

Experimental and theoretical studies on cis-dioxomolybdenum(VI) complexes of ONN-donor thiosemicarbazone

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Abstract: Cis-dioxomolybdenum(VI) chelate complexes with 5-chloro-2-hydroxybenzophenone S-methyl-4-phenylthiosemicarbazone (**L**) were synthesized in the general formula (MoO₂(L)D), where D is an odd- or even-numbered alcohol (methanol (**1**), ethanol (**2**), n-propanol (**3**), n-butanol (**4**), and allyl alcohol (**5**)). The structures of **1–5** were verified by elemental analysis, Fourier transform infrared (FT-IR), and ¹H NMR spectra. Complex **5** crystallizes in the monoclinic space group P21/n, and its crystalline data showed a dimeric structure formed by a pair of intermolecular hydrogen bonds with 1.92 Å. These dimers are stacked in a similar crystalline structure as a single molecule. The experimental data were compared with the theoretical results obtained by the quantum chemical calculations of the DFT/B3LYP method with LANL2DZ basis set. A detailed interpretation of the FT-IR spectra of the studied compounds was performed based on the total energy distribution. In order to investigate the electronic structures and the UV-Vis spectrum of complex **5**, time-dependent density functional theory calculation was taken into account. The interaction energies between the odd- and even-numbered alcohols and remaining parts of complexes **1–4** were evaluated with the help of natural bonding orbital analysis. In addition, the basis set superposition error correction energies were calculated. The results were evaluated by considering the coordinated alcohols with an even number of carbon atoms to have much higher interaction energy than the next lower homologous alcohols with an odd number of carbon atoms.

Key words: Thiosemicarbazone, vibrational spectra, density functional theory, time-dependent density functional theory, basis set superposition error, natural bonding orbital

1. Introduction

Thiosemicarbazones with versatile ligand features have been involved in numerous structural analysis studies. Also, since the 1950s, thiosemicarbazones and their metal complexes have been the subject of pharmaceutical research.^{1–6} Some thiosemicarbazones have been used in clinical drug trials as triapine (3-aminopyridine 2-carboxaldehyde thiosemicarbazone).^{7,8}

Molybdenum is a biologically important trace element that acts in the redox-active sites of molybdoenzymes involved in nitrogen, sulfur, or carbon metabolism.^{9–11} Some dioxomolybdenum(VI) complexes have an ability to participate in the reversible oxo-transfer process of aldehyde oxidase and xanthine dehydrogenase.^{12–14}

Dioxomolybdenum(VI) complexes formed by bidentate ligands such as O₂¹⁵ or N₂¹⁶ and polydentate ligands having donor sets O₂N¹⁷, O₂N₂¹⁸, SO₂N₂¹⁹, or S₂N₂²⁰ can catalyze oxo-atom transfer reactions.^{21–23}

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Molybdenum complexes consisting of 2-hydroxyarylidene thiosemicarbazones with N_2O ^{24,25} or ONS ^{26,27} donor sets are particularly preferred for biological activity tests.

This work contains the preparation, structural characterization, and theoretical calculations of five cis-dioxomolybdenum(VI) complexes with a new ligand, namely 5-chloro-2-hydroxybenzophenone S-methyl-4-phenylthiosemicarbazone (**L**) (Figure 1).

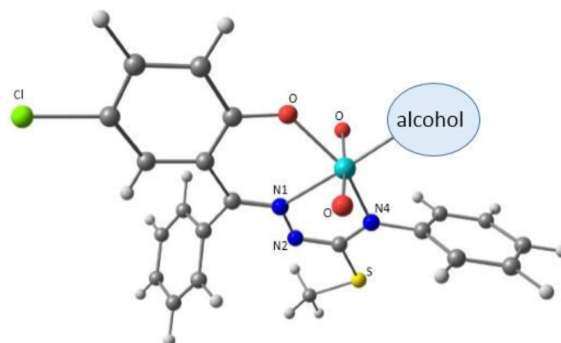


Figure 1. 3D representation of the complexes. Alcohols: MeOH (**1**), EtOH (**2**), n-PrOH (**3**), n-BuOH (**4**), allylOH (**5**).

The compounds were experimentally characterized by elemental analyses, Fourier transform infrared spectroscopy (FT-IR), and ¹H NMR spectra. The molecular and crystal structures of the cis-dioxomolybdenum(VI) complex (**5**), which contains allyl alcohol, was studied by single-crystal X-ray diffraction technique for the first time.

Density functional theory (DFT) calculations perform well with respect to the molecular geometry and vibrational properties of organic compounds. The quantum-mechanical calculations and structural parameters of thiosemicarbazone metal complexes were reported in previous studies.^{28,29} DFT studies will not only help in definitive investigation of molecular properties and in clarifying experimental data, but will also be the base of further studies of cis-dioxomolybdenum(VI) complexes. The experimental results were compared with theoretical calculations based on the DFT technique. The electronic transitions of complex **5** were observed using the UV-Vis spectrum and calculated by time-dependent DFT. Chemical bond characteristics of complex **5** were examined by means of the natural bonding orbital (NBO).

2. Results and discussion

2.1. Some physical properties of the compounds

The thiosemicarbazone ligand was obtained as a crystalline powder, and it was soluble in alcohols and donor solvents such as dimethyl sulfoxide (DMSO). Although complexes **1–5** have different shades of orange, these shades are indistinguishable. The complexes are in the form of fine crystals, moderately soluble in chlorinated hydrocarbons, but highly soluble in dimethyl formamide and DMSO. Despite the decrease of brightness of the crystals in the course of time, the chemical compositions of **1–5** do not change in air for several months, but if left in solution, they slowly decompose within a few days. Transformation of the complexes occurs more quickly in a warm solution, and as a result of decomposition, blackish-green substances are obtained in any case.

2.2. Spectral data

The selected, observed, and calculated wavenumbers of fundamental bands along with their total energy distribution (TED) are summarized in Table S1. The TED values, the calculated vibrational wavenumbers

of the ligand, and complex 5 wavenumbers are given in Tables S2 and S3, respectively. The atom-numbering scheme of the ligand and complex 5 are shown in Figures S1 and S2. Moreover, FT-IR spectra of the complexes are presented in Figure 2.

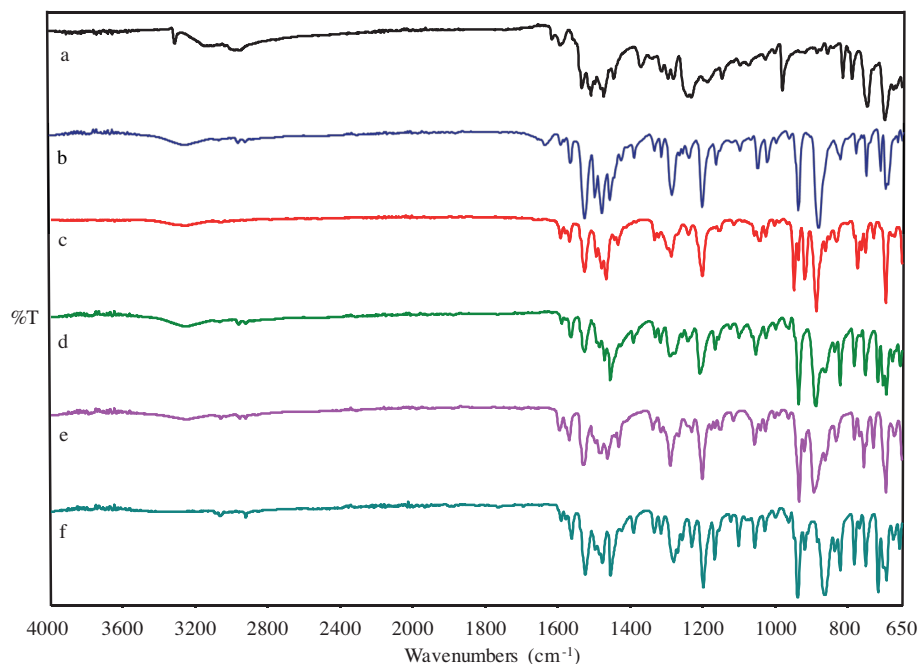


Figure 2. FT-IR spectra of a) ligand, b) $[\text{MoO}_2(\text{L})\text{MeOH}]$ (**1**), c) $[\text{MoO}_2(\text{L})\text{EtOH}]$ (**2**), d) $[\text{MoO}_2(\text{L})\text{PrOH}]$ (**3**), e) $[\text{MoO}_2(\text{L})\text{BuOH}]$ (**4**), f) $[\text{MoO}_2(\text{L})\text{allylOH}]$ (**5**).

