

Thermodynamic Description of Oxotransfer Processes Involving Molybdenum and Tungsten Enzyme Models: DFT Calculations and Calorimetry

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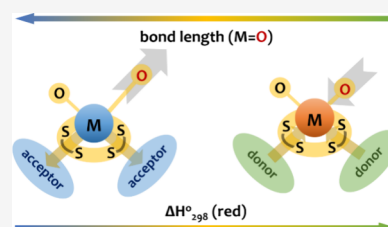


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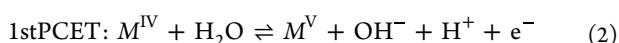
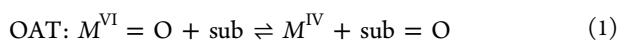
ABSTRACT: The enthalpy of the oxotransfer reaction of $[\text{Bu}_4\text{N}]_2[\text{WO}_2(\text{mnt})_2]$ (where mnt^{2-} is maleonitriledithiolate) with PPh_3 in an inert atmosphere in an acetonitrile solution was determined by calorimetry. The obtained enthalpy value (-93 ± 5) kJ mol^{-1} differs from the enthalpy value of the reaction carried out by us earlier under aerobic conditions by (16 ± 9) kJ mol^{-1} . The obtained results indicate the participation of atmospheric oxygen in the catalytic process. DFT calculations of the structures $[\text{MO}_x(\text{LL})_2]^{2-}$ (where $M = \text{Mo}$ or W , $x = 1$ or 2 , and LL is dithiolene ligand) were carried out. DFT calculations of the thermodynamic potential values for the oxygen transfer reaction in the system $[\text{M}^{\text{IV}}\text{O}_2(\text{LL})_2]^{2-} - [\text{M}^{\text{VI}}\text{O}(\text{LL})_2]^{2-}$ were also carried out. It was shown that the determining contribution to these processes is made by the enthalpy changes. The enthalpies of these processes depend on the donor–acceptor characteristics of the dithiolene ligands. In the case of good acceptors, the oxidation process is more exothermic. The opposite picture is observed for the reduction processes of the complex. The $M=\text{O}$ bond length can be used as a quantitative criterion for donor–acceptor properties of the ligands. Also, for molybdenum complexes, reduction processes are more favorable, while for tungsten complexes, oxidation processes are more favorable. The calculations agree well with experimental data that prove the validity of the model used for DFT calculations.



1. INTRODUCTION

Currently, one of the modern areas of bioinorganic chemistry is the study of molybdenum and tungsten-containing enzymes.^{1,2} For this purpose, complex compounds of these metals with dithiolene ligands are synthesized and studied, which model the natural active centers of enzymes.^{3,4} A lot of different dithiolene ligands and molybdenum and tungsten complexes with these ligands have already been obtained and characterized.⁵ As a result, these model compounds are structural or functional analogues of metalloenzymes.^{6–8}

Oxygen atom transfer (OAT) or oxotransfer is the main process involving molybdenum and tungsten enzymes.^{9,10} This reaction is the OAT between the substrate and the active center of the enzyme (eq 1, sub = substrate accepting an oxygen atom and M = metal center). The active center is regenerated by two stages of proton-coupled electron transfer (PCET, eqs 2 and 3):



Initially, kinetic studies of synthesized model complexes of molybdenum and tungsten with various substrates have been carried out, simulating the OAT process.^{11–13} However, a thermodynamic description for these systems is practically

absent, although thermodynamic potentials are the driving force of the OAT processes. Thus, the description of oxotransfer processes using a thermodynamic approach is of crucial importance. This path allows us to identify the driving force of the reactions taking place and determine the influence of the electronic and steric effects of structural fragments on the oxidation–reduction properties of the model compounds. As a result, it becomes possible to come closer to understanding the development and functioning of living organisms on Earth. By fine-tuning the properties of these complexes, it is possible to determine the most effective molybdenum and tungsten model compounds as biomimetic catalysts in various oxidation–reduction processes.¹⁴

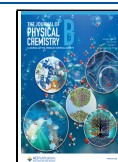
In this article, data on the thermodynamics of oxotransfer processes are obtained using DFT calculations. This approach is much faster than the experimental determination of the corresponding values provided that such calculations are in good agreement with experimental data.

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2. EXPERIMENTAL METHODS

2.1. Materials and Methods. Commercial grade $[\text{Bu}_4\text{N}]\text{-Br}$, NaHSO_3 , $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, CH_3COOH , and PPh_3 and solvents (EtOH , $i\text{PrOH}$, $i\text{BuOH}$, Et_2O , and DMF) were used without additional purification. CH_3CN was dried using 4 Å molecular sieves. Na_2mnt (where mnt^{2-} is maleonitriledithiolate) and $[\text{Bu}_4\text{N}]_2[\text{WO}_2(\text{mnt})_2]$ were synthesized under aerobic conditions as described in literature.^{15,16}

IR spectra were recorded using an IRAffinity-1 mid-IR Fourier IR spectrometer in the range 4000–400 cm^{-1} in KBr pellets. Energy-dispersive X-ray fluorescence spectrometry was performed under air atmosphere using an EDX-800P, and the spectrum was recorded on two channels: Na–Sc (0.00–4.40 keV) and Ti–U (0.00–40.00 keV). NMR spectra were obtained using a Bruker 400 MHz Avance III NMR spectrometer with $d_6\text{-DMSO}$ as solvents. UV–vis spectra were obtained using a UV-1800 scanning double-beam spectrophotometer in the range of 200–700 nm in acetonitrile solution (for results, see SI).

2.2. Calorimetric Measurements. Calorimetric measurements were carried out using a Calvet-type heat-conducting calorimeter designed by Yu. V. Kondratiev et al. (KYV calorimeter).^{17,18} The calorimeter was equipped with two differential calorimetric cells. The cell volume for KYV was 50 mL. The thermal effect of the reaction was determined by dissolving a solid sample of the substance in 25 mL of acetonitrile in the presence of a dissolved reducing agent (PPh_3). The substance was placed in a glass ampule. The mass of the sample was defined as the difference between the masses of a filled and empty ampule.

