

Polyoxometalates

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Abstract

Quantum chemical methods have been applied to calculate the molecular structure and properties of a series of molybdenum and tungsten polyoxometalates. These were of the Lindqvist, Keggin, Wells–Dawson, and Preyssler type, respectively. Force field parameters for tungsten polyoxometalates were derived from the obtained data, compatible with the AMBER force field. Molecular dynamics simulations, which are based on classical mechanics, were then performed for tungsten polyoxometalates encapsulated with dendrimeric amphiphilic cations, in trichloromethane as solvent. The term ‘dendrzymes’ has been introduced for such dendrimer-encapsulated polyoxometalates, since they may serve in the future as homogeneous redox catalysts with enzyme-like substrate specificity, regioselectivity and stereospecificity.

Quantum chemical study of polyoxometalates

Many chemical and physical properties of molecular systems can be understood from their electron density distributions. Nowadays, good to excellent approximations to such distributions can be calculated with various software tools, all of which apply quantum mechanical methods. In *ab initio* methods, an approximate wave function is calculated, from which the electron density distribution is easily obtained, whereas methods relying on density functional theory (DFT) give this distribution in a more direct way. Both kinds of approach can be combined with effective core potentials, so that the atomic cores (and a corresponding number of electrons) can be removed from the explicit calculation, and all efforts can thus be focused on the determination of only a valence part of the electron density distribution. In this project, density functional methods were applied to calculate properties of molybdenum and tungsten polyoxometalates of the following types (the highest possible symmetry group is indicated in parentheses; see also figure 1):

the Lindqvist type $[(O)M_6O_{18}]^{2-}$ (O_h ; $M = Mo$ or W), the α -Keggin type $[(XO_4)M_{12}O_{36}]^{q-}$ (T_d ; $M = Mo$ or W ; $q = 3$ for $X = P$, or $q = 6$ for $X = Zn$), the α -Wells–Dawson type $[(XO_4)_2M_{18}O_{54}]^{6-}$ (D_{3h} ; $M = Mo$ or W ; $X = P$), and the Preyssler type $[(XO_4)_5M_{30}O_{90}]^{15-}$ (D_{5h} ; $M = W$; $X = P$). All species of these types can be understood formally as being built up from central anions (determining the total charge) surrounded by a neutral polyoxometalate cage, but this point of view has no physical basis. Direct results from the quantum chemical calculations are, e.g., optimized molecular structures (also known as equilibrium structures, i.e. the spatial arrangement of the atomic nuclei giving the lowest value for the total energy) together with the associated electron density distribution. From these results, other quantities, like partial atomic charges (located at the positions of the atomic nuclei) or the molecular electrostatic potential, have been calculated. Molecular structures and molecular electrostatic potentials served as ingredients for the next step, the derivation of force field parameters.

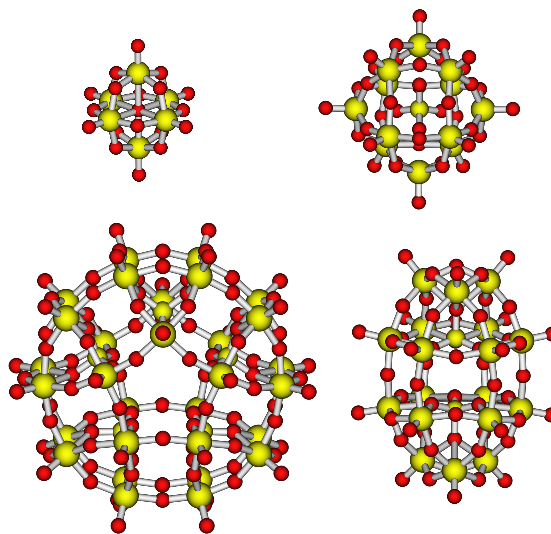


Fig. 1: Molecular structures of the studied polyoxometalate types (clockwise, from the upper left corner: Lindqvist, α -Keggin, α -Wells–Dawson, and Preyssler type; oxygen in red, other atoms in yellow).

Derivation of force field parameters for polyoxotungstates

A force field for molecular dynamics (MD) simulations represents the potential energy of a molecular system as a sum of classical terms for the various degrees of freedom (changes of bond lengths, bond angles, etc.), and terms for van-der-Waals and electrostatic interactions. Every term depends on some empirical parameters, like force constants and equilibrium values of coordinates, which must be de-

terminated before the force field can be used. This has to be done for all atom types, pairs of atom types, etc., involved in the force field to be used. In this project, the so-called ‘generalized AMBER force field’ (GAFF) was to be used in MD simulations of dendrimer-encapsulated α -Keggin ions ($M = W$) in trichloromethane solution (see below), since parameters for the organic molecules, the dendrimers and the solvent molecules, are already available. Hence, force field parameters for the α -Keggin ions were required. These were generated from the results previously obtained for the series of polyoxotungstates, so that equilibrium structures, molecular electrostatic potentials, and normal mode frequencies from the force field are in good to reasonable agreement with the corresponding results from quantum chemical calculations. During this process, emphasis was laid on the α -Keggin type of ions, since it is involved in the final part of this work. But the other polyoxometalates (Lindqvist, Wells–Dawson, and Preyssler) were nevertheless kept in the set, in the hope to make the resulting force field more robust and perhaps more widely applicable (within the series of polyoxotungstates).

