

The Syntheses and Vibrational Spectra of ^{16}O - and ^{18}O -Enriched *cis*- MO_2 (M = Mo, W) Complexes

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Abstract: In this contribution, we report convenient synthetic approaches for obtaining $^{16}\text{O}/^{18}\text{O}$ -enriched dioxidometal^{VI} complexes, $\text{MO}_2(\text{L})$ (W, Mo), with a linear, tetradentate amine phenolate ligand *N,N*-dimethyl-*N,N'*-bis(2-hydroxy-3,5-dimethylbenzyl)ethylenediamine (H_2L) and describe their characterization by IR and Raman spectroscopy complemented by DFT computational analysis. The isotopologues of $\text{WO}_2(\text{L})$ were made of tungsten^{VI} trisglycolate $\text{W}(\text{eg})_3$ ($\text{eg} = 1,2$ -ethanediolate dianion) and ligand H_2L in the presence of either $\text{H}_2[^{16}\text{O}]$ or $\text{H}_2[^{18}\text{O}]$, whereas $\text{Mo}^{16}\text{O}_2(\text{L})$ was made using $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ which was converted to $\text{Mo}^{18}\text{O}_2(\text{L})$ by oxido substitution using $\text{H}_2[^{18}\text{O}]$. The complementary IR and Raman analyses show the $\nu(\text{MO}_2)_s$ and $\nu(\text{MO}_2)_a$ at 934 and 899 cm^{-1} for $\text{W}^{16}\text{O}_2(\text{L})$ and at 914 and 898 cm^{-1} for $\text{Mo}^{16}\text{O}_2(\text{L})$, respectively. In the vibrational spectra of the ^{18}O substituted derivatives, the $\nu(\text{MO}_2)_s$ were shifted to lower energy by 43 cm^{-1} for $\text{W}^{18}\text{O}_2(\text{L})$ and by 41 cm^{-1} for $\text{Mo}^{18}\text{O}_2(\text{L})$ whereas asymmetric MO_2 stretches in the IR were partially overlapped by an organic ligand related stretch. However, Raman spectroscopy, accompanied by DFT calculations, allowed the deciphering the $\nu(\text{MO}_2)_a$ shifts of 47 cm^{-1} for $\text{W}^{18}\text{O}_2(\text{L})$ and 31 cm^{-1} for $\text{Mo}^{18}\text{O}_2(\text{L})$.

Introduction

A number of dioxidotungsten^{VI} and -molybdenum^{VI} compounds have been prepared for catalytic applications in important industrial processes, such as olefin epoxidation.^[1, 2] Such complexes are also considered as soluble molecular models for metal oxide catalysts.^[3] Moreover, tungsten and molybdenum are found in nature as water-soluble and biologically available high-valent oxido species and are used by a variety of metalloenzymes that take part in oxygen atom transfer (OAT) reactions. In such reactions, an oxygen atom is transferred from an oxygen donor to a biologically relevant acceptor molecule or vice versa.^[1, 2, 4, 5] Bearing in mind these important biological functions, many examples of tungsten- and molybdenum-containing model compounds for OAT studies have been prepared.^[6–10] We have previously synthesized a number of tungsten^{VI} complexes with amine bisphenolate ligands using tungsten^{VI} alkoxide $\text{W}(\text{eg})_3$ ($\text{eg} = \text{ethylene glycolate dianion}$) as a precursor and found that the

number of terminal oxido ligands in the formed complex depends on the denticity of the amine bisphenol. That is, tridentate ligands (H_2ONO) yield monooxido complexes $\text{WO}(\text{eg})(\text{ONO})$ whereas the use of tetradentate ligands (H_2ONOX , X = a neutral donor atom) leads to the formation of dioxido complexes $\text{WO}_2(\text{ONOX})$.^[11–13] However, the origin of these terminal oxido ligands in the reactions of a trisglycolate precursor is not unambiguous. Water is the most likely source of the oxo-groups, but, on the other hand, it is known that high-valent molybdenum, tungsten and rhenium alkoxides can decompose by an elimination process, which yields an ether and the corresponding oxidometal species.^[14, 15] We decided to investigate the mechanism of the formation of the oxido species by reacting $\text{W}(\text{eg})_3$ with an amine bisphenol ligand in the presence of either $\text{H}_2[^{16}\text{O}]$ or $\text{H}_2[^{18}\text{O}]$ to form a dioxido complex $\text{WO}_2(\text{L})$. If the formation of the WO_2^{2+} moiety occurs due to ether elimination, $\text{W}^{16}\text{O}_2(\text{L})$ is expected to form regardless of whether $\text{H}_2[^{16}\text{O}]$ or $\text{H}_2[^{18}\text{O}]$ is used, whereas the hydrolytic cleavage of the alkoxide bonds should lead to the formation of $\text{W}^{16}\text{O}_2(\text{L})$ and $\text{W}^{18}\text{O}_2(\text{L})$, correspondingly. These two isotopologues can be easily differentiated by the mass spectroscopy and are expected to have distinctive vibrational spectra as well.