FT-IR spectra of the ligand and all complexes were investigated. In the FT-IR spectra of the ligand, the stretching vibrations of the N^4H , $\text{C}=\text{N}^1$, and $\text{N}^2=\text{C}$ groups are clearly observed. The $\nu(\text{N}^4\text{H})$ band disappears in the spectra of the complexes due to the coordination of the deprotonated phenolate and N^4 nitrogen. As a result of the $\text{Mo}-\text{N}^1$ bond formed in the complex, the $\text{C}=\text{N}^1$ stretching mode of the complexes shifts to lower frequencies, whereas the N^1-N^2 stretching mode of complexes shifted to higher frequencies than the ligand.^{30,31}

The N^1-N^2 stretching mode was assigned at 1057 cm^{-1} for **5**, 1058 cm^{-1} for **4**, 1055 cm^{-1} for **3**, 1043 cm^{-1} for **2**, and 1053 cm^{-1} for **1**. The $\text{C}-\text{N}^1$ and $\text{C}-\text{N}^2$ stretching modes were assigned at 1578 and 1525 cm^{-1} for **5**, 1569 and 1531 cm^{-1} for **4**, 1565 and 1527 cm^{-1} for **3**, 1597 and 1527 cm^{-1} for **2**, and 1578 and 1523 cm^{-1} for **1**.

Characteristic antisymmetric stretching bands $\nu_{asym}(\text{MoO}_2)$ and symmetric stretching bands $\nu_{sym}(\text{MoO}_2)$ were observed in the FT-IR spectra of the complexes. The ν_s and ν_{as} bands of the *cis*- MoO_2 group of the complexes can be observed, as strong stretching modes, at $935\text{--}949$ and $864\text{--}895\text{ cm}^{-1}$, respectively.^{32,33} The corresponding bands were observed at $864\text{--}939\text{ cm}^{-1}$ for **5**, $895\text{--}935\text{ cm}^{-1}$ for **4**, $889\text{--}936\text{ cm}^{-1}$ for **3**, $887\text{--}949\text{ cm}^{-1}$ for **2**, and $892\text{--}946\text{ cm}^{-1}$ for **1**. The TED contributions of the MoO_2^{2+} antisymmetric and symmetric stretching modes were approximately 80%.

Bands at 699 , 694 , 696 , 694 , and 696 cm^{-1} due to the $\text{C}-\text{S}$ stretching modes were observed for the ligand and complexes containing allyl alcohol (**5**), n-butanol (**4**), n-propanol (**3**), ethanol (**2**), and methanol (**1**) as the auxiliary ligand, respectively.

The ^1H NMR spectrum of the ligand showed the expected signals arising from the protons due to the phenolic group, aromatic ring, S-methyl, and N^4H groups.^{34–36} The deprotonation (and simultaneous coordination) of the phenolic oxygen and thioamide nitrogen (N^4) can be checked by the ^1H NMR spectra of the complexes. The OH and N^4H proton signals of complexes **1–5** disappear due to chelation, and the singlet-shaped peak for the S-methyl protons shifted upfield from 2.65 ppm to 1.95–1.98 ppm. After coordination of the ligand to the molybdenum center, the chemical shifts of the aromatic protons (a, b, and c) did not show a significant change.

The ^1H NMR spectra of the complexes clearly showed the proton-based signals of the coordinated alcohols (D). The shift values and peak patterns of the alcohols were as expected.^{37,38} The chemical shifts of the hydroxyl protons of the alcohols in the spectra of complexes **1–4** were in the range of 4.12–4.32 ppm, but an equivalent proton of allyl alcohol in complex **5** had a shift of 4.69 ppm, such as the one in a similar structure.³¹ The difference probably arises from allyl alcohol, as it is an unsaturated molecule.

The ^{13}C NMR spectrum of the ligand (**L**) showed the expected chemical shift values. Upon coordination, some chemical shifts of its corresponding dioxomolybdenum(VI) complex (**5**) were observed compared to the free ligand. The remarkable shifts (about 7 ppm) are for the carbon atoms, C2 and C15, which are connected/bonded to donor nitrogen atoms (N^1 and N^4) (Figure 3). The data are significant enough to demonstrate the coordination bonds, $\text{N}^1\text{-Mo}$ and $\text{N}^4\text{-Mo}$, and the functionality of the ON^1N^4 donor set on the ligand backbone, considered together with deprotonated phenolic oxygen. After formation of chelate complexes, the other carbon atoms are not affected much (at only 1–2 ppm shifts), and these values indicate that the benzene rings are not distorted to a noticeable extent. Additionally, the shift values of 62.5 (CH_2), 139.8 ($-\text{CH}=\text{}$), and 114.0 ($=\text{CH}_2$) show the presence of allyl alcohol as the second ligand in the complex.

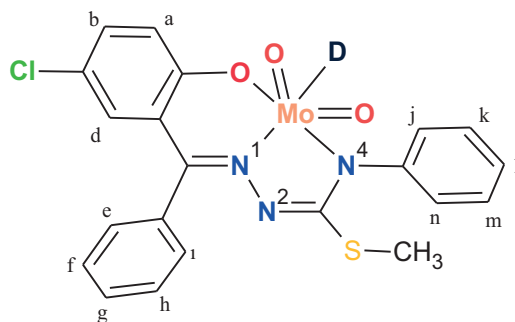


Figure 3. General formula of the complex molecule.

Consequently, the ^1H and ^{13}C NMR spectra confirm the complex structure's ON^1N^4 chelating ligand system and also the coordination of the second ligands (D).

2.3. Crystal structure of complex **5**

A single crystal of complex **5**, suitable for crystal structure analysis, was obtained by recrystallization from a chloroform-allyl alcohol mixture (10:1, v:v). Complex **5** is formed by the chelation of the doubly deprotonated thiosemicarbazone with an ON^1N^4 donor set that consists of a phenoxy oxygen atom and azomethine and thioamide nitrogen atoms. Allyl alcohol (D) is weakly attached to the molybdenum center with a bond distance of 2.380(2). This bond distance was 2.3613(14) Å.³⁰ The bond distances and angles indicate the three-axis

distorted octahedral environments of the molybdenum center. In the structure, the oxo-oxygens are in the cis-position and allyl alcohol is in the trans-position to one of the oxygens (O2) (Figure 4). The double-bonded C23 and C24 atoms of the allyl moiety exhibit disorder.

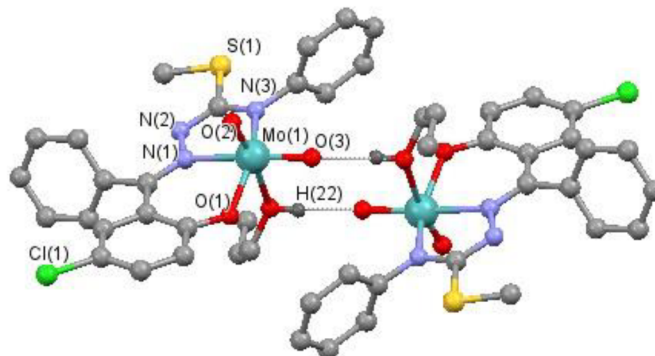


Figure 4. Dimeric structure of complex **5**, showing an intermolecular hydrogen bond of 1.92 Å.

Complex **5** crystallizes in the monoclinic space group P21/n with Z = 4. The crystalline structure includes an intermolecular hydrogen bond involving the hydroxyl proton of the allyl alcohol. The bond parameters are as follows: O4-H22 0.81 Å (calculated 1.0 Å), H22···O3 1.92 Å (calculated 1.62 Å), O3-O4 2.728 Å (calculated 2.737 Å), \angle O4-H22···O3 171.57° (calculated 177.119 Å), (i) 2-x, -y, 2-z. Selected torsion angles and molybdenum-centered angular values of **5** are shown in Tables 1 and 2.

