-coordinate Mo(VI) complexes of **DAB-G_2-PPI-$(NH_2)_8$** and DAB-G_4-PPI-$(NH_2)_{32}$ dendrimers, used as catalyst for alkenes epoxidation [13]. Compulsory starting step was to select the most suitable theoretical model for the studied systems. Therefore, we compared the structural parameters calculated by five different DFT functionals (B3LYP, B2LYP, O3LYP, M05 and M06) and five different basis sets (6-31G(d,p), 6-311G, 6-311G(d,p), D95 and D95V for all non-metals) with available crystallographic data on similar cis-dioxo Mo(VI) complexes. It should be noted that there are no reports on crystal structures of MoO_2^{2+} complexes of dendrimers. That is why we mostly compared our calculated results with reported crystallographic data on cis-dioxo Mo(VI) complexes of three- or tetra- dentate Schiff bases or hydrazones that coordinate by at least one or two N-donor atoms [31-36]. In most of these cases the sixth coordination site of Mo(VI) is occupied by an weakly bound solvent molecule (e.g. alcohol). However, there are also recent data on five-coordinate Mo(VI) complexes that have been isolated and their crystal structures were solved [37]. The basic finding of our calculations suggested that the most suitable method is M06/6-31G(d,p)-(LanL2DZ; Mo) giving acceptable Mo-N distances. Only this method gave lengths of the Mo-N bonds shorter than 2.230 Å (for the terminal amino groups) and Mo-Nm bond (with the tertiary amino group) shorter than 2.270 Å (Table 1 and Fig. 2). Although these bond lengths are longer than 2.180 Å, they are fairly acceptable if compared with the crystallographic data for Mo(VI) complexes with tridentate ligands that coordinate with three [38] or two N-donor atoms [32] in which the longest Mo-N bonds range from 2.31 to 2.42 Å. These data let us conclude that M06/6-31G(d,p) optimized structure of the five-coordinate cis-dioxo Mo(VI) complex with the tridentate dendrite fragment **L-N3** is possible and confirms the feasibility of the experimentally suggested coordination mode of the **DAB-G_2-PPI-$(NH_2)_8$** and DAB-G_4-PPI-$(NH_2)_{32}$ dendrimers [13]. All other functionals, we have tested, predicted Mo-N bonds shorter or equal to 2.310 Å for the five-coordinate cis-dioxo Mo(VI) complexes $[MoO_2(L\text{-}N3)]^{2+}$. However, these values are larger by *ca*. 1% than the Mo-N bonds calculated with the M06 functional and the same holds for the Mo-O bonds. Therefore, we selected the M06/6-31G(d,p)-(LanL2DZ; Mo) method for geometry optimization of other possible complex structures. The model of a six-coordinate cis-dioxo Mo(VI) complex with one chloride ligand added, $[MoO_2(L\text{-}N3)Cl]^{+}$, resulted in strong elongation of the M-Nm bond to 2.592 Å and elongation of the Mo-O bonds by 0.02 Å (Table 1 and Fig. 2). These results indicate that the supposed Cl-bound six-coordinate Mo(VI) complex is less probable.

To further elaborate the expected high possibility for six-coordinate Mo(VI) complexes we made a model with coordinated water molecule

$[MoO_2(L\text{-}N3)(H_2O)]^{2+}$. In this case successful convergence was achieved using the B3LYP functional, and therefore, it was the method of choice for the water-bound complex. For the sake of comparison the results obtained with the B3LYP/6-31G(d,p) and B3LYP/6-311G(d,p) methods for five- and six- coordinate Mo(VI) complexes are listed in Table 1 and the optimized geometries are depicted in Fig. 3. It can be noted that appreciable elongation resulted only for the Mo-Nm bond (by *ca*. 0.13 Å). Despite the elongation, calculated bond lengths for the water-bound complex remain in the range of experimentally reported ones for cis-dioxo Mo(VI) complexes coordinated with a tridentate ligand and a solvent molecule (with Mo-O distances within the 2.319 – 2.385 Å range) [33-37]. This let us propose that the optimized five-coordinate Mo(VI) complexes of the studied PPI dendrimer, although probable, preserves the potential to coordinate additional O-donor solvent molecule. Similarly, it can be supposed that the Mo-centers of the modeled metallodendrimer are available for coordination with a hydroperoxide that is used as an oxygen source for the catalytic epoxidation of alkenes. This possibility is yet to be confirmed by our ongoing theoretical studies on the catalytic steps of olefin epoxidation by metallodendrimers and TBPH.