For the investigation of the $^{16}\text{O}/^{18}\text{O}$ labelling in the synthesized dioxido complexes we selected IR spectroscopy which is a powerful tool in probing the *cis*- MO_2 (M = Mo, W) unit as it usually generates two characteristic strong to medium absorption bands around 900 cm^{-1} in the IR spectrum. Since the pioneering work by Griffith in the late 1960's, these IR absorptions are generally assigned as symmetric and asymmetric O=M=O stretches, respectively.^[16, 17] Specifically, molecular complexes $[\text{MoO}_2(\text{L})_n]$ show two distinctive absorption maxima at 915–935 and 890–905 cm^{-1} , respectively, whereas complexes $[\text{WO}_2(\text{L})_n]$ display typically two strong vibrational bands at ca. 930–960 and 870–920 cm^{-1} in their IR spectra.^[4, 6–10, 12, 18–22] Generally, these two bands show a difference of 20–35 cm^{-1} . For tungsten complexes, the former bands usually occur at 10–25 cm^{-1} higher frequencies than those of their molybdenum congeners. For example, the resonances $\nu(\text{MO}_2)_s$ and $\nu(\text{MO}_2)_a$ for $[\text{MO}_2(\text{ONNO}^{\text{H}})]$ (M = Mo, W; $\text{H}_2\text{ONNO}^{\text{H}} = \text{N,N}$ -bis(2-hydroxyphenyl)ethane-1,2-diamine) are seen as strong absorptions at 937 and 916 cm^{-1} for Mo and at 951 and 911 cm^{-1} for W complexes, respectively.^[7]

To date, numerous dioxidotungsten^{VI} and -molybdenum^{VI} complexes with tetradentate amine phenolate ligands have been prepared and their IR spectra have been reported.^[6, 7, 12, 23, 24] We have earlier prepared the structurally identical complexes of tungsten and molybdenum using *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)-*N,N'*-dimethylethane-1,2-diamine (H_2L) ligand with a natural isotope distribution (Figure 1).^[13, 25, 26] Both these complexes show four strong to medium intensity absorptions in the region typical for the *cis*- MO_2 moiety. These are 959(m), 934(vs), 899 (vs) and 868(m) cm^{-1} for $\text{WO}_2(\text{L})$ and, respectively, 949(m), 914(s), 903(vs) and 868(m) cm^{-1} for $\text{MoO}_2(\text{L})$. Following the generally accepted definition, the strong bands at 934 and 899

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cm^{-1} for $\text{WO}_2(\text{L})$ and corresponding bands at 914 and 903 cm^{-1} for complex $\text{MoO}_2(\text{L})$ were assigned as $\nu(\text{MO}_2)_s$ and $\nu(\text{MO}_2)_a$, respectively. However, at the time it was not possible to unambiguously verify the correct assignment of the vibrational spectra. A significant aspect in the present study is to use the ^{18}O labelling of the terminal oxido-groups to acquire more evidence for the assignment of above-mentioned absorption bands. Therefore, we have prepared not only the ^{18}O labelled $\text{MO}_2(\text{L})$ complexes of tungsten^{VI} but also molybdenum^{VI} and compared their vibrational spectra with the complexes having a natural isotope distribution. In addition, the established reaction routes for the $\text{M}^{18}\text{O}_2(\text{L})$ complexes allowed us to investigate the lability of the terminal oxide ligands in the $\text{WO}_2(\text{L})$ complex in respect to the analogous $\text{MoO}_2(\text{L})$ complex.

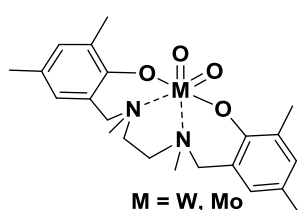


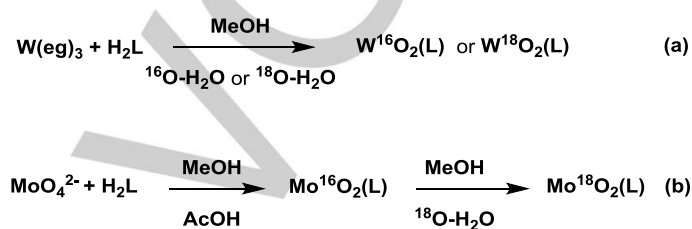
Figure 1. The molecular structure of the studied complexes.