Table 1. Selected torsion angles of complex **5** (°).

| | | | |
|---------------|---------|-------------|----------|
| Mo1-N3-C16-N2 | -0.6(4) | C1-C2-C7-N1 | -15.9(3) |
| Mo1-O1-C1-C2 | 43.7(3) | C1-C2-C7-O3 | 0.7(5) |

Table 2. The molybdenum-centered angular values of complex **5** (°).

| | | | |
|-----------|-----------|------------|-----------|
| O1-Mo1-O2 | 98.28(9) | O3-Mo1-N1 | 157.66(8) |
| O1-Mo1-O3 | 105.98(8) | O3-Mo1-N3 | 93.69(8) |
| O1-Mo1-O4 | 77.26(7) | O4-Mo1-N1 | 78.06(8) |
| O1-Mo1-N1 | 80.80(7) | O4-Mo1-N3 | 78.8(1) |
| O1-Mo1-N3 | 146.79(8) | N1-Mo1-N3 | 72.1(1) |
| O2-Mo1-O3 | 105.8(1) | Mo1-O4-C22 | 132.7(2) |
| O2-Mo1-O4 | 171.31(9) | Mo1-N1-C7 | 127.9(2) |
| O2-Mo1-N1 | 93.9(1) | Mo1-N1-N2 | 117.0(1) |
| O2-Mo1-N3 | 101.8(1) | Mo1-N3-C14 | 118.1(1) |
| O3-Mo1-O4 | 82.69(9) | Mo1-N3-C16 | 121.9(2) |

For analogous cis-MoO₂⁺ complexes obtained from 2-hydroxyarylidene thiosemicarbazones, a hydrogen bond (1.767 Å), which is between the hydroxy proton of the coordinated alcohol and terminal oxo-oxygen of another complex molecule, was first reported in a previous article.³¹ In the single crystal of complex **5**,

an intermolecular hydrogen bond, which is shorter than the σ -coordination bonds, was 1.92 Å. The crystal structure does not contain remarkable short contacts, except the hydrogen bond. Hydrogen bonding connects two molecules consisting of a dimer, and these supramolecular-like structures are stacked in a crystalline structure resembling a single molecule (Figure 5).

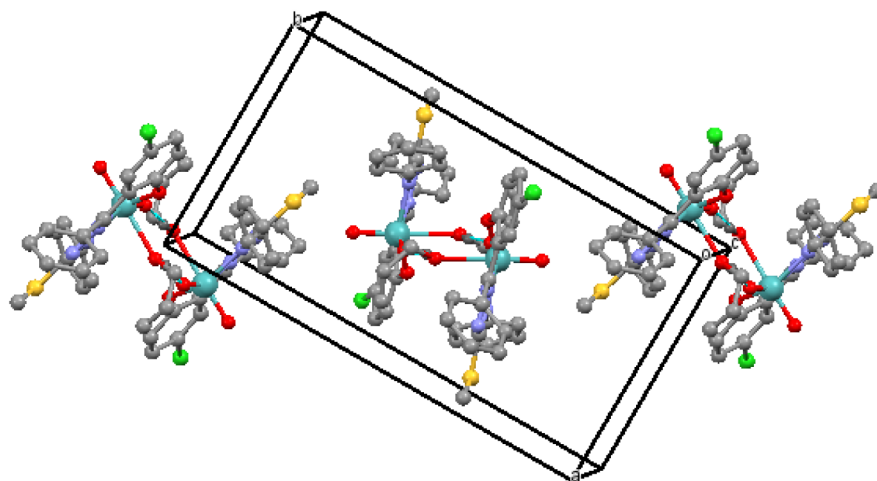


Figure 5. Unit cell packing diagram of complex **5** dimers.

Mo-O1, Mo-O2, Mo-O3, Mo-O4, Mo-N1, and Mo-N3 bond lengths were 1.965 Å, 1.735 Å, 1.745 Å, 2.529 Å, 2.284 Å, and 2.076 Å, respectively. Corresponding experimental bond lengths were 1.934 Å, 1.684 Å, 1.711 Å, 2.380 Å, 2.245 Å, and 2.059 Å. N1-N2 bond lengths were 1.266 Å in the ligand and 1.408 Å in the allyl alcohol-bound molecule (this value was 1.393 Å with experiments).

O4-Mo-O2, O3-Mo-N1, O1-Mo-N3, O4-Mo-O1, O4-Mo-O3, O4-Mo-N1, O4-Mo-N3, and N2-N1-Mo bond angles were 176.94°, 154.37°, 146.05°, 100.45°, 107.31°, 97.18°, 101.18°, and 115.06°, respectively. Corresponding experimental values were 171.31°, 157.66°, 146.79°, 77.26°, 82.69°, 78.06°, 79.08°, and 117.0°. The rest of the experimental and computed molecular geometric parameters are given in Table S1 and compared. The results show that there is reasonable agreement between calculated and experimental geometric parameters.

2.4. TD-DFT

The electronic transitions of complex **5** were observed via the UV-Vis spectrum and calculated by TD-DFT/B3LYP with the LANL2DZ basis set. The lowest 45 singlet-to-singlet spin-allowed excitation states were calculated with the same functional and basis set. TD-DFT calculation in chloroform as the solvent was performed. The calculated results involving oscillator strength (f), wavelength (scaled by 0.862)³⁷, and major contributions of the most intense transitions were obtained and compared with measured experimental wavelengths listed in Table S4. Experimental absorption bands were interpreted by means of theoretical results. The experimental and calculated UV-Vis spectra are provided in Figure 6.

A 1×10^{-4} M solution of complex **5** was prepared in chloroform. Complex **5** displayed six bands in the UV-Vis spectrum. The bands at 240 and 251 nm were assigned to the $\pi \rightarrow \pi^*$ transitions. The absorption bands at 310 nm ($f = 4.19$) and 358 nm ($f = 3.92$) were associated with $n \rightarrow \pi^*$ transitions. According to results of TD-DFT calculation, the bands at 310 nm (mainly (S3-2pz) and (S3-1pz) \rightarrow (Mo1-1dyz) and (Mo1-1dx²-y²)) and 435 nm (mainly (N9-1pz) and (N9-2pz) \rightarrow (Mo1-1dyz) and (Mo1-1dx²-y²)) were attributed

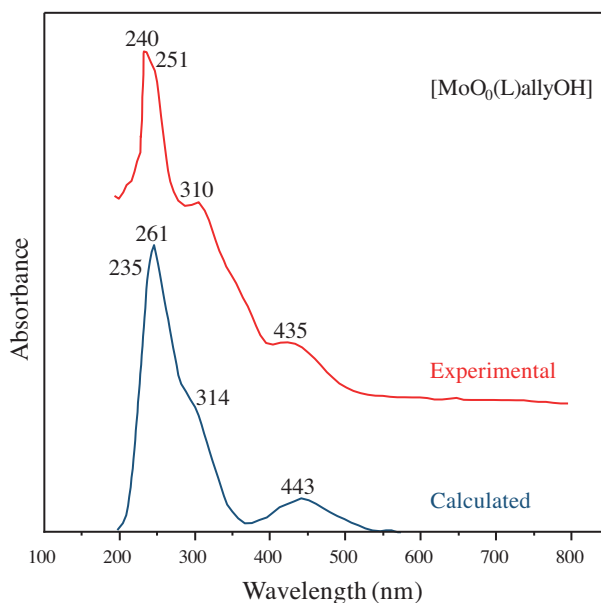


Figure 6. The experimental and DFT-generated UV spectra of $[\text{MoO}_2(\text{L})\text{allyOH}]$ (**5**).

to charge transfer transitions from the ligand to metal. The calculated oscillator strength values near unity represent strong transitions, while the values near 0.001 represent quantum-mechanically forbidden transitions. The most intense electronic transitions predicted by TD-DFT at 443 nm ($f = 0.0406$), 314 nm ($f = 0.0731$), and 235 nm ($f = 0.1438$) are consistent with the experimental data of 435 nm, 310 nm, and 251 nm.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the most significant orbitals in the molecules for reactivity and kinetic stability. Therefore, some parameters (ionization energy, electron affinity, global hardness, and chemical potential)³⁸ obtained from the HOMO and the LUMO were calculated by B3LYP with the LANL2DZ basis set.³⁹ The results are listed in Table S5. The atomic orbital compositions of the HOMO and LUMO are shown in Figure 7.

2.5. NBO analysis

NBO analysis is important for understanding the delocalization effect from the donor to the acceptor.³⁹ The stabilization energy $E(2)$, derived from the interactions between the donor and acceptor orbitals, was estimated by second-order perturbation interaction energy in the NBO.^{29,30} The second-order perturbation energies $E(2)$ (donor \rightarrow acceptor), which involve the most important delocalization energies of the ligand, methanol-, ethanol-, n-propanol-, n-butanol-, and allyl alcohol-bearing complexes, are given in Tables S6–S11, respectively. The important interaction in the ligand has a lone N2 pair with anti- π bonding C=N4. The result of the stabilization was 64.89 kcal/mol. The stabilization energies of these interactions were obtained as 11.82, 11.80, 5.92, 0.89, and 0.45 kcal/mol for n-butanol-, ethanol-, n-propanol-, allyl alcohol-, and methanol-bearing complexes, respectively.

The calculation results are compatible with the molecule including a molybdenum ion and thiosemicarbazone ligand.^{40,41}

The contributions of the stabilization energies for the $E \rightarrow \pi - \pi^*$ charge transfers of the ligand and relevant complexes were obtained as 455.92 kcal/mol for **L**, 521.11 kcal/mol for **4**, 519.96 kcal/mol for **2**, 560.45 kcal/mol for **5**, 274.59 kcal/mol for **3**, and 249.80 kcal/mol for **1**.