The calorimetric cells were preliminarily calibrated using the thermal effect of KCl dissolution in water (eqs 4):

$$Q = (-\Delta H_{\text{sol}}^0(\text{KCl})) \cdot \nu \quad (4)$$

$$K = S/Q \quad (5)$$

where K is the calorimeter constant (W J^{-1}); S is the area under the curve, corresponding to the fixed thermal effect (W); and ν is the amount of substance (mol).

Calibration provided the calorimeter constant K . After the reaction was carried out with an unknown thermal effect, the area under the curve (S) was calculated. Knowing the calorimeter constant K , we used eq 5 to find the thermal effect of the reaction. To determine the standard enthalpies of the processes, measurements were carried out at 298 K.

Calorimetric experiments were carried out in an inert atmosphere. The system was degassed by an argon stream for 2 h, assembled as a three-necked flask, a calorimetric cell, and an argon cylinder setup (Figure S1). One neck of the flask was closed with a septum with a needle to release excess pressure, the second neck was closed with a stopper equipped with a Teflon capillary and connected through a hose to the argon cylinder, and the third neck was closed with a stopper with a long Teflon capillary lowered into a prepared calorimetric cell with a weighed PPh_3 sample and a sealed ampule with the complex inside. 25 mL of acetonitrile was placed in the flask, and an argon stream was blown through the capillary lowered into the solvent. The blowing was accompanied by ultrasound treatment using short pulses in an ultrasound bath. After this, the end of the long capillary was lowered to the bottom of the flask, and the outlet to the atmosphere through the needle was closed. The excess pressure allowed all of the degassed solvent to be transferred through the capillary directly to the

calorimetric cell. The prepared cell was placed in the calorimeter, and the accessible outlets of the cell were closed with the ball filled with argon to prevent oxygen from entering the system during thermostating.

3. THEORETICAL CALCULATIONS

The calculations were performed using the Gaussian 16 program (revision A.03) on a virtual machine of the St. Petersburg State University resource center “Computing Center”.¹⁹ All structures were fully optimized, and the energy minima were checked by the analytical calculation of the frequencies of normal vibrations. Geometry optimizations, calculations of the frequencies of normal vibrations, and determinations of thermodynamic potentials were performed at the DFT level using the B3LYP function.^{20–22} The LANL08(f) basis set was chosen for the tungsten atom.^{23,24} For the remaining elements, the 6-311++G(2d,2p) basis set was used.^{25,26} Calculations in the solvent were performed using the polarized continuum model (PCM).²⁷ Acetonitrile ($\epsilon = 35.688$) was used as a solvent. In order to reduce the time, all calculations were performed only for the anionic part of the complex compounds. The total charge of all particles was -2 . This approximation was valid, since the complex compounds dissociated in the acetonitrile solution.¹⁶ Thus, the role of the counterion was insignificant in calculating the thermodynamic functions of the oxotransfer process. The Chemcraft program was used to visualize the optimized geometries and normal vibrations.²⁸

4. RESULTS AND DISCUSSION

4.1. Calculated Structures of Model Complexes. The main quantum chemical calculations’ objective is to obtain the values of thermodynamic potentials for the oxygen transfer reaction in the system $[\text{M}^{\text{IV}}\text{O}_2(\text{LL})_2]^{2-} - [\text{M}^{\text{VI}}\text{O}(\text{LL})_2]^{2-}$, where LL is the dithiolene ligand and $\text{M} = \text{Mo}, \text{W}$. This method is much faster and less labor-intensive than the experimental calorimetry determination. Thus, they allow us to determine trends in the behavior of enzyme active center analogs depending on the structure of the model complex. Quantum chemical calculations using a correct model are able to predict changes in the properties of the system (in our case, changes in the enthalpy of oxotransfer) when varying the structure of the active center.

The optimized structures of $[\text{WO}_2(\text{mnt})_2]^{2-}$ and $[\text{WO}(\text{mnt})_2]^{2-}$ are shown in Figures 1 and 2. The starting geometry is the X-ray experimentally determined structure of the corresponding anion.¹⁶ Tables S1 and S2 show the calculated

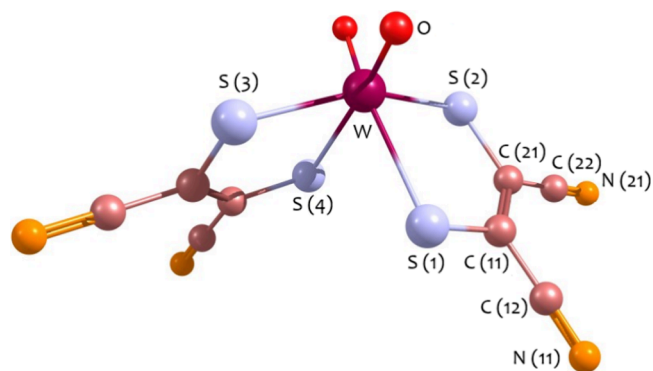


Figure 1. Calculated structure of $[\text{WO}_2(\text{mnt})_2]^{2-}$.

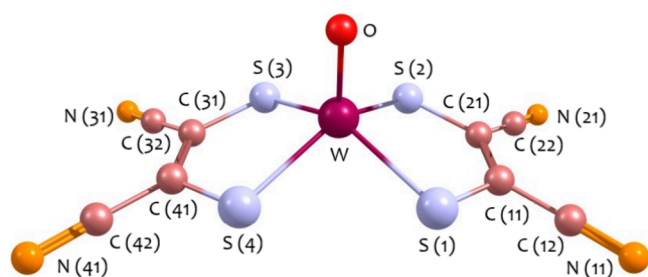


Figure 2. Calculated structure of $[\text{WO}(\text{mnt})_2]^{2-}$.

geometric parameters for the complexes and the results of their X-ray structural analysis.