Results and Discussion

Syntheses and Reactivity

The tungsten compounds $\text{W}^{16}\text{O}_2(\text{L})$ and $\text{W}^{18}\text{O}_2(\text{L})$ used in this study were prepared following the known procedure, *i.e.* by the reaction of $\text{W}(\text{eg})_3$ (eg = ethylene glycolate dianion) with the ligand precursor in the presence of $\text{H}_2[^{16}\text{O}]$ or $\text{H}_2[^{18}\text{O}]$ (Scheme 1a). In principle, the formation of a WO_2^{2+} moiety using triglycolate precursor may be due to the ether elimination process of the alkoxide groups^[14, 15] or by hydrolysis. The mass and IR spectra (see below) show that the addition of either $\text{H}_2[^{16}\text{O}]$ or $\text{H}_2[^{18}\text{O}]$ in the reaction mixture leads to the clean formation of the respective isotopologue which demonstrates that the formation of dioxidotungsten centre is caused by the hydrolysis reaction wherein the included water acts as the oxide source. The molybdenum complex $\text{Mo}^{16}\text{O}_2(\text{L})$ was prepared by the reaction of sodium molybdate with the ligand precursor H_2L in an acidic methanol solution.^[26] The ^{18}O enriched complex $\text{Mo}^{18}\text{O}_2(\text{L})$ was obtained straightforwardly by heating $\text{Mo}^{16}\text{O}_2(\text{L})$ with an excess of $\text{H}_2[^{18}\text{O}]$ in methanol solution and allowing the complex to crystallize upon cooling (Scheme 1b). The tungsten complex

$\text{W}^{16}\text{O}_2(\text{L})$ can be made of sodium tungstate following the identical procedure applied for the preparation of $\text{Mo}^{16}\text{O}_2(\text{L})$. However, the oxygen atom exchange with $\text{H}_2[^{18}\text{O}]$ was found unproductive. All products were identified by ^1H and ^{13}C NMR spectroscopy, which show expected chemical shifts for the octahedral complexes with C_2 rotation axis.^[13, 25] The isotopic purity of the compounds was unequivocally confirmed by mass spectrometry. We also studied the possibility of structural polymorphs forming upon the ^{18}O substitution, but the measured powder X-ray diffraction patterns (PXRD) of all four studied complexes demonstrated the isostructural nature of the bulk samples and their distinctive correspondence to the simulated PXRD patterns of the respective single crystal structures^[25, 26] (see Figure S1 in the Supporting Information).



Scheme 1. Preparation of studied complexes.

Spectral characterization

The general features of IR spectra of all studied compounds are very similar apart from strong absorptions around 900 cm^{-1} ; *i.e.* the anticipated spectral region of the *cis*- MO_2 related absorptions (Figure 2). The IR frequencies for the *cis*- MO_2 related absorptions are expected to show shifts to the lower energy upon ^{18}O substitution assuming that the lattice parameters and atomic positions remain the same. It was also anticipated that the isotope substitutions would shift the frequencies of both symmetric and asymmetric *cis*- MO_2 stretches roughly 5% ($[\nu(\text{Mo}^{16}\text{O})/\nu(\text{Mo}^{18}\text{O})] = 1.051$)^[27], that is ca. 50 cm^{-1} .^[28-33] These presumptions in mind we carried out an initial assignment of the $\nu(\text{MO}_2)_s$ and $\nu(\text{MO}_2)_a$ modes as follows: for the complexes with natural isotope distribution the symmetric and asymmetric *cis*- MO_2 stretches were found at 914 and 898 cm^{-1} in case of $\text{Mo}^{16}\text{O}_2(\text{L})$ whereas for $\text{W}^{16}\text{O}_2(\text{L})$ the respective IR absorption bands were found at 934 and 899 cm^{-1} . While these absorption bands were straightforward to decipher we experienced difficulties in identifying the $\nu(\text{MO}_2)_a$ modes of the ^{18}O enriched complexes. The parameter $\Delta = \nu(\text{MO}_2)_s - \nu(\text{MO}_2)_a$ (cm^{-1}) can be used to position these absorption bands; in related *cis*- MO_2 complexes Δ is typically ca. 33 cm^{-1} for tungsten^[24] and ca. 22 cm^{-1} for molybdenum.^[5] The $\nu(\text{MO}_2)_s$ bands for $\text{Mo}^{18}\text{O}_2(\text{L})$ and $\text{W}^{18}\text{O}_2(\text{L})$ were seen at 873 and 891 and cm^{-1} , respectively, but

Table 1. The experimental (IR and Raman) and calculated (RI-PBE/def2-TZVP) *cis*- MO_2 related symmetric (s) and asymmetric (a) vibrational frequencies (in cm^{-1}) for all studied complexes.