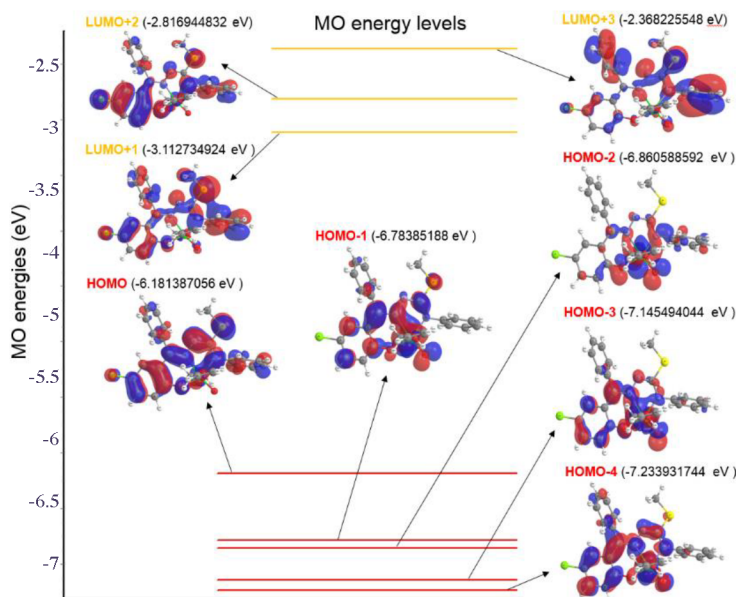


Figure 7. The MO energy levels of $[\text{MoO}_2(\text{L})\text{allylOH}]$ (**5**).

According to the NBO, the electronic arrangement of the Mo in complexes **1–5** are respectively as follows: $(\text{Kr})5\text{S}(0.22)4\text{d}(4.09)5\text{p}(0.50)5\text{d}(0.05)$, $(\text{Kr})5\text{S}(0.22)4\text{d}(4.07)5\text{p}(0.32)5\text{d}(0.05)6\text{p}(0.18)$, $(\text{Kr})5\text{S}(0.22)4\text{d}(4.07)5\text{p}(0.49)5\text{d}(0.05)$, $(\text{Kr})5\text{S}(0.22)4\text{d}(4.07)5\text{p}(0.32)5\text{d}(0.05)6\text{p}(0.18)$, and $(\text{Kr})5\text{S}(0.22)4\text{d}(4.07)5\text{p}(0.32)5\text{d}(0.05)6\text{p}(0.18)$, with 4.81489, 4.78063, 4.78142, 4.78145, and 4.78170 valence electrons. Natural charges were 1.15860, 1.19667, 1.19600, 1.19551, and 1.19590, respectively.

The dimeric structure of complex **5** is a supramolecular-like structure formed by the hydrogen-bonding interaction between two adjacent monomers. In this structure, charge transfer has taken place.

2.6. Odd- and even-numbered alcohols as second ligands

The stabilization and interaction energies of the molybdenum-alcohol system were calculated by means of the NBO and BSSE (Figure 8). In light of the obtained results, the relationship between the carbon chain of alcohols and the $\text{Mo-O}_{\text{alcohol}}$ bond energy is discussed.

The carbon atoms of the alcohols (D) are arranged in a zig-zag manner. In odd-numbered alcohols, methyl and OH groups can be placed on the same and opposite sides. Alcohols with opposite terminal groups have higher symmetry and so the molecules result in a more regular crystal.⁴²

According to the interaction energies obtained from NBO and BSSE calculations of complexes **1–4**, electron density is on the carbon atoms placed at the end of the zig-zag chain and stabilization energy of $\pi \rightarrow \pi^*$ shows a zig-zag change as a result of the different molecular weights of the alcohols with odd and even numbers of carbon atoms, as seen in Figure 8.

Carbon atoms of even-numbered alcohols are closely packed in the crystal lattice.⁴² Hence, the van der Waals forces of even-numbered alcohols are stronger than those of odd-numbered alcohols in the solid state. This is referred to as the alternation effect due to the differences in the shape, size, and packing of the alcohols, which means that alcohols with an even number of carbon atoms have much higher interaction energy than the next lower homologous alcohols with an odd number of carbon atoms. In addition, alcohols

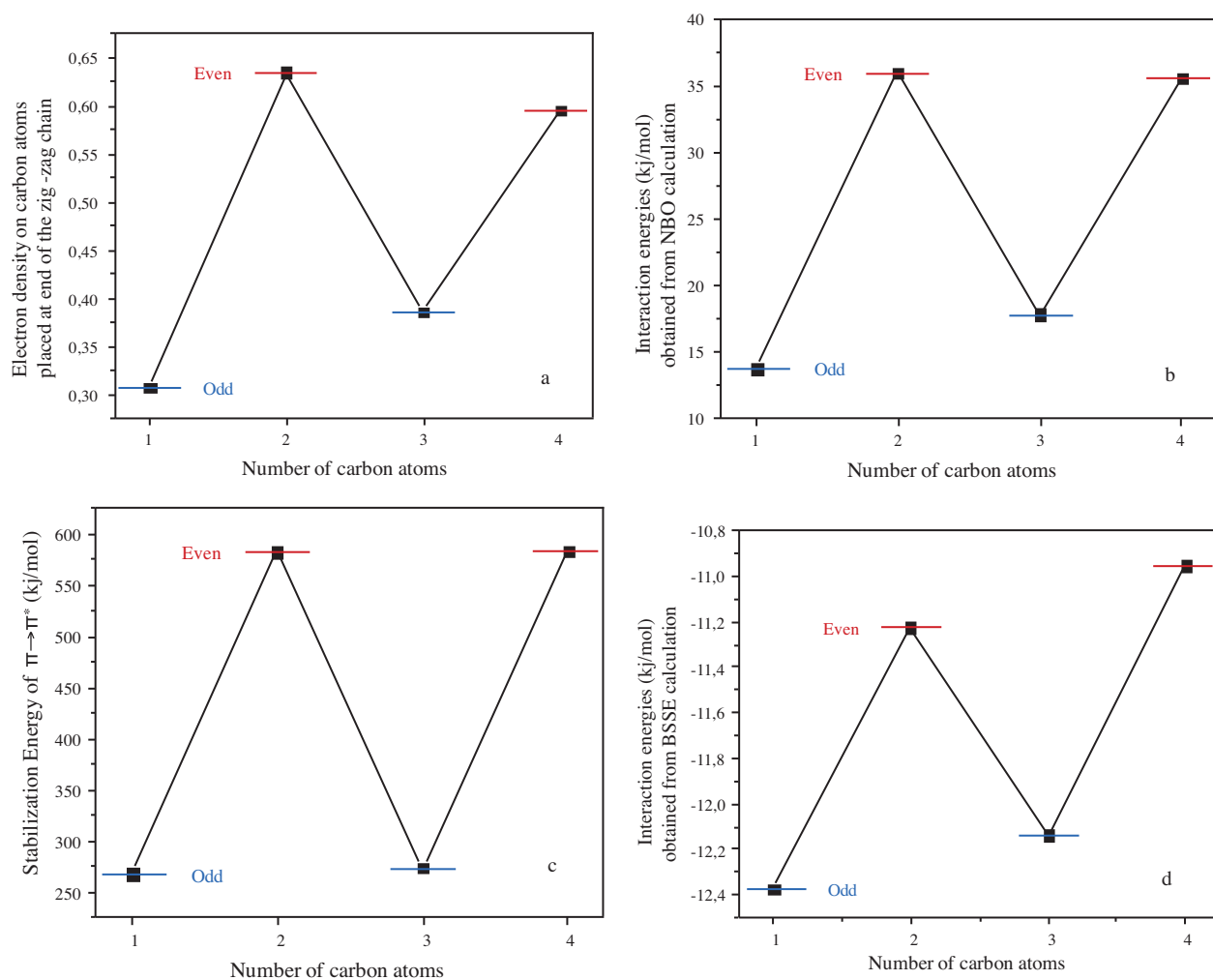


Figure 8. Plot of number of carbon atoms versus: a) electron density on carbons atoms placed at the end of the zig-zag chain; b) interaction energies (kJ/mol) obtained from NBO calculation; c) stabilization energy of $\pi \rightarrow \pi^*$ (kJ/mol); d) interaction energies (kJ/mol) obtained from BSSE calculation.

with odd and even numbers of C atoms have different chain lengths and different molecular arrangements. The electron-withdrawing effect from the O atom to the C atoms occurs in the chain of the alcohols.^{42,43} Theoretical calculations confirmed that the electron density is much higher in the last C atom of the alcohols (Figure 8). In light of the results discussed above, it can be suggested that odd-numbered alcohols show a globular structure, while even-numbered alcohols show an oblate structure.