For the oxidized form, only the hydrate crystal $[\text{Ph}_4\text{P}]_2[\text{WO}_2(\text{mnt})_2] \cdot 2\text{H}_2\text{O}$ is described. The presence of crystallization water molecules as well as the packing of particles in the crystal can lead to a distortion of the structure parameters. This is manifested in a noticeable difference in the lengths of the $\text{C}\equiv\text{N}$ bonds in the same ligand (0.116 nm for $\text{N}(11)\equiv\text{C}(12)$ and 0.114 nm for $\text{N}(21)\equiv\text{C}(22)$). The effect of packing in the solid state also affects the same bonds in the reduced form, where all four CN groups are nonequivalent. The lengths of the $\text{C}\equiv\text{N}$ bonds differ noticeably within one ligand and not so significantly between ligands. The calculation model does not assume that such interactions are taken into account; therefore, the obtained structures have the same or very close values of the $\text{C}\equiv\text{N}$ bonds in these groups.

The calculated bond lengths and angles are in good agreement with the majority of the X-ray data.¹⁶ This means that the chosen model is suitable for further consideration and satisfactorily describes the model systems. The comparison of the results obtained by calculation in the gas phase and in acetonitrile solution shows that the parameters appear to be similar to each other. In general, for the oxidized form, the bond lengths and angles calculated in the solution are closer to the experimental values. The exceptions are the $\text{W}=\text{O}$ and $\text{W}-\text{S}(1)$ bonds, which are in better agreement with the calculation in the gas. For the reduced form, some parameters are better in gas, while others are better in the acetonitrile solution.

In addition to the systems with mnt^{2-} ligand experimentally described in this work, complex anions with other dithiolene ligands described in the literature have been calculated.^{3,29} The structures of the ligands and their codes are listed in Figure 3. The geometry optimization is performed using the solution model only.

Table S3 summarizes the parameters of all calculated structures with tungsten as the metal center. A detailed analysis reveals some regularities. The coordination environment of tungsten in the reduced form is a distorted tetragonal pyramid, but the structure distortions are very small; therefore,

the complexes can be considered almost symmetrical. The oxidized form of tungsten is a distorted trigonal antiprism. In general, the oxidized form is characterized by greater asymmetry in the structure than the reduced form. The reason for this may be due to the arrangement of the ligands and their donor abilities. Terminal oxygen is a good π -donor due to its unshared electron pairs and supplies more electron density to the metal center than sulfur in the trans position to it. According to Pearson's concept,^{30–32} the hard oxygen atom is more attracted to the hard tungsten atom than the softer sulfur atom. Thus, sulfur atoms in the trans position to each other donate more electron density to the metal center than sulfur atoms in the trans position to the terminal oxygen atom. Thus, the $\text{W}-\text{S}$ bond in the trans position to the oxygen is longer than the $\text{W}-\text{S}$ bond in the trans position to the S of the other ligand. Therefore, there is significant asymmetry in the oxidized forms. Such a phenomenon is very clearly seen in the calculated structures.

The $\text{W}=\text{O}$ bond length decreases with the transition from the oxidized form to the reduced form for all the calculated complexes as well as the $\text{C}=\text{C}$ bond length. The shortest $\text{C}=\text{C}$ bond is in the complexes with edt^{2-} ligand, 0.1340 nm for $[\text{WO}_2(\text{edt})_2]^{2-}$, and 0.1333 nm for $[\text{WO}(\text{edt})_2]^{2-}$. Also, the highest value of the $\text{S}-\text{C}=\text{C}$ valence angle is in the case of the edt^{2-} ligand (123.5° and 121.6° for the reduced and oxidized forms, respectively). It means that the $\text{C}=\text{C}$ atoms can "fit" closer to each other, which can be explained by the absence of steric hindrance. In the edt^{2-} complex, hydrogen atoms, which have a small size, act as substituents for multiple bonds. Such compact substituents do not prevent bond shortening. The bulk substituent (methyl groups in mdt^{2-} and aromatic systems, e.g., in bdt^{2-}) hinders this, causing the $\text{C}=\text{C}$ bonds to be longer and the $\text{S}-\text{C}=\text{C}$ angles to be larger compared to complexes with edt^{2-} .

The valence angle $\text{S}-\text{C}=\text{C}$ values show that the nitrile substituent at the double bond as in the case of hydrogen substituent at the double bond does not create steric difficulties. In $[\text{WO}_2(\text{mnt})_2]^{2-}$, the $\text{S}-\text{C}=\text{C}$ angle is 123.2°, and in $[\text{WO}(\text{mnt})_2]^{2-}$, this angle is 121.5°. The CN group has a small substituent volume, because it contains a $\text{C}\equiv\text{N}$ triple bond lying in the plane of the dithiolene moiety and forms a linear fragment with the C atom of the double bond. In addition, the CN substituents are strong π -acceptors and repel each other as far away as possible, allowing the atoms of the $\text{C}=\text{C}$ bond to come closer as the CN groups reduce the electron density on the carbon atoms. In the case of reduced forms, the pdt^{2-} complex is also similar (121.6° for $\text{S}-\text{C}=\text{C}$ angle and 0.1334 nm for $\text{C}=\text{C}$ bond).

The $\text{W}=\text{O}$ bond length changes significantly compared across a ligand range for the same oxidation state of the tungsten. The presence of electron acceptor substituents (such as nitrile) shifts the electron density toward dithiolene ligands.