Attempts to model a neutral complex of bidentately coordinating **L-N3** fragment with MoO_2Cl_2 core, and complex composition $MoO_2(L\text{-}N3)Cl_2$, proved that such coordination mode of the PPI dendrimer is sterically hindered.

Table 1. Calculated (M06 and B3LYP) bond lengths (in Å) of the cis-dioxo Mo(VI) complexes with the PPI dendrimer **DAB-G$_2$-PPI-(NH$_2$)$_8$**, $[(MoO_2)_4DAB\text{-}G_2]^{8+}$, or with its smallest tridentate fragment (**L-N3**) and having the following compositions: $[MoO_2(L\text{-}N3)]^{2+}$, $[MoO_2(L\text{-}N3)Cl]^{+}$ or $[MoO_2(L\text{-}N3)(H_2O)]^{2+}$. The ECP basis set LanL2DZ is used for Mo. In the six-coordinate complexes the axial ligand is either water (Ow) or a chloride (Cl). The Nm notation is used for the tertiary amine from the tridentate fragment of the dendrimer.

Comput. method	M06 optimized structures 6-31G(d,p)			B3LYP optimized structures 6-31G(d,p)/		6-311G(d,p)/	
Structure / Bond distances	$[MoO_2(L\text{-}N3)]^{2+}$	$[MoO_2(L\text{-}N3)Cl]^{+}$	$[(MoO_2)_4DAB\text{-}G_2]^{8+}$	$[MoO_2(L\text{-}N3)]^{2+}$	$[MoO_2(L\text{-}N3)(H_2O)]^{2+}$	$[MoO_2(L\text{-}N3)]^{2+}$	$[MoO_2(L\text{-}N3)(H_2O)]^{2+}$
Mo-O1	1.686	1.705	1.674 ÷ 1.681	1.694	1.700	1.697	1.703
Mo-O2	1.678	1.691	1.675 ÷ 1.680	1.688	1.689	1.691	1.691
Mo-N	2.229	2.227	2.217 ÷ 2.229	2.244	2.249	2.245	2.248
Mo-Nm	2.267	2.592	2.366 ÷ 2.373	2.293	2.430	2.289	2.416
Mo-Ow					2.396		2.407
Mo-Cl		2.451					

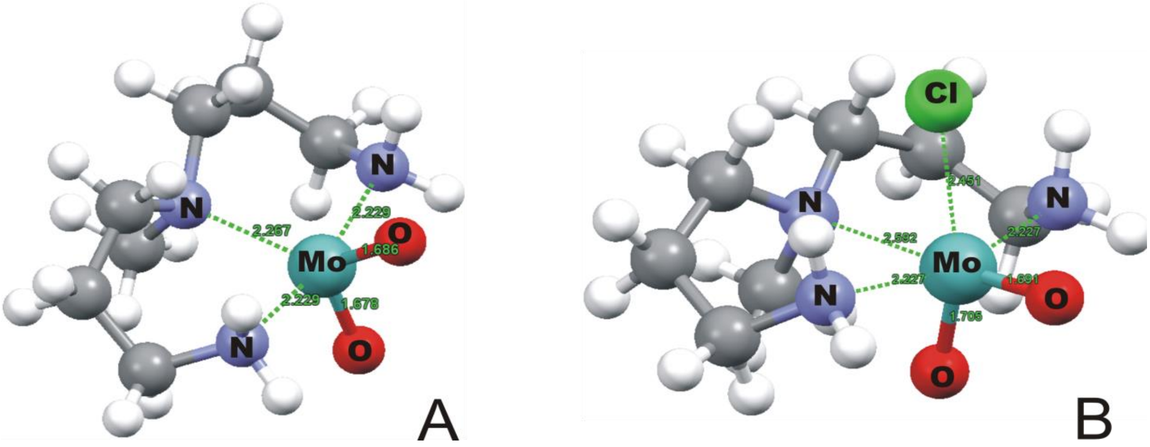


Fig. 2. Optimized (M06/6-31G(d,p)-(LanL2DZ; Mo)) structures of the five- and six- coordinate cis-dioxo Mo(VI) complexes having the compositions: A) $[MoO_2(L\text{-}N3)]^{2+}$ and B) $[MoO_2(L\text{-}N3)Cl]^{+}$. The dotted lines represent the coordination bonds Mo-N or Mo-Cl, and the numbers give the corresponding distances, listed also in Table 1.