2.7. Conclusions

Five new cis-MoO₂ complexes (**1–5**) of an ON¹N⁴-chelating thiosemicarbazone were synthesized and characterized. The crystal structure of complex **5** (which has allyl alcohol as the coligand) showed a quite strong intermolecular hydrogen bond with a length of 1.92 Å, shorter than the coordination bonds in the complex molecule. Geometric calculation showed that the relatively short intermolecular connection was 1.62 Å. These interactions resulted in a dimer-resembling supramolecular structure, with the dimers packed as singular molecules in the crystal.

Complexes bearing methanol, ethanol, *n*-propanol, *n*-butanol, and allyl alcohol as the coligands were also investigated with DFT, TD-DFT, and NBO methods and BSSE approximation.

NBO methods indicate that the different stabilization energies of complex molecules coordinated odd and even alcohols, probably because of globular and oblate structures of odd- and even-numbered alcohols, respectively. The calculated values are 274.59–268.05 kcal/mol for odd-numbered alcohols and 583.53–582.40 kcal/mol for even-numbered alcohols.

The differences between the experimental and theoretical values are quite large. This can be explained by the fact that the calculations assume an isolated molecule where the intermolecular interactions are absent in the gaseous phase, while the experimental results are based on interacting molecules in the solid phase.

3. Experimental

3.1. General remarks

Analytical data were obtained with a Thermo Finnigan Flash EA 1112 analyzer (Waltham, MA, USA). ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer (Billerica, MA, USA). The FT-IR spectra of the complexes were measured using a PerkinElmer Spectrum 400 FT-Mid-IR with an ATR unit (Pike Technologies, Madison, WI, USA; Gladi ATR, 3 mm diameter, 45° angle of incidence). The system spectrometer operates in the 4000–600 cm⁻¹ range. The spectral resolution was 4 cm⁻¹ and 200 scans were performed. UV-Vis spectra were obtained using an ATI-Unicam UV/visible spectrophotometer (Markham, ON, Canada).

X-ray measurements were performed on a Rigaku (The Woodlands, TX, USA) RAXIS RAPID imaging plate area detector with graphite monochromated MoK α radiation ($\lambda = 0.71070 \text{ \AA}$). The data were corrected for Lorentzian and polarization effects. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.79 to 1.00. The molecular and crystal structures were solved by direct methods implemented in the program SIR92.⁴⁴ Hydrogen atoms were refined using the riding model and the nonhydrogen atoms were refined anisotropically. All calculations were performed with the crystal structure obtained from the crystallographic software package (Mercury v3.3; Cambridge Structural Database System, Cambridge, UK).^{45,46}

3.2. Preparation of the compounds

The yellow thiosemicarbazone ligand (**L**) was synthesized by the method appearing in the literature.⁴⁷ The general formula is given in Figure 5. Detailed ¹H NMR and ¹³C NMR results are shown in Figures S3–S10 and Tables S12 and S13. Elemental analysis (C, H, N, S) results were in good agreement ($\pm 0.2\%$) with the calculated values.

5-Chloro-2-hydroxobenzophenone-N⁴-phenyl-S-methyl-thiosemicarbazone (**L**): Yellow, yield (%): 45, mp 170.2 °C. For C₂₁H₁₈ClN₃OS (395.91 g/mol), found (calc.): C, 63.81 (63.71); H, 4.71 (4.58); N, 10.38 (10.61); S, 5.89 (6.10). ¹H NMR (DMSO-d₆, δ in ppm): 13.02 (s, 1H, OH) 8.6 (s, 1H, NH), 7.56–6.76 (doublet and triplets, 13H, aromatic rings), 2.65 (s, 3H, S-CH₃). ¹³C NMR (DMSO-d₆, δ in ppm): C1(171.24), C2(158.63), C3(119.60), C4(159.41), C5(120.56), C6(121.66), C7(163.14), C8(135.36), C9(129.88), C10–14(128.72), C11–13(123.22), C12(131.24), C15(140.61), C16–20(128.92), C17–19(129.07), C18(122.62), C21(14.57).

Complex **1** was prepared according to the literature-based method with small modifications as follows: the ligand (0.345 g, 1.0 mmol) was dissolved in absolute methanol (2.0 mL) by heating. The hot solution was treated with 2.0 mL of a methanolic solution of $\text{MoO}_2(\text{acac})_2$ (0.325 g, 1.1 mmol). The reaction mixture was stirred at 60 °C for 5 h and then allowed to stand at room temperature overnight. The orange precipitate was collected by filtration and washed twice with 2–4 mL of cold methanol. Recrystallization of the product from methanol yielded an analytical-grade pure compound. The crystalline powder was dried for 12 h in air.^{32,48}

In order to synthesize complex **5**, we used chloroform as a solvent, and the synthesis was accomplished by eliminating bound *n*-propanol according to the following procedure: 300 mg (0.05 mmol) of complex **3** (having *n*-propanol as the second ligand) was dissolved in chloroform (5 mL) and then 0.007 mL (0.1 mmol) of allyl alcohol was added to the solution. The mixture was allowed to stand at room temperature overnight. The precipitated orange solid product was filtered, recrystallized from chloroform-allyl alcohol mixture (10:1, v:v), and dried in air.

Samples **1–5** were subjected to all analyses mentioned above. Yield (%), mp (°C, uncorrected), microanalysis, and ¹H NMR and ¹³C NMR (DMSO-*d*₆, ppm) data of the second ligands (D) are given below. Elemental analysis (C, H, N, S) results were in good agreement (±0.4%) with the calculated values.

Cis-dioxo (5-chloro-2-hydroxobenzophenone-*N*⁴-phenyl-*S*-methyl-thiosemicarbazonato *N,N,O*)-methanol-molybdenum(VI) (**1**): 51, 264.7. For $\text{C}_{22}\text{H}_{20}\text{ClMoN}_3\text{O}_4\text{S}$ (553.87 g/mol), found (calc.): C, 47.46 (47.71); H, 4.07 (3.64); N, 7.53 (7.59); S, 6.08 (5.79). ¹H NMR chemical shift values of aromatic hydrogens: 6.79 (d, 1H, a), 7.45 (d-d, 1H, b), 6.99 (d, 1H, d) 7.40 (d, 2H, e, i), 7.51–7.56 (m, 3H, f, g, h), 7.33(t, 2H, j, n), 7.21 (t, 3H, k, l, m), D (CH₃OH): 4.12 (s, 1H, OH), 3.16 (s, 3H, CH₃).

Cis-dioxo (5-chloro-2-hydroxobenzophenone-*N*⁴-phenyl-*S*-methyl-thiosemicarbazonato *N,N,O*)-ethanol-molybdenum(VI) (**2**): 70, 260.9. For $\text{C}_{23}\text{H}_{22}\text{ClMoN}_3\text{O}_4\text{S}$ (567.90 g/mol), found (calc.): C, 49.09 (48.64); H, 4.33 (3.90); N, 7.53 (7.40); S, 5.45 (5.65). ¹H NMR for D (HOCH₂CH₃): 4.32 (s, 1H, OH), 3.41–3.45 (m, 2H, CH₂), 1.05 (t, 3H, CH₃).

Cis-dioxo (5-chloro-2-hydroxobenzophenone-*N*⁴-phenyl-*S*-methyl-thiosemicarbazonato *N,N,O*)-propanol-molybdenum(VI) (**3**): 25, 258.8. For $\text{C}_{24}\text{H}_{24}\text{ClMoN}_3\text{O}_4\text{S}$ (581.92 g/mol) found (calc.): C, 49.95 (49.54); H, 4.26 (4.16); N, 7.40 (7.22); S, 5.27 (5.51). ¹H NMR for D (HOCH₂CH₂CH₃): 4.32 (s, 1H, OH), 3.31–3.34 (m, 2H, CH₂), 1.38–1.42 (m, 2H, CH₂), 0.82 (t, 3H, CH₃).

Cis-dioxo (5-chloro-2-hydroxobenzophenone-*N*⁴-phenyl-*S*-methyl-thiosemicarbazonato *N,N,O*)-butanol-molybdenum(VI) (**4**): 64, 259.8. For $\text{C}_{25}\text{H}_{26}\text{ClMoN}_3\text{O}_4\text{S}$ (595.95 g/mol) found (calc.): C, 50.59 (50.38); H, 4.83 (4.40); N, 7.00 (7.05); S, 5.08 (5.38). ¹H NMR for D (HOCH₂CH₂CH₂CH₃): 4.29 (s, 1H, OH), 3.34–3.38 (m, 2H, CH₂), 1.36–1.39 (m, 2H, CH₂), 1.27–1.30 (m, 2H, CH₂), 0.85 (t, 3H, CH₃).