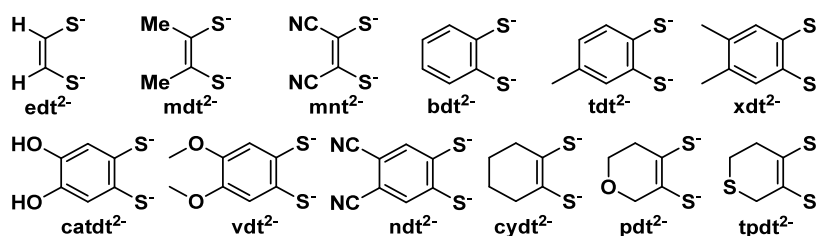


Figure 3. Structures of dithiolene ligands used in calculations.

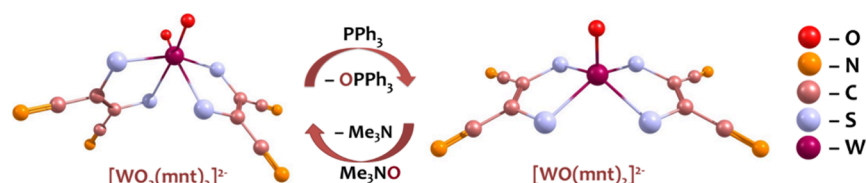


Figure 4. Scheme of the oxotransfer process involving dithiolene complexes of tungsten.

The central atom is depleted in electron density and becomes a harder Lewis acid. The donor properties of the oxygen show up better in this case. As a result, the bond between the terminal oxygen and the metal center is shorter than that for other compounds. The acceptor substituent effect is most clearly seen for mnt^{2-} as a ligand, since the CN group is located directly at the double bond. The $\text{W}=\text{O}$ bond in $[\text{WO}_2(\text{mnt})_2]^{2-}$ is 0.1727 nm and in $[\text{WO}(\text{mnt})_2]^{2-}$ is 0.1707 nm, while for bdt^{2-} , these values are 0.1739 and 0.1720 nm, respectively. A smaller but quite noticeable influence is exerted by the $-\text{CN}$ substituents in the aromatic system, as in ndt^{2-} (0.1732 and 0.1712 nm for the oxidized and reduced forms, respectively). The described phenomenon is also evident for the S–C bonds. In contrast, the influence of acceptor substituents on the W–S bond length is not observed in these structures.

The CN groups also affect the value of the $\text{O}=\text{W}=\text{O}$ valence angle. In the case of a strong acceptor in the ligand structure, this angle increases. The strengthening of oxygen donor abilities leads to the fact that π -binding orbitals of the W–O bond become more populated; thus, their electron density is higher compared to the case of the absence of the acceptor substituent. This means a stronger repulsion of terminal oxo-ligands between each other, which manifests itself in an increase in the valence angle between them. The maximum value of the $\text{O}=\text{W}=\text{O}$ angle (103.7°) is observed for mnt^{2-} complex. For the same ligand, the shortest $\text{W}=\text{O}$ bond length was 0.1727 nm. A slightly higher value of bond length and a lower value of valence angle are observed in the structure with ndt^{2-} ligand in which the corresponding parameters values are 0.1732 nm and 103.2° , respectively.

The described pattern is also preserved with a good donor substituent. For example, in mdt^{2-} , the ligand contains two methyl groups, which have the best donor abilities among the other selected substituents. In the mdt^{2-} complex, the donor abilities of oxygen are lower; as a result, the binding to the metal center is worse, and the repulsion of $\text{W}=\text{O}$ bonds from each other becomes lower than that for the other ligands. Hence, the $\text{W}=\text{O}$ bond of 0.1726 nm is the longest and the valence angle of $\text{O}=\text{W}=\text{O}$ 101.9° is the smallest compared to the other structures. The complexes with cydt^{2-} and pdt^{2-} ligands, which also contain good donor fragments, also have comparable values for the discussed parameters. By replacing the metal center from W to Mo and subsequent geometry optimization, the structures of similar dithiolene molybdenum complexes in an acetonitrile solution are obtained (Tab. S4).

The donor–acceptor properties of the substituents in the dithiolene ligands certainly affect the structural parameters of the calculated complexes. In general, the following important trends can be noted. When the nature of the substituent in the ligand changes from donor to acceptor, the $\text{M}=\text{O}$ bond shortens. This effect is associated with other structural changes. When the $\text{W}=\text{O}$ bond shortens, the W–S and C=C bond lengths increase and the S–C bond length decreases. In the

oxidized forms of the complexes, the $\text{O}=\text{W}=\text{O}$ angle becomes larger, and the S–C=C angle decreases with an increase in $\text{W}=\text{O}$ length in both the oxidized and reduced forms of the complexes. The dependence of the discussed structural parameters is not strictly monotonic but rather reflects general trends in the rearrangement of the metal center ligand environment. These trends are most clearly manifested when a strong acceptor substituent is introduced into the ligand structure (Tables S3, S4). When the results are obtained for mnt^{2-} , anomalous deviations are observed in some cases. Nevertheless, correlations between bond lengths and angles are clearly traced in all other calculated molybdenum and tungsten complexes. Certainly, the most convenient structural parameter that describes the donor–acceptor properties of substituents in dithiolene ligands is the length of the $\text{M}=\text{O}$ bond, since in this case significant differences in the ligand structure (the presence of cyclic forms or heteroatoms) do not have a decisive steric effect on this parameter.

4.2. Quantum Chemical Description of the Oxotransfer Process. Complex anions $[\text{MO}_2(\text{LL})_2]^{2-}$ and $[\text{MO}(\text{LL})_2]^{2-}$, where $\text{M} = \text{Mo}, \text{W}$, with optimized structures, were used to calculate the oxotransfer reaction thermodynamic potentials. The oxotransfer process scheme in the case of mnt^{2-} tungsten complexes is shown in Figure 4. Me_3NO as an oxidizing agent and PPh_3 as a reducing agent were chosen in the model processes.