Compound	IR			Raman			Calculated		
	$\nu(\text{MO}_2)_s$	$\nu(\text{MO}_2)_a$	Δ^a	$\nu(\text{MO}_2)_s$	$\nu(\text{MO}_2)_a$	Δ	$\nu(\text{MO}_2)_s$	$\nu(\text{MO}_2)_a$	Δ
$\text{W}^{16}\text{O}_2(\text{L})$	934	899	35	933	900	33	947	918	29
$\text{W}^{18}\text{O}_2(\text{L})$	891	– ^b	–	891	863-872 ^b	19-28	898	872	26
$\text{Mo}^{16}\text{O}_2(\text{L})$	914	898	16	914	897	17	948	936	12
$\text{Mo}^{18}\text{O}_2(\text{L})$	873	859	14	873	ca. 860	13	900	894	6

^a $\Delta = \nu(\text{MO}_2)_s - \nu(\text{MO}_2)_a$, ^bPartially obscured by amine phenolate ligand-M $\nu(\text{O}-\text{M}-\text{O})_a$ at 850-860 cm^{-1} region.

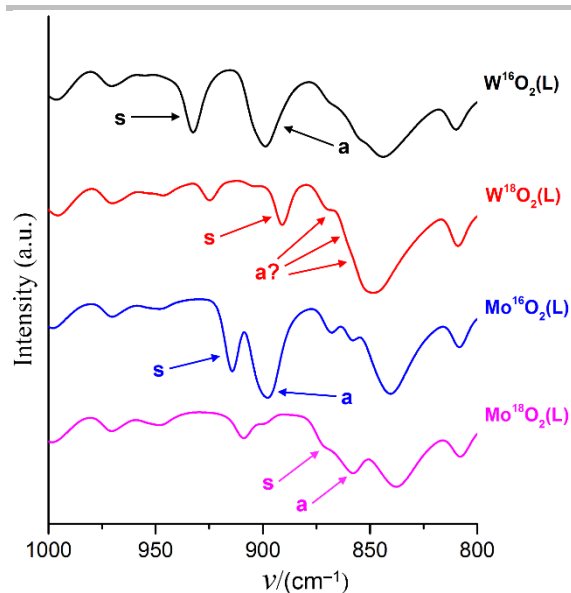


Figure 2. The Infrared spectra of $W^{16}O_2(L)$ (black), $W^{18}O_2(L)$ (red), $Mo^{16}O_2(L)$ (blue) and $Mo^{18}O_2(L)$ (violet) with assigned symmetric and asymmetric *cis*- MO_2 vibrations marked with “s” and “a”, respectively.

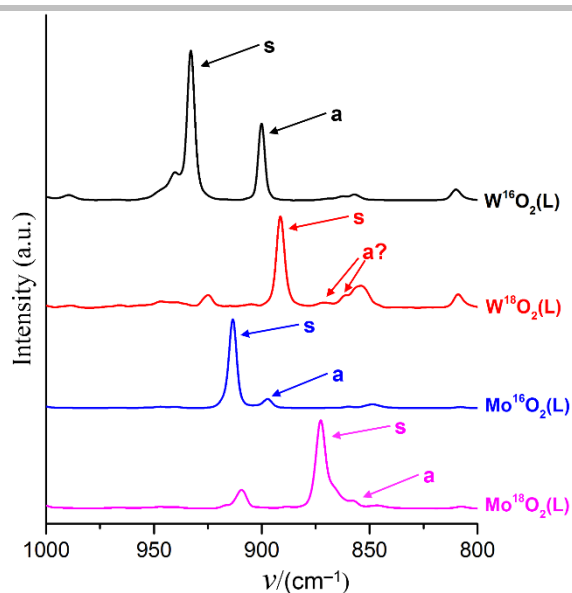


Figure 3. The Raman spectra of $W^{16}O_2(L)$ (black), $W^{18}O_2(L)$ (red), $Mo^{16}O_2(L)$ (blue) and $Mo^{18}O_2(L)$ (violet) with assigned symmetric and asymmetric *cis*- MO_2 vibrations marked with “s” and “a”, respectively.

the corresponding $\nu(MO_2)_a$ bands, which were expected to emerge in the 840–870 cm^{-1} region, were obscured by strong absorptions arising from the bisphenolate-metal O–M–O modes. As a result, we were unable to reliably determine these asymmetric $M^{18}O_2$ stretches from IR spectra alone.