Cis-dioxo (5-chloro-2-hydroxobenzophenone-*N*⁴-phenyl-*S*-methyl-thiosemicarbazonato *N,N,O*)-2-propen-1-ol (allyl-alcohol)-molybdenum(VI) (**5**): 38, 268.5. For $\text{C}_{24}\text{H}_{22}\text{ClMoN}_3\text{O}_4\text{S}$ (579.91 g/mol) found (calc.): C, 50.07 (49.71); H, 4.03 (3.82); N, 7.11 (7.25); S, 5.80 (5.53). UV-Vis [λ (nm)/log ϵ (L mol⁻¹ cm⁻¹)] 240 (4.41), 251 (4.38), 310 (4.19) 435 (3.68). ¹H NMR for D (HOCH₂CH=CH₂): 4.69 (t, 1H, OH), 3.92 (t, 2H, CH₂), 5.87–5.97 (m, 1H, -CH=), 5.01 (d-d, 2H, =CH₂); ¹³C NMR: C1(170.65), C2(151.34), C3(121.16), C4(158.45), C5(124.49), C6(125.37), C7(160.87), C8(133.02), C9(129.69), C10–14(128.89), C11–13 (127.43), C12 (131.87), C15 (133.53), C16–20 (129.18), C17–19(129.32), C18(127.07), C21(15.02), C22(62.48), C23(139.75), C24(114.02).

For X-ray diffraction analysis of complex **5**, crystallographic data and structure refinement parameters are presented in Table 3. Selected bond distances and angles of complex **5** are given in Table S3.

Table 3. Crystal data and structure refinement details for complex **5**.

| | |
|---|---|
| CCDC deposition number | 971335 |
| Chemical formula | C ₂₄ H ₂₂ N ₃ O ₄ ClMoS |
| Crystal habit | Block |
| Crystal size (mm) | 0.60 × 0.40 × 0.20 mm |
| Formula weight (g/mol) | 579.91 |
| Temperature (K) | 294 |
| Wavelength (Å) | 0.71070 |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /n (#14) |
| Unit cell parameters | |
| <i>a, b, c</i> (Å) | 9.7723(3), 17.8540(4), 15.1974(5) |
| γ, β, V | 90°, 101.084(2)°, 2602.10(13) Å ³ |
| Cell volume (Å ³) | 2602.10(13) |
| <i>Z</i> | 4 |
| Density (g/cm ³) | 1.480 |
| Absorption coefficient (mm ⁻¹) | 0.204 |
| <i>F</i> ₀₀₀ | 1176.00 |
| Index ranges | -13 ≤ <i>h</i> ≤ 13, -25 ≤ <i>k</i> ≤ 25, -21 ≤ <i>l</i> ≤ 21 |
| Reflections collected | 7836 |
| Independent reflections | 6617 |
| <i>R</i> _{int} | 0.028 |
| Data reflections / parameters | 147206 / 332 |
| Goodness of fit indicator | 1.026 |
| Final <i>R</i> indices [<i>I</i> > 3σ(<i>I</i>)] | R1 = 0.046, wR2 = 0.062 |
| Δ <i>p</i> max, Δ <i>p</i> min (e/Å ³) | 1.43, -0.68 |

a, b, c: Cell parameters, β : cell angles, *V*: cell size, *Z*: the unit number of molecules in crystal cells, *R*: residual.

3.3. Computational section

The optimized geometries of the monomeric and dimeric structures of complex **5** were obtained via the DFT/B3LYP method combined with the LANL2DZ basis set, employing Gaussian 09 software (Gaussian, Inc., Wallingford, CT, USA) in order to determine the change in the geometric structure of the synthesized complexes.³⁹ The same calculations were repeated for complexes **1–4**. In order to evaluate the optimized geometries, the initial geometries of all complexes and the dimeric structure of complex **5** were constructed based on the crystallographic data of complex **5**. The harmonic wavenumbers of the complexes were calculated by the DFT with the same functional and basis set. The selected bond lengths and angles for the calculated and experimental data are compared in Table S14. The theoretically optimized parameters were slightly less than the experimental values due to disparity of the phase of the complexes: the gaseous phase for theoretical and the solid phase for experimental analysis.

The probable donor–acceptor interactions and electronic transitions of complex **5** were examined with Gaussian 09 software, utilizing the NBO with the DFT/B3LYP and TD-DFT/B3LYP methods combined with the LANL2DZ basis set, respectively. Systematic values of calculated coordination bond energies for the odd- and even-numbered alcohols bound to the molybdenum center were suggested by means of BSSE approximation.

3.4. Supplementary data

CCDC number 971335 contains the supplementary crystallographic data for complex **5** (C₂₄H₂₂ClMoN₃O₄S). The data can be obtained, free of charge, via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or email: deposit@ccdc.cam.ac.uk.

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Supplementary

Table S1. Selected calculated wavenumbers, experimental wavenumbers, and TED values of the ligand and related complexes.

| Assign. | Ligand | | | Complex | | | | | |
|--------------------------------------|--------|------|---|----------|------|---|---------|------|--|
| | E | C | TED (>10%) | Methanol | | | Ethanol | | |
| | E | C | TED (>10%) | E | C | TED (>10%) | E | C | TED (>10%) |
| v(OH) | - | 3675 | (94)v(O-H) | - | 3675 | (100)v(O-H) | - | 3672 | (100)v(O-H) |
| v(NH) | 3303 | 3401 | (100)v(N-H) | | | | | | |
| v(C=N ¹) | 1592 | 1602 | (45)v(C-N ₁), (15)v(C-N ₂) | 1578 | 1554 | (35)v(C-N ₁) | 1579 | 1548 | (39)v(C-N ₁), (20)v _{ring} , |
| | | | | | | (23)v _{ring} , (14)δ(CH) _{ring} | | | (16)δ(CH) _{ring} |
| v(C=N ²) | 1532 | 1412 | (23)v(C-N ₂), (12)v(C-N ₄) | 1523 | 1453 | (41)v(C-N ₂), (11)δ(CH) _{ring} | 1527 | 1483 | (24)v(C-N ₂), (15)v(C-N ₁) |
| | | 1354 | | | | | | | |
| δ(COH) | 1241 | 1378 | (29)v _{ring} , (16)δ(CH) _{ring} , | 1265 | 1345 | (40)δ(COH), (25)v _{ring} , | 1272 | 1340 | (40)δ(COH), (23)v _{ring} , |
| | | 1196 | (15)δ(COH) | | | (18)δ(CH) _{ring} | | | (14)δ(CH) _{ring} |
| v(CO) | 1230 | 1259 | (37)v(C-O), (25)v _{ring} , | 1241 | 1269 | (35)v(C-O), (27)v _{ring} , | 1240 | 1270 | (42)v(C-O) |
| | | | (18)δ(CH) _{ring} | | | (17)δ(CH) _{ring} | | | |
| v(C-S) | 699 | 657 | (75)v(C-S), (10)δ _{ring} , | 697 | 656 | (68)v(C-S) | 696 | 660 | (88)v(C-S) |
| v(N-N) | 980 | 1581 | (32)v(N-N), (16)v _{ring} , | 1053 | 1057 | (29)v _{ring} , (21)δ _{ring} , | 1043 | 1039 | (29)v _{ring} , |
| | | | (14)v(C-N ₁), (9)v(C-N ₄) | | | (17)δCH _{ring} , (14)v(N-N) | | | (24)v(N-N), (21)δ _{ring} |
| v(MoO ₂) _{asym} | | | | 941 | 953 | (78)v(O=Mo), (10)δ _{ring} , | 949 | 1123 | (89)v(Mo=O) |
| | | | | | | (10)γ(CH) _{ring} | | | |
| v(MoO ₂) _{sym} | | | | 885 | 935 | (83)v(O=Mo), (10)v(C-O) | 887 | 1074 | (47)v(Mo=O), (11)δ(COH) |
| v(Mo-N) | | | | 435 | 453 | (33)τ _{ring} , (20)v(N-Mo), | 445 | 463 | (30)v(C-Cl), (15)v(O-Mn) |
| | | | | | | (15)δ _{ring} | | | (15)v(N-Mo) |