Table 1 contains data on ΔH°_{298} , ΔS°_{298} , and ΔG°_{298} values for the OAT reactions in the acetonitrile solution. The entropy value changes in the reactions are quite small. Indeed, the number of reactants particles is equal to the number of products in the same phase in both oxotransfer directions. The process itself consists only in the transfer of one oxygen atom between the reactants. Thus, the contribution of the entropic factor to the Gibbs energy can be neglected in these systems. It is the enthalpic contribution that plays the main role in the OAT, and its change reflects the change in the properties of the model complexes. It is worth noting that the experimental description also focuses on the change in the enthalpy of reactions. That is why the results of the calorimetric experiment used to determine ΔH°_{298} in oxotransfer processes are the most important.

Comparison of the values of two separate OAT directions allows us to trace the reverse dependence: favorable oxidation in the case of one complex leads to unfavorable reduction and vice versa. In addition, molybdenum complex anions are worse oxidized and better reduced than tungsten-containing anions, which seems quite reasonable. Oxidation state +6 for the tungsten is the most stable in solution, therefore W^{IV} undergoes the oxidation process to W^{VI} easily. Molybdenum is characterized by a lower oxidation state in the solution, which is apparent for complexes in the reduced state. Mo^{VI} is the best oxidizing agent and readily transforms to Mo^{IV} .

In the case of W^{IV} oxidation by Me_3NO , some regularities in the enthalpy changes are observed. The value of the minimum

Table 1. Calculated Thermodynamic Parameters for the Oxotransfer Process

LL ²⁻	$[M^{IV}O(LL)_2]^{2-} + (CH_3)_3NO = [M^{VI}O_2(LL)_2]^{2-} + (CH_3)_3N$					
	$\Delta H_{298}^\circ, \text{kJ mol}^{-1}$		$\Delta G_{298}^\circ, \text{kJ mol}^{-1}$		$\Delta S_{298}^\circ, \text{J K}^{-1} \text{mol}^{-1}$	
	W	Mo	W	Mo	W	Mo
edt ²⁻	-209	-102	-209	-109	1	22
mdt ²⁻	-201	-109	-206	-109	17	-1
mnt ²⁻	-176	-83	-175	-81	-4	-9
bdt ²⁻	-196	-95	-198	-97	8	6
tdt ²⁻	-195	-95	-199	-99	13	15
xdt ²⁻	-197	-97	-195	-95	-6	-4
vd ²⁻	-193	-94	-197	-96	12	8
catdt ²⁻	-194	-95	-194	-93	0	-8
ndt ²⁻	-190	-90	-191	-87	5	-11
cydt ²⁻	-205	-105	-208	-103	9	-8
pdt ²⁻	-205	-106	-208	-107	8	5
tpdt ²⁻	-198	-100	-202	-104	13	13

LL ²⁻	$[M^{VI}O_2(LL)_2]^{2-} + Ph_3P = [M^{IV}O(LL)_2]^{2-} + Ph_3PO$					
	$\Delta H_{298}^\circ, \text{kJ mol}^{-1}$		$\Delta G_{298}^\circ, \text{kJ mol}^{-1}$		$\Delta S_{298}^\circ, \text{J K}^{-1} \text{mol}^{-1}$	
	W	Mo	W	Mo	W	Mo
edt ²⁻	-60	-167	-59	-159	-4	-25
mdt ²⁻	-68	-160	-62	-160	-20	-1
mnt ²⁻	-93	-186	-94	-188	1	6
bdt ²⁻	-73	-174	-70	-171	-11	-9
tdt ²⁻	-74	-174	-69	-169	-16	-18
xdt ²⁻	-72	-173	-73	-173	3	2
vd ²⁻	-76	-175	-72	-172	-15	-11
catdt ²⁻	-75	-174	-74	-175	-2	5
ndt ²⁻	-80	-179	-77	-182	-8	9
cydt ²⁻	-64	-164	-61	-166	-12	6
pdt ²⁻	-64	-164	-61	-161	-11	-8
tpdt ²⁻	-71	-169	-66	-164	-16	-16

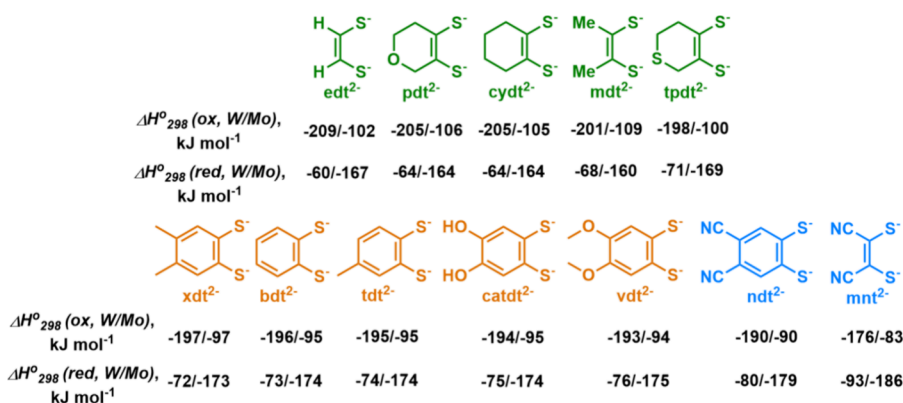
oxidation enthalpy for both W and Mo is for mnt²⁻ (−176 kJ mol^{−1} for W and −83 kJ mol^{−1} for Mo). Larger absolute enthalpy change values are observed in the case of ndt²⁻ (−190 kJ mol^{−1} for W and −90 kJ mol^{−1} for Mo). Both ligands contain strong π -acceptor −CN groups. The terminal oxygen atom has a higher electronegativity than the metal center and pulls down the electron density from the polar M=O bond. Acceptor ligands compete with oxo-ligands, as they are also able to shift the electron density from the metal center to

themselves. Upon oxidation, when an additional electro-negative oxygen atom appears in the molecule, the electron density attributable to mnt²⁻ will decrease. For this reason, the presence of strong acceptor ligands in the complex structure leads to less favorable oxidation than complexes with other ligands. Conversely, the reduction process will be more favorable: −93 kJ mol^{−1} for [WO₂(mnt)₂]²⁻ and −186 kJ mol^{−1} for [MoO₂(mnt)₂]²⁻.