Using the selected superior method for our system, M06/6-31G(d,p)-(LanL2DZ; Mo), we optimized the structure of the Mo(VI) complex of the **DAB-G$_2$-PPI-(NH$_2$)$_8$** dendrimer, referred to as $[(MoO_2)_4DAB\text{-}G_2]^{8+}$. Two views of the optimized structure are depicted in Fig. 4 and selected bond lengths are given in Table 1. The four metal centers exhibit virtually the same geometry. The slight variations in the lengths of the molybdenum bonds are indicated with the given range (Table 1). All optimized bond distances are virtually equal to the ones obtained for the similar monomeric complex with the **L-N3** fragment, except for the Mo-Nm (with the tertiary amine) which elongates by *ca.* 0.10 Å in the tetrameric complex. Thus, the longest calculated Mo-N distances approach 2.37 Å but still remain within the range of experimentally reported ones for a complex with sterically crowded tetradentate ligand coordinating with two tertiary amine groups to cis-dioxo Mo(VI) [32], where the Mo-N bonds are estimated to 2.260 - 2.423 Å.

The calculated vibrational frequencies of the five-coordinate monomeric and tetrameric complexes, $[MoO_2(L\text{-}N3)]^{2+}$ and $[(MoO_2)_4(DAB\text{-}G_2)]^{8+}$, agree with the experimentally reported ones for the stretching modes involving the metal center. The M06/6-31G(d,p) calculated stretching vibrations of Mo-N in $[MoO_2(L\text{-}N3)]^{2+}$ are 423 and 431 cm^{-1}, which are very close to the experimental data of 405 to 430 cm^{-1} [13]. The most intense vibrations of the Mo=O bonds appear at 1016 and 1049 cm^{-1} in the calculated $[MoO_2(L\text{-}N3)]^{2+}$ model structure and at 1013 and 1021 - 1024 cm^{-1} for $[(MoO_2)_4(DAB\text{-}G_2)]^{8+}$. These unscaled values would become closer to the experimental data (of 900 - 950 cm^{-1}) if a scaling factor of *ca.* 0.90 is used.