| Assign. | n-Propanol | | | n-Butanol | | | Allyl alcohol | | |
|--------------------------------------|------------|------|--|-----------|------|--|---------------|-------|--|
| | E | C | TED (>10%) | E | C | TED (>10%) | E | C | TED (>10%) |
| v(OH) | | 3694 | (100)v(O-H) | | 3677 | (100)v(O-H) | | 3664 | (94)v(O-H) |
| v(C=N ¹) | 1565 | 1548 | (38)v(C-N1), (19)v _{ring} , (18) δ (CH) _{ring} | 1569 | 1547 | (36)v(C-N1), (17)v _{ring} , (16) δ (CH) _{ring} | 1578 | 1547 | (35)v(C-N1), (17)v _{ring} , (16) δ (CH) _{ring} |
| v(C=N ²) | 1527 | 1482 | (28)v(C-N2), (18) δ (CH) _{ring} , (15)v(C-N1), (13)v(C-N4) | 1531 | 1482 | (24)v(C-N2), (15) δ (CH) _{ring} , (12)v(C-N1), (11)v(C-N4) | 1525 | 1481 | (23)v(C-N2), (17) δ (CH) _{ring} , (12)v(C-N1) |
| δ (COH) | 1279 | 1343 | (44) δ (COH), (26)CH ₂ twist, (14)CH ₂ rock, (12)CH ₂ wag | 1267 | 1344 | (44) δ (COH), (26)CH ₂ twist, (14)CH ₂ rock, (12)CH ₂ wag | 1270 | 1341 | (33)CH ₂ twist, (21)tetra O7, (18) δ (COH) |
| v(CO) | 1242 | 1270 | (40)v(C-O), (25)v _{ring} , (16) δ (CH) _{ring} | 1242 | 1270 | (38)v(C-O), (26)v _{ring} , (18) δ (CH) _{ring} | 1257 | 1269 | (39)v(C-O), (26)v _{ring} , (18) δ (CH) _{ring} |
| v(C-S) | 694 | 660 | (80)v(C-S) | 696 | 657 | (78)v(C-S) | 694 | 657 | (79)v(C-S) |
| v(N-N) | 1055 | 1039 | (36)v _{ring} , (25) δ _{ring} , (19) δ (CH) _{ring} , (13)v(N-N) | 1058 | 1057 | (34)v _{ring} , (22) δ _{ring} , (18) δ (CH) _{ring} , (11)v(N-N) | 1057 | 1057* | (32)v _{ring} , (22) δ _{ring} , 1040* |
| v(MoO ₂) _{asym} | 936 | 1118 | (25)v(O-Mo), (19)v(C-O), (18) δ (C-H ₃) | 935 | 952 | (21)v(O-Mo), (19)v(C-O), (18) δ (C-H ₃) | 939 | 947 | (41)v(O-Mo), (16) δ _{ring} , (11)v _{ring} , |
| v(MoO ₂) _{sym} | 889 | 1069 | (65)v(O-Mo), (15) γ (CH) _{ring} | 895 | 937 | (61)v(O-Mo), (14) γ (CH) _{ring} | 864 | 940 | (54)v(O-Mo), (10) γ (CH) _{ring} |
| v(Mo-N) | 405 | 440 | (39) τ _{ring} , (25)v(N-Mo), (22) γ (CH) _{ring} | 410 | 435 | (20) δ _{ring} , (20)v(N-Mo), (10)v(C-Cl) | 395 | 423 | (22) tetrapyrimidine Mo, (20) v(N-Mo), (13) δ (CCS) |

E = Experimental wavenumbers, C = calculated wavenumbers, TED = total energy distribution; v = stretching; δ = in-plane ring bending; γ = out-of-plane ring bending vibrations.

| Table S2. The calculated wavenumbers (cm ⁻¹) and TED (%) of the ligand (L). | |
|---|--|
| Calculated wavenumbers | TED (%), >10% |
| 18 | (66) τ C13-N, (23) δ (CN1N2) |
| 24 | (60) τ N5-N, (12) τ C13-N |
| 31 | (76) τ C13-N, (22) τ N5-N |
| 40 | (52) τ C14-C, (11) δ (CN1N2), (10) δ (CC) |
| 46 | (44) τ C13-N, (19) τ C14-C, (12) δ (CN1N2) |
| 55 | (35) τ C14-C, (14) δ (CC), (13) γ (CC) |
| 70 | (43) τ C21-S, (15) τ C14-C, (10) τ C13-N, (10) τ_{ring} |
| 77 | (26) τ C14-C, (13) γ (CC), (12) τ C21-S, (11) τ_{ring} , (10) τ C13-N |
| 92 | (20) τ_{ring} , (15) τ C13-N, (12) δ (CCN) |
| 99 | (24) τ C21-S, (19) τ C13-N, (11) δ (CN1N2) |
| 112 | (20) τ C13-N, (18) τ_{ring} , (18) δ (CCN), (14)tetra C20, (11) τ C21-S |
| 130 | (50) τ_{ring} , (15)wag CCl |
| 151 | (15) δ (CCN), (13) δ (CN1N2), (12)rock NC, (10)rock CCl |
| 163 | (71) τ C21-S |
| 185 | (22) τ C21-S, (18) τ C13-N, (16) τ_{ring} , (13) tetra C20 |
| 205 | (26) τ_{ring} , (15)rock CCl, (11) τ C13-N |
| 218 | (19) δ (CC), (19) τ_{ring} |
| 240 | (24) τ_{ring} , (10) δ (CC) |
| 246 | (44) δ (CCS), (13) τ_{ring} , (11) δ (CN1N2) |
| 268 | (24) δ (CCS), (14)rock NC |
| 294 | (19) δ_{ring} , (17)rock CCl, (17) ν (C-C), (14) δ (CC) |
| 313 | (42) τ_{ring} , (30)wag CCl, (14) γ (C=O) |
| 338 | (16) ν (C-Cl), (10) δ_{ring} , (10) ν (C-S) |
| 366 | (21) δ_{ring} , (18) τ_{ring} , (17) ν (C-Cl), (13) τ C13-N |
| 382 | (19)tetra C20, (17) δ_{ring} , (14) τ C13-N, (14) τ_{ring} |
| 405 | (26) τ_{ring} , (15) δ_{ring} , (10) δ (CN1N2) |
| 423 | (100) τ_{ring} |
| 423 | (100) τ_{ring} |
| 451 | (27) δ_{ring} , (26) τ_{ring} |
| 467 | (51) τ_{ring} , (21) γ (CC) |
| 479 | (24) τ_{ring} , (15) δ (CN1N2), (15) δ_{ring} , (10)C20 umbrella |
| 507 | (27) δ (C=O), (19) τ_{ring} |
| 540 | (37) τ_{ring} , (15) γ (C=O), (15)wag CCl |
| 550 | (22) τ_{ring} , (14) δ (C=O), (12)wag NC |
| 566 | (25) τ_{ring} , (15)wag NC, (13) ν (C-S) |
| 581 | (20) ν (C-S), (15) δ_{ring} , (13) δ (CCN), (13)rock NC |
| 616 | (33) δ_{ring} , (24)C20 umbrella, (11)tetra C20 |
| 632 | (77) δ_{ring} |
| 634 | (68) δ_{ring} , (16) ν (C-S) |
| 637 | (68) δ_{ring} , (12) ν_{ring} , (11) ν (C-Cl) |
| 657 | (75) ν (C-S) |
| 668 | (38) δ_{ring} , (10) τ_{ring} |
| 677 | (24) τ_{ring} , (14) δ_{ring} |
| 715 | (27) δ_{ring} , (13) δ (CN1N2), (13) ν_{ring} , (11) τ_{ring} |