The reverse situation is observed for ligands containing good donor substituents. The largest in absolute values of the oxidation processes enthalpy changes are observed in edt²⁻ complexes (−209 kJ mol^{−1} for W and −102 kJ mol^{−1} for Mo), pdt²⁻ complexes (−205 kJ mol^{−1} for W and −106 kJ mol^{−1} for Mo), cydt²⁻ (−205 kJ mol^{−1} for W and −105 kJ mol^{−1} for Mo), and mdt²⁻ complexes (−201 kJ mol^{−1} for W and −109 kJ mol^{−1} for Mo).

Thus, the ligands can be divided into three conventional groups. The first group includes ligands with substituents that exhibit strong donor abilities (edt²⁻, cydt²⁻, pdt²⁻, mdt²⁻, and tpdt²⁻), and the second group includes ligands with strong acceptor substituents (mnt²⁻ and ndt²⁻). The last group includes ligands that do not show strong donor–acceptor properties: catdt²⁻, bdt²⁻, xdt²⁻, tdt²⁻, and vdt²⁻ (Figure 5). For the first group ligands (with donor substituents), the greatest absolute value of enthalpy changes in oxidation processes is observed, and for the ligands of the second group (with acceptor substituents), the smallest. In the case of reduction processes, the reverse dependence is observed: the greatest absolute value of enthalpy changes is for the second group of the ligands, containing acceptor substituents.

The bond length between the metal atom and terminal oxygen atom M=O can be used as a quantitative criterion for dividing the ligands into these three groups. Figure 6 shows the dependence of the enthalpy change in the metal center oxidation process on the M=O bond length. Ligands with strong acceptor properties (second group ligands, Figure 5) such as strongly pull the electron density from the metal center, shortening the M=O bond. In this case, the values of the enthalpy change in the calculated oxidation processes decrease in absolute value (Table 1). Conversely, ligands with significant donor characteristics (first group ligands, Figure 5) increase the electron density on the metal atom, increasing the length of this M=O bond and increasing the thermal effect of these reactions in absolute value. A more exothermic character

**Figure 5.** Division of ligands into groups based on their effect on the enthalpy of oxotransfer in the corresponding complex (green, first group; blue, second group; orange, third group).

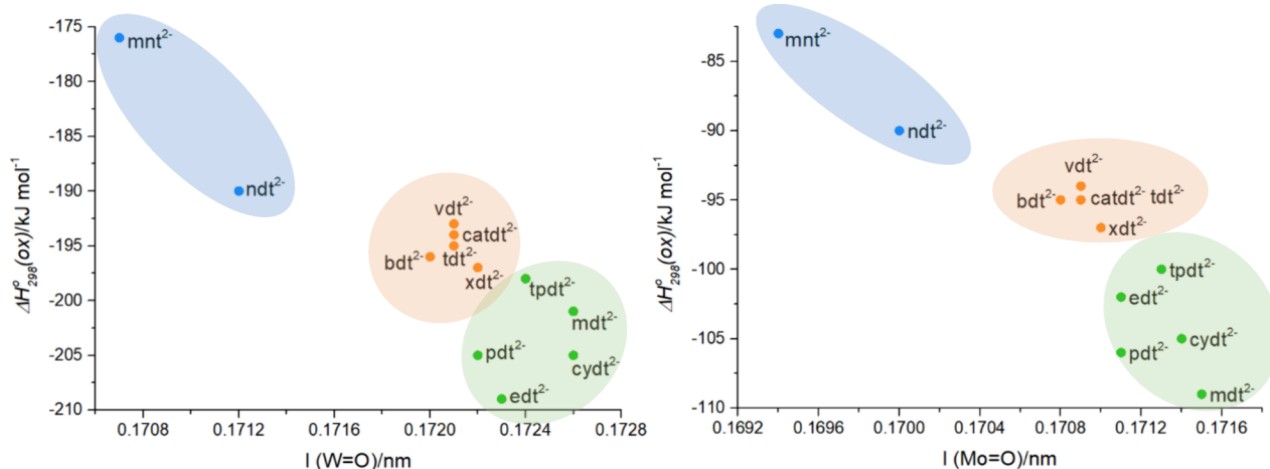


Figure 6. Dependence of the enthalpy change in the metal center oxidation process on the $M=O$ bond length

of the metal center oxidation process is observed in the case of ligands with donor properties (first group ligands, Figure 5).

The $C=C$ bond length of the dithiolene fragment can also serve as a criterion for dividing the ligands into three groups. Strong acceptor ligands lead to a decrease in the bonding orbital population of the $C=C$ double bond, leading to its elongation (Tables S3 and S4). However, in this case, probably, the structural features of the ligand do not allow to unambiguously assign the ligands to one of the groups based on the length of the $C=C$ bond. In particular, in the case of $-CN$ substituents in the mnt^{2-} ligand, the length of the double bond is abnormally short. Therefore, we believe that the most convenient criterion is the length of the $M=O$ bond, which very well reflects the donor–acceptor characteristics of dithiolene ligands.

In the case of reduction processes, the $M=O$ bond length can also serve as a criterion for describing donor–acceptor properties of ligands (Figure S7). Thus, the $M=O$ bond length in both oxidized and reduced forms of molybdenum and tungsten dithiolene complexes allows one to predict the thermal effect of the oxotransfer processes; involving them without carrying out complete thermodynamic calculations limited to calculating the structure of the complex only.