To further extend our analysis of the vibrational modes we recorded the Raman spectra of all studied compounds. Due to the approximate C_2 symmetry of the complexes, we expected to see all the vibrational modes both IR and Raman active but the difference in the relative intensities of the peaks given by the two methods could provide useful information upon the correct assignment of the *cis*- MO_2 stretching modes. The observed Raman spectra exhibit nearly identical modes compared to IR in the 900 ± 50 cm^{-1} area, but show significant differences in their relative intensities (Figure 3). Especially, Raman intensities of $\nu(MO_2)_s$ modes appear much greater than $\nu(MO_2)_a$ which is in stark contrast to the corresponding IR vibration intensities since the symmetric stretch induces a greater change in the dipole moment compared to the asymmetric stretch. The measured Raman spectra therefore support the assignment of 914 and 873 cm^{-1} to the $\nu(Mo^{16}O_2)_s$ and $\nu(Mo^{18}O_2)_s$ modes, respectively, whereas the corresponding symmetric stretching modes of W analogues are observed at 933 and 891 cm^{-1} . This assignment of $\nu(MO_2)_s$ also supports the one done according to the IR spectra (*vide supra*).

To aid in interpreting the experimental IR and Raman spectra we conducted a computational analysis of the natural and ^{18}O enriched complexes by DFT. The experimental single crystal X-ray derived structures of $Mo^{16}O_2(L)$ and $W^{16}O_2(L)$ were first normalized in regard to the C–H distances and then the full geometries were relaxed at the RI-PBE/def2-TZVP level of theory. The optimized geometrical parameters are, at large, in good agreement with the experimental single crystal X-ray bond structures of the complexes. Only the M–N bond lengths deviate slightly from experimental values as they are overestimated by roughly 0.1 Å by the RI-PBE/def2-TZVP method. The optimized

geometries were used to produce the corresponding IR and Raman spectra of ^{16}O and ^{18}O analogues of both Mo and W complexes (Figure S2, see further information in computational details). The geometries exhibit C_2 symmetry and thus all calculated vibrational modes are both IR and Raman active and the calculated IR and Raman spectra of corresponding complexes differ only in their relative intensities. The spectral data showed no significant mixing of the *cis*- MO_2 stretching with other modes thus it was possible to unambiguously assign the symmetric and asymmetric *cis*- MO_2 stretching frequencies of all complexes from the calculated spectra. The relevant calculated vibrational data is shown in Table 1

The general tendency of PBE functional to underestimate the vibrational frequencies results in a good overall agreement between the experimental and calculated frequencies without an external scaling factor. For the $Mo^{16}O_2(L)$ complex the calculated $\nu(MoO_2)_s$ modes appear at 948 and 900 cm^{-1} (experimental 914 and 873 cm^{-1} , in IR) whereas for $Mo^{18}O_2(L)$ the $\nu(MoO_2)_a$ modes are calculated to be at 936 and 894 cm^{-1} (experimental 897 and ca. 860 cm^{-1} , Raman). The calculated differences (Δ) of 12 and 6 cm^{-1} between the symmetric and asymmetric MoO_2 stretching modes of $Mo^{16}O_2(L)$ and $Mo^{18}O_2(L)$ support that the shoulder, observed in the Raman spectrum of $Mo^{18}O_2(L)$ at about 860 cm^{-1} , corresponds to the $\nu(MoO_2)_a$ mode.