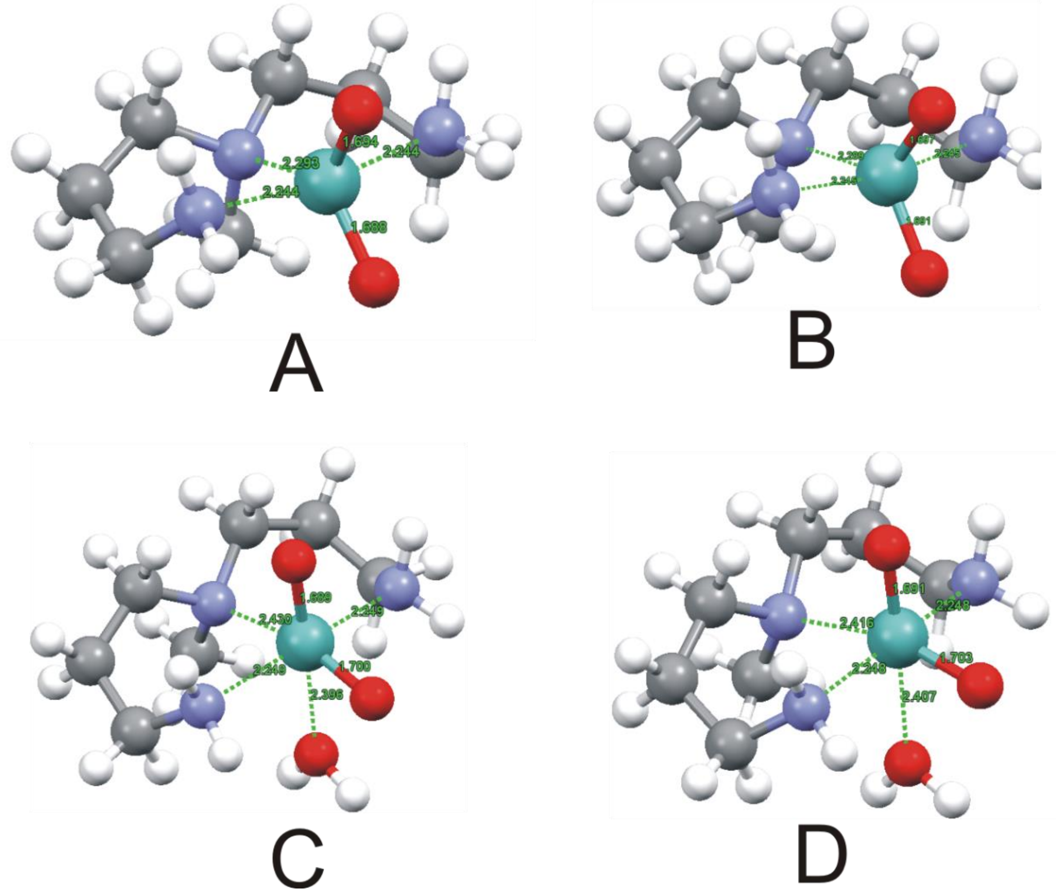


Fig. 3. Comparison of the B3LYP optimized geometries of five- and six- coordinate cis-dioxo Mo(VI) complexes with compositions $[MoO_2(L\text{-}N3)]^{2+}$ (in A and B) and $[MoO_2(L\text{-}N3)(H_2O)]^{2+}$ (in C and D), and using different basis sets for the light elements - the 6-31G(d,p) in A and C or 6-311G(d,p) in B and D. The dotted lines represent the coordination bonds Mo-N and Mo-OH$_2$, and the numbers giving the corresponding distances are listed in Table 1. The same color code for all heteroatoms is used as in Fig. 2.