4.3. Experimental Determination of the Enthalpy Change in the Oxotransfer Reaction. Previously, we experimentally determined the reduction enthalpy between $[WO_2(mnt)_2]^{2-}$ complex and PPh_3 in acetonitrile under aerobic conditions.³³ This reaction is a catalytic process, which can be described as PPh_3 oxidation by dissolved oxygen in the presence of the tungsten complex as a catalyst (Figure 7).

The enthalpy value in the 1:1 molar ratio was $\Delta H^\circ_{298, r(1+2)} = (-109 \pm 4) \text{ kJ mol}^{-1}$. This value corresponds to the total effect of all of the reaction stages taking place in solution. The oxidation of the formed catalyst, i.e., its regeneration, contributes to the total thermal effect (Figure 7, stage 2).

Removal of oxygen from the reaction system allows the last stage. The thermal effect in this case should correspond only to the oxotransfer process (Figure 7, stage 1). In this work, the calorimetric experiment in an inert atmosphere was performed under experimental conditions (concentrations, ratio) similar to those used previously.³³

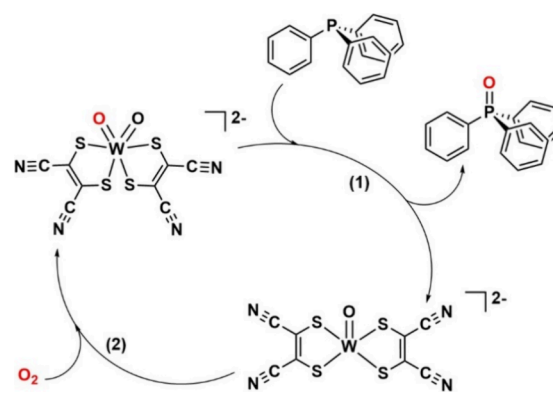
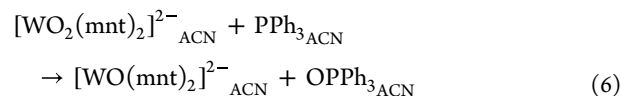


Figure 7. Scheme of the catalytic reaction that occurs during the interaction of $[WO_2(mnt)_2]^{2-}$ and PPh_3 under air (step 1: oxidation of PPh_3 , step 2: regeneration of $[WO_2(mnt)_2]^{2-}$). Reprinted with permission from ref. (33). Copyright 2024, Springer Nature.

The calorimetric curve obtained for the oxotransfer reaction (eq 6) in argon atmosphere ($[WO_2(mnt)_2]^{2-}$: PPh_3 molar ratio 1:1) is shown in Figure 8B:



The curve is similar to those measurements under aerobic conditions (Figure 8A). The curves clearly show the endothermic dissolution process of the solid $[Bu_4N]_2[WO_2(mnt)_2]$ in the acetonitrile solution containing PPh_3 . This process is accompanied by heat release due to the redox reaction (eq 6), which is expressed as a broad extended exothermic peak. In the inert atmosphere case, it can be seen that the “tail” of the baseline is decreased. As we have shown earlier, this area in aerobic condition (Figure 8A) corresponds to the oxidation of the reduced form $[WO(mnt)_2]^{2-}$ by oxygen.³³ The tail decrease in anaerobic conditions (Figure 8B) corresponds to the absence of the oxidation step of $[WO(mnt)_2]^{2-}$.

The dissolution of a solid $[Bu_4N]_2[WO_2(mnt)_2]$ heat effect ($\Delta H^\circ_{298, sol}$) was obtained from an independent experiment.³³ The dissolution enthalpy of $[Bu_4N]_2[WO_2(mnt)_2]$ ($\Delta H^\circ_{298, sol}$) was subtracted from the total value $\Delta H^\circ_{298, sum}$, which corresponds to the total area under the calorimetric curve.

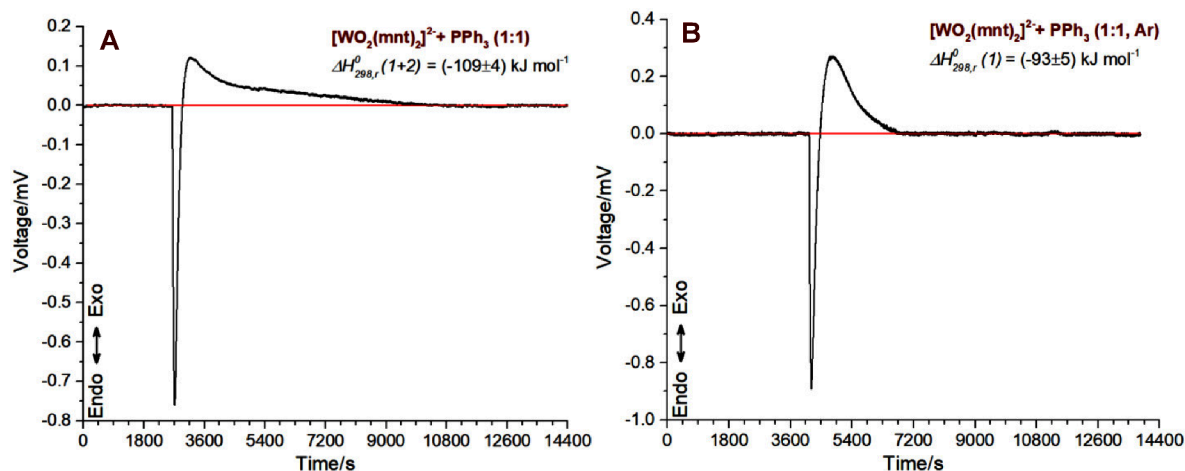


Figure 8. Calorimetric curves of the dissolution of $[\text{Bu}_4\text{N}]_2[\text{WO}_2(\text{mnt})_2]$ in acetonitrile with PPh_3 in a molar ratio of 1:1 in air (A) and argon (B). Reprinted in part with permission from ref. (33). Copyright 2024, Springer Nature.