In the case of $W^{16}O_2(L)$, the $\nu(WO_2)_s$ is calculated to be 947 cm^{-1} (experimental 934 cm^{-1}) and $\nu(WO_2)_a$ is 918 cm^{-1} (experimental 900 cm^{-1}). For $W^{18}O_2(L)$, the Raman spectrum clearly reveals the $\nu(WO_2)_s$ band at 891 cm^{-1} , even if it is more difficult to assign the $\nu(WO_2)_a$ mode. However, according to the calculated $W^{18}O_2(L)$ frequencies the $\nu(WO_2)_a$ mode should be red shifted ca. 26 cm^{-1} to roughly 865 cm^{-1} . Indeed, this region shows changes upon ^{18}O substitution in both experimental vibrational spectra but particularly in Raman wherein a peak value of either 863 or 872 cm^{-1} can be suggested for the asymmetric stretch. Although we cannot unambiguously assign either of the two to $\nu(W^{18}O_2)_a$ mode, the proposed interpretation indicates that the absorptions at 909

FULL PAPER

cm^{-1} and 925 cm^{-1} in the spectra of ^{18}O substituted Mo and W complexes, respectively, are not related to *cis*- MO_2 modes.

Conclusions

The ^{18}O labelled dioxidometal^{VI} complexes $\text{MO}_2(\text{L})$ ($\text{M} = \text{W}, \text{Mo}$) with a linear, tetradentate amine phenolate ligand (L) were prepared and their IR and Raman spectra were compared with the complexes having a natural isotope distribution. $\text{WO}_2(\text{L})$ was made by the reaction of tungsten(VI) alkoxide $\text{W}(\text{eg})_3$ ($\text{eg} =$ ethylene glycolate dianion) with an amine bisphenol ligand in the presence of either $\text{H}_2[^{16}\text{O}]$ or $\text{H}_2[^{18}\text{O}]$. In both syntheses, the compounds were isolated as pure isotopologues. The formation of two isotopologues confirms that the formation of the oxido ligands is due to the hydrolytic cleavage of the alkoxide bonds instead of possible ether elimination. This reaction provides an easy route to the ^{17}O or ^{18}O dioxido-labelled dioxidotungsten^{VI} complexes. On the other hand, $\text{Mo}^{16}\text{O}_2(\text{L})$ was made of sodium molybdate and converted to $\text{Mo}^{18}\text{O}_2(\text{L})$ by ligand substitution using $\text{H}_2[^{18}\text{O}]$ as an oxide source, which demonstrates the different chemical reactivity of structurally identical W and Mo complexes.

The IR and Raman spectroscopic studies showed that although plenty of earlier experimental data of MoO_2 and WO_2 is available, which aids in characterization of their analogous complexes, the assignment of their symmetric and asymmetric *cis*- MO_2 stretching modes is not trivial. After recognizing the partial overlapping of $\nu(\text{WO}_2)_a$ modes with vibrational modes arising from the ligand backbone, we were able to show, by using experimental IR and Raman and computational analyses, that the symmetric and asymmetric *cis*- MoO_2 stretches of $\text{Mo}^{16}\text{O}_2(\text{L})$ were at ca. 914 and 898 cm^{-1} . The corresponding bands for $\text{W}^{16}\text{O}_2(\text{L})$ were found at ca. 934 and 899 cm^{-1} . In the ^{18}O substituted derivatives, the $\nu(\text{MO}_2)_s$ were shifted to the lower energy by 41 cm^{-1} for $\text{Mo}^{18}\text{O}_2(\text{L})$ and by 43 cm^{-1} for $\text{W}^{18}\text{O}_2(\text{L})$ whereas the corresponding asymmetric stretches shift ca. 39 and $28\text{--}37 \text{ cm}^{-1}$. The rather exhaustive vibrational analyses demonstrate that it is often reasonable to use complementary spectroscopic methods in order to avoid the misinterpretation of spectroscopic data.

Supporting Information Summary

Experimental details, computational details, IR and Raman spectra and X-ray powder diffraction data are available in SI.

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Keywords: DFT, isotopologues, molybdenum, tungsten, vibrational spectra

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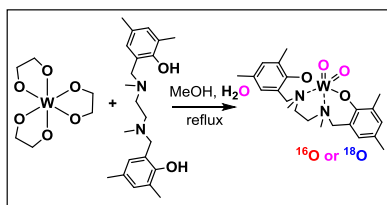
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Entry for the Table of Contents

FULL PAPER

The ^{16}O - and ^{18}O -enriched dioxidotungsten^{VI} and – molybdenum^{VI} complexes with a tetradentate amine phenolate ligand were prepared, whereas their IR and Raman spectra were compared with the complexes having a natural isotope distribution. The clear isotopic shifts to the lower energy were seen in the symmetric and asymmetric stretches attributed to the *cis*- MO_2 moiety. The DFT theoretical calculations support the experimental results.

**Vibrational spectra**

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Page No. – Page No.

The Syntheses and Vibrational Spectra of ^{16}O - and ^{18}O -Enriched *cis*- MO_2 (M = Mo, W) Complexes