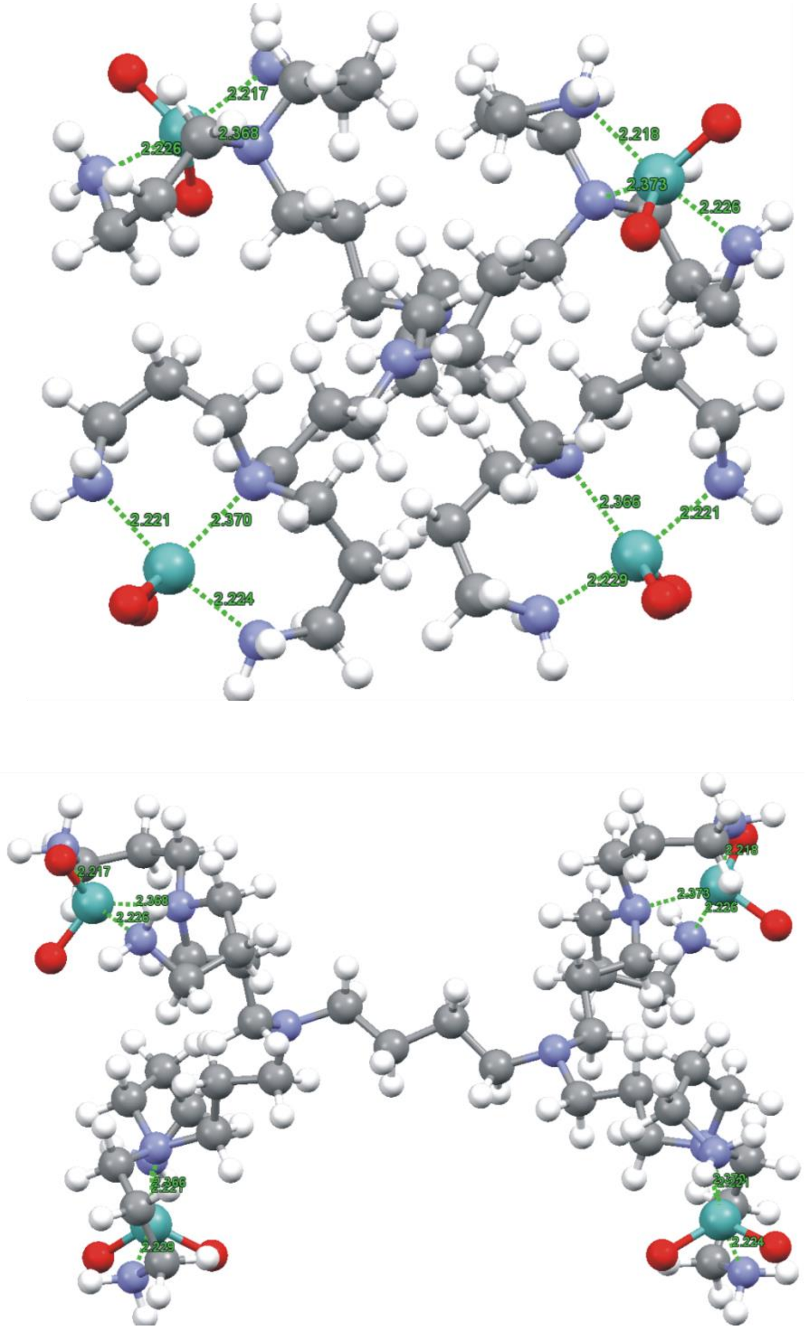


Fig. 4. Two different views of the M06/6-31G(d,p)-(LanL2DZ; Mo) optimized structure of the tetrameric cis-dioxo Mo(VI) complex of the second generation PPI dendrimer **DAB-G$_2$-PPI-(NH$_2$)$_8$** with composition $[(MoO_2)_4(DAB\text{-}G_2)]^{8+}$. Top view is oriented normal to the core diaminobutane chain and the bottom view depicts the structure along that chain. The dotted lines represent the Mo-N coordination bonds and the corresponding distances are listed in Table 1. The same color code for all heteroatoms is used as in Fig. 2.

In conclusion, the investigated rare case of five-coordinate Mo(VI) complexes appeared as the most plausible structure for the PPI dendrimers, which we confirmed by the current detailed computational study. Moreover, the suggested structure agrees with available crystallographic data on similar system of cis-dioxo Mo(VI) complexes with two- or three- N-donor atoms. The obtained optimized structure of $[(MoO_2)_4(DAB\text{-}G_2)]^{8+}$ can be further elaborated to evaluate the catalytic steps of the cyclohexene epoxidation, in which the studied system performed as an excellent catalyst.

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МЕТАЛОДЕНДИМЕРИ ЗА КАТАЛИТИЧНО ЕПОКСИДИРАНЕ - ТЕОРЕТИЧНИ ПОЗНАНИЯ ЗА СТРУКТУРАТА НА Mo (VI) КОМПЛЕКСИ НА ПОЛИ (ПРОПИЛЕН ИМИН) ДЕНДРИМЕРИ

В. Трифонова[1], К. Василев[2], А. Ахмедова[3]*,

[1] *Катедра Аналитична и неорганична химия, Университет "Проф. Асен Златаров", ул. "Проф. Якимов" 1, 8010 Бургас, България*

[2] *Катедра "Биотехнология", Университет "Проф. Асен Златаров", ул. "Проф. Якимов" 1, 8010 Бургас, България*

[3] *Факултет по химия и фармация, Софийски университет "Св. Климент Охридски", ул. "Дж. Бучър" 1, 1164 София, България*

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(Резюме)

Настоящото теоретично изследване е фокусирано върху подробното структурно описание на комплекс на Mo (VI) с полипропилен-иминов дендример от второ поколение, DAB-G_2-PPI-$(NH_2)_8$, който по-рано бе синтезиран и оценен като катализатор за епоксидиране на алкени с органични хидропероксиди. За да се провери предложената геометрия с пет координирани метални центрове, което е рядък случай за Mo (VI), ние извършихме структурно описание на възможните комплекси чрез квантово-химични (DFT) изчисления. Това беше постигнато чрез моделиране и геометрична оптимизация на MoO_2^{2+} комплекс с най-малкия триаминов фрагмент на дендримера. Бяха взети под внимание моделни комплекси с различен състав и бяха използвани множество комбинации от DFT функционали (B3LYP, B2LYP, O3LYP, M05 и M06) и базисни функции. Изчисленията с метода M06/6-31G(d,p)-(LanL2DZ; Mo) дадоха най-добро съгласие с наличните кристалографски данни за подобни комплекси на цис-диоксо Mo(VI). Поради това, този метод бе използван за оптимизиране на структурата на тетрамерния Mo(VI) комплекс на DAB-G_2-PPI-$(NH_2)_8$. Резултатите сочат, че оптимизираната с M06/6-31G (d,p) метода структура на пет-координирания цис-диоксо Mo(VI) комплекс с тридентатните дендримерни фрагменти е възможна, потвърждавайки експериментално предложения начин на координация на DAB-G_2-PPI-$(NH_2)_8$. Изчисленията върху комплекс с допълнително координирана водна молекула показват, че пет-координираните комплекси на Mo(VI) с PPI дендример съхраняват възможността да координират и една молекула разтворител с O-донор. Тези структурни характеристики могат да обяснят способността на молибденовите центрове в моделирания металодендимер да координират и хидропероксидите, използвани като източници на кислород за каталитично епоксидиране на алкени, и по този начин да осигурят осъществяването на решаващ каталитичен етап в реакциите на епоксидиране на олефини.