Based on Hess's law, the obtained value of $\Delta H_{298,r}^{\circ}(1)$ corresponds to the reaction enthalpy $[\text{WO}_2(\text{mnt})_2]^{2-}$ with PPh_3 in a 1:1 molar ratio in an inert atmosphere:

$$\begin{aligned}\Delta H_{298,r}^{\circ}(1) &= \Delta H_{298,\text{sum}}^{\circ} - \Delta H_{298,\text{sol}}^{\circ} \\ &= (-93 \pm 5) \text{ kJ mol}^{-1}\end{aligned}$$

The obtained $\Delta H_{298,r}^{\circ}(1)$ agrees with our quantum chemical calculations for oxotransfer processes in the acetonitrile solution: $\Delta H_{298,\text{red}}^{\circ} = -93 \text{ kJ mol}^{-1}$ (Table 1).

The difference of the thermal effects obtained in an inert atmosphere and in air, according to Hess's law, allows estimating the enthalpy change during the oxidation of the forming tungsten complex (eq 7):

$$\begin{aligned}\Delta H_{298,r}^{\circ}(\text{W}^{\text{IV}} \rightarrow \text{W}^{\text{VI}}) &= \Delta H_{298,r}^{\circ}(1+2) - \Delta H_{298,\text{red}}^{\circ}(1) \\ &= (-109) \text{ kJ mol}^{-1} - (-93) \text{ kJ mol}^{-1} \\ &= (-16 \pm 9) \text{ kJ mol}^{-1}\end{aligned}\quad (7)$$

The UV-spectra for equimolar mixtures of $[\text{WO}_2(\text{mnt})_2]^{2-}$ and PPh_3 in air and an argon atmosphere are presented in Figure 9. The purple line corresponds to the absorption

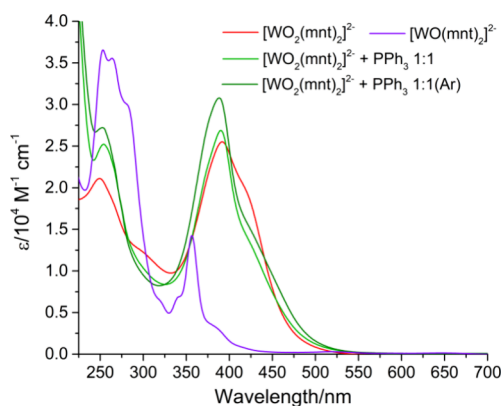


Figure 9. Comparison of the electronic absorption spectra of reaction mixtures of $[\text{WO}_2(\text{mnt})_2]^{2-} + \text{PPh}_3$ in air and argon atmospheres with the spectra of individual substances.

spectrum of the expected product, the reduced form of $[\text{WO}(\text{mnt})_2]^{2-}$, while the red line corresponds to the initial complex $[\text{WO}_2(\text{mnt})_2]^{2-}$.³³ Absorption is observed in the 225–325 nm region, which is due to the presence of PPh_3 and significant amounts of the corresponding OPPh_3 in the solution. In the spectra for the solutions after calorimetric experiments, the peak at 357 nm referring to the reduced form of the tungsten complex is absent. The absorption maximum is observed at 392 nm, which corresponds to the oxidized form of $[\text{WO}_2(\text{mnt})_2]^{2-}$.

We assume that the oxidation of the reduced complex $[\text{WO}(\text{mnt})_2]^{2-}$ occurs when the solution is allowed to stand in the calorimetric cell for a long time to reach the baseline. Because of the argon atmosphere, this process is very slow. Nevertheless, it proceeds after consumption of the reducing agent (PPh_3). The heat effect of the oxidation stage is not detected by the calorimeter because of its low intensity. This can be seen on the curve by the time to reach the baseline. The whole duration of the heat exchanges decreased significantly when oxygen was removed. Thus, we believe that we were able to separate the two stages of the process of catalytic oxidation of phosphine and register the thermal effect of the OAT reaction.

5. CONCLUSIONS

For the first time, the change in enthalpy for the model oxotransfer reaction between $[\text{WO}_2(\text{mnt})_2]^{2-}$ and PPh_3 was determined: $(-93 \pm 5) \text{ kJ mol}^{-1}$. For this purpose, a calorimetric cell was constructed, allowing thermal effects to be determined under inert conditions.

The scheme to determine thermodynamic characteristics of the model oxotransfer process using DFT calculations is proposed. This calculation scheme is confirmed by the experimental results. The calculated structural parameters are close to crystallographic ones, and the calculated change in the enthalpy for the reaction between $[\text{WO}_2(\text{mnt})_2]^{2-}$ with PPh_3 (-93 kJ mol^{-1}) corresponds to the calorimetrically obtained value. The calculations performed allowed us to divide the dithiolene ligands into three groups based on their donor–acceptor properties. It is convenient to use the length of the $\text{M}=\text{O}$ bond as a quantitative criterion. The shorter this bond, the stronger the acceptor characteristics of the dithiolene ligand and, accordingly, the more exothermic the oxidation

process of the complex will be. Vice versa, for ligands with donor properties, the length of the $M=O$ bond is higher, and the process of metal center reduction is more exothermic. Therefore, the distance between the M and the O atoms in both the oxidized and reduced forms of molybdenum and tungsten dithiolene complexes can be used to predict the thermal effects of reactions involving these complexes, without the need for extensive thermodynamic calculations that would involve determining the structure of the complex.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcb.4c06967>.

Additional results of quantum chemical calculations and characterization, including photographs of experimental setup (PDF)

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Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by V.M.S. Project supervision and conceptualization were performed by V.D.K. The experimental planning and spectral data interpretation were carried out by O.N.P. The first draft of the manuscript was written by V.M.S., V.D.K., and B.P.E.. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Notes

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■ ABBREVIATIONS

OAT, oxygen atom transfer, oxotransfer; PCET, proton-coupled electron transfer; DFT, density functional theory; PCM, polarized continuum model; LL, dithiolene ligand

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