Molecular dynamics simulations of dendrzyme model systems

From the previous part, a complete set of parameters (compatible with the GAFF format) for all required atom types was at hand. This set was used now in the last part of this project for MD simulations of dendrzyme model systems. Two of the model systems studied in this project are presented in figure 2 (hydrogen atoms are not shown): The α -Keggin ion $[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]^{3-}$ surrounded by three dendrimers derived from the bis(3,5-dimethoxybenzyl)dimethylammonium ion, $[\text{C}_{52}\text{H}_{60}\text{NO}_{12}]^+$ (upper part), and the α -Keggin ion $[(\text{ZnO}_4)\text{W}_{12}\text{O}_{36}]^{6-}$ surrounded by six *N*-methyl-3,5-bis(3,5-di-*tert*-butylphenyl)pyridinium ions, $[\text{C}_{34}\text{H}_{48}\text{N}]^+$ (lower part). The MD simulations were done for trichloromethane solutions of these ion clusters (with concentrations about 10 mmol/l in the former case and 20 mmol/l in the latter case, respectively). An *NVE* ensemble with periodic boundary conditions was imposed (keeping constant the particle number, the cell volume and the total energy). Such MD simulations, where the content of the cell (ion cluster and solvent molecules in our case) is allowed to evolve according to the laws of classical mechanics, primarily yield a set of positions in space as function of time (‘trajectories’) for every atom in the simulation cell. Methods from statistical mechanics and statistical thermodynamics can be used then to analyze these trajectories. An enzyme-like substrate specificity, that has already been seen in experiments with dendrzyme model systems based on redox-active polyoxometalates, can partially be

supported by our results: Whether a substrate is able to approach the central polyoxometalate or not depends (i) on the fraction of polyoxometalate surface covered by the dendrimers, and (ii) on the spatial requirements of the dendrimer molecules (steric hindrance of substrate access).

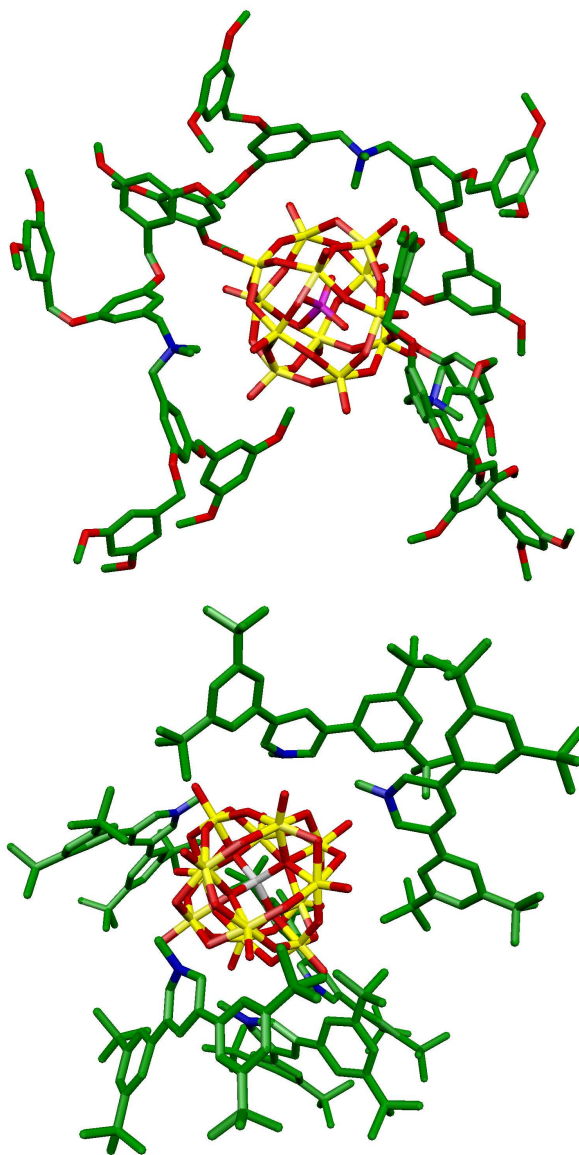


Fig. 2: Molecular structures of dendrimer-encapsulated α -Keggin ions (from snapshots of the molecular dynamics simulations; solvent molecules and hydrogen atoms of the dendrimers are not shown; see text for further details).

References

Volkmer, D. *et al.* (2002) *J. Am. Chem. Soc.* 124, 10489–10496

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