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| 717 | (73) τ_{ring} , (17) $\gamma(\text{CH})_{\text{ring}}$ |
| 728 | (76) τ_{ring} , (19) $\gamma(\text{CH})_{\text{ring}}$ |
| 744 | (22) ν_{ring} , (18) $\delta(\text{CN1N2})$, (16) δ_{ring} |
| 781 | (31) $\gamma(\text{CH})_{\text{ring}}$, (29) τ_{ring} , (15) $\gamma(\text{C=O})$, (15) $\gamma(\text{CC})$ |
| 801 | (59) $\gamma(\text{CH})_{\text{ring}}$, (19)wag NC, (18) τ_{ring} |
| 811 | (46) $\gamma(\text{CH})_{\text{ring}}$, (17) $\gamma(\text{CC})$, (15) τ_{ring} |
| 830 | (51) ν_{ring} , (24) δ_{ring} |
| 860 | (26) ν_{ring} , (15)tetra C20, (15) δ_{ring} , (11) $\nu(\text{C-N})$ |
| 865 | (59) $\gamma(\text{CH})_{\text{ring}}$, (27) $\gamma(\text{C=O})$ |
| 874 | (99) $\gamma(\text{CH})_{\text{ring}}$ |
| 894 | (100) $\gamma(\text{CH})_{\text{ring}}$ |
| 933 | (100) $\gamma(\text{CH})_{\text{ring}}$ |
| 956 | (40) δ_{ring} , (22) ν_{ring} , (15) $\gamma(\text{CH})_{\text{ring}}$ |
| 957 | (86) $\gamma(\text{CH})_{\text{ring}}$ |
| 976 | (31) $\nu(\text{C-N2})$, (19) $\gamma(\text{CH})_{\text{ring}}$, (11) $\delta(\text{CH}_3)$, (10)tetra C20 |
| 984 | (91) $\gamma(\text{CH})_{\text{ring}}$ |
| 1012 | (65) $\delta(\text{CH}_3)$, (18) δ_{ring} , (13) ν_{ring} |
| 1013 | (100) $\gamma(\text{CH})_{\text{ring}}$ |
| 1014 | (32) δ_{ring} , (28) $\delta(\text{CH}_3)$, (21) $\gamma(\text{CH})_{\text{ring}}$, (20) ν_{ring} |
| 1014 | (57) δ_{ring} , (33) ν_{ring} , (10) $\gamma(\text{CH})_{\text{ring}}$ |
| 1016 | (90) $\gamma(\text{CH})_{\text{ring}}$, (10) δ_{ring} |
| 1032 | (100) $\gamma(\text{CH})_{\text{ring}}$ |
| 1037 | (100) $\gamma(\text{CH})_{\text{ring}}$ |
| 1045 | (67) $\delta(\text{CH}_3)$, (13) ν_{ring} |
| 1047 | (58) ν_{ring} , (18) $\delta(\text{CH})_{\text{ring}}$, (11) $\delta(\text{CH}_3)$ |
| 1049 | (100) $\gamma(\text{CH})_{\text{ring}}$ |
| 1053 | (54) ν_{ring} , (16) $\delta(\text{CH})_{\text{ring}}$, (14) $\gamma(\text{CH})_{\text{ring}}$, (11) δ_{ring} |
| 1079 | (61) ν_{ring} , (22) $\delta(\text{CH})_{\text{ring}}$, (11) $\nu(\text{C-Cl})$ |
| 1110 | (54) ν_{ring} , (40) $\delta(\text{CH})_{\text{ring}}$ |
| 1114 | (53) ν_{ring} , (32) $\delta(\text{CH})_{\text{ring}}$ |
| 1139 | (27) ν_{ring} , (18) δ_{ring} , (15) $\nu(\text{C-N1})$, (15) $\delta(\text{CH})_{\text{ring}}$ |
| 1162 | (45) $\delta(\text{CH})_{\text{ring}}$, (30) ν_{ring} |
| 1203 | (84) $\delta(\text{CH})_{\text{ring}}$, (15) ν_{ring} |
| 1211 | (85) $\delta(\text{CH})_{\text{ring}}$, (15) ν_{ring} |
| 1216 | (63) $\delta(\text{CH})_{\text{ring}}$, (19) ν_{ring} |
| 1224 | (46) $\delta(\text{CH})_{\text{ring}}$, (27) ν_{ring} |
| 1236 | (76) $\delta(\text{CH})_{\text{ring}}$, (24) ν_{ring} |
| 1239 | (25) $\nu(\text{C-N})$, (24) $\delta(\text{CH})_{\text{ring}}$, (23) ν_{ring} |
| 1296 | (41) $\delta(\text{CH})_{\text{ring}}$, (18) $\nu(\text{C-C})$, (16) ν_{ring} |
| 1326 | (46) ν_{ring} , (29) $\delta(\text{CH})_{\text{ring}}$, (16) $\nu(\text{C-C})$ |
| 1349 | (47) $\delta(\text{CH})_{\text{ring}}$, (47) ν_{ring} |
| 1362 | (71) ν_{ring} , (23) $\delta(\text{CH})_{\text{ring}}$ |
| 1367 | (40) $\delta(\text{CH})_{\text{ring}}$, (27) ν_{ring} , (15) $\nu(\text{C=O})$ |
| 1378 | (53) ν_{ring} , (47) $\delta(\text{CH})_{\text{ring}}$ |
| 1387 | (75) $\delta(\text{CH})_{\text{ring}}$, (25) ν_{ring} |
| 1399 | (100) $\delta(\text{CH}_3)$ |
| 1430 | (42) ν_{ring} , (19) $\nu(\text{C=O})$, (13) $\nu(\text{C-C})$, (11) $\delta(\text{CH})_{\text{ring}}$ |

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| 1471 | (47) $\delta(\text{CH})_{\text{ring}}$, (29) ν_{ring} , (12) $\nu(\text{C-C})$ |
| 1475 | (53) $\delta(\text{CH})_{\text{ring}}$, (36) ν_{ring} |
| 1478 | (57) $\delta(\text{CH})_{\text{ring}}$, (37) ν_{ring} |
| 1495 | (100) $\delta(\text{CH}_3)$ |
| 1516 | (53) $\delta(\text{CH})_{\text{ring}}$, (27) ν_{ring} , (15) $\delta(\text{CH}_3)$ |
| 1518 | (80) $\delta(\text{CH}_3)$, (12) $\delta(\text{CH})_{\text{ring}}$ |
| 1522 | (52) $\delta(\text{CH})_{\text{ring}}$, (29) ν_{ring} |
| 1537 | (26) ν_{ring} , (23) $\nu(\text{C-C})$, (22) $\nu(\text{C=O})$, (18) $\delta(\text{CH})_{\text{ring}}$ |
| 1546 | (66) ν_{ring} , (11) $\nu(\text{N-N})$ |
| 1581 | (51) $\nu(\text{N-N})$, (16) ν_{ring} , (14) $\nu(\text{C-N1})$ |
| 1616 | (66) ν_{ring} , (17) $\delta(\text{CH})_{\text{ring}}$ |
| 1619 | (70) ν_{ring} , (20) $\delta(\text{CH})_{\text{ring}}$ |
| 1638 | (48) ν_{ring} , (16) $\nu(\text{C-N4})$, (15) $\delta(\text{CH})_{\text{ring}}$ |
| 1645 | (67) ν_{ring} , (19) $\delta(\text{CH})_{\text{ring}}$, (10) δ_{ring} |
| 1651 | (66) ν_{ring} , (17) $\delta(\text{CH})_{\text{ring}}$, (10) δ_{ring} |
| 1660 | (53) $\nu(\text{C-N4})$, (27) ν_{ring} |
| 3085 | (100) $\nu(\text{CH}_3)$ |
| 3194 | (100) $\nu(\text{CH})_{\text{ring}}$ |
| 3199 | (100) $\nu(\text{CH})_{\text{ring}}$ |
| 3204 | (96) $\nu(\text{CH})_{\text{ring}}$ |
| 3205 | (96) $\nu(\text{CH}_3)$ |
| 3208 | (100) $\nu(\text{CH})_{\text{ring}}$ |
| 3219 | (100) $\nu(\text{CH})_{\text{ring}}$ |
| 3220 | (99) $\nu(\text{CH})_{\text{ring}}$ |
| 3222 | (98) $\nu(\text{CH})_{\text{ring}}$ |
| 3223 | (98) $\nu(\text{CH}_3)$ |
| 3228 | (99) $\nu(\text{CH})_{\text{ring}}$ |
| 3230 | (99) $\nu(\text{CH})_{\text{ring}}$ |
| 3238 | (99) $\nu(\text{CH})_{\text{ring}}$ |
| 3238 | (99) $\nu(\text{CH})_{\text{ring}}$ |
| 3245 | (99) $\nu(\text{CH})_{\text{ring}}$ |
| 3252 | (99) $\nu(\text{CH})_{\text{ring}}$ |

| Table S3. The calculated wavenumbers (cm ⁻¹) and TED (%) of [MoO ₂ (L)allylOH] (5). | |
|--|---|
| Calculated wavenumbers | TED (%), >10% |
| 16 | (33) τ MoN, (16) τ CN, (10) τ NN |
| 23 | (49) τ CN, (24) τ CC, (12) τ CO |
| 35 | (39) τ MoO, (21) τ CN, (10) τ CO |
| 40 | (24) τ MoO |
| 42 | (63) τ CN |
| 51 | (20) tetra N10, (18) τ _{ring} , (10) C26 umbrella |
| 57 | (21) τ _{ring} , (15) tetra C17, (13) C18 umbrella, (11) τ CS |
| 63 | (22) τ MoO, (12) τ CN, (10) τ MoN, (10) τ _{ring} |
| 66 | (32) τ CS, (14) tetra N10, (13) τ _{ring} |
| 75 | (26) τ CS, (16) τ CN, (12) τ CO |
| 96 | (23) τ CO, (16) τ _{ring} , (10) τ CS |
| 101 | (11) tetra C24, (10) τ CO |
| 113 | (68) ν (O-Mo), (15) δ (OCC), (6) τ CO |
| 116 | (25) τ _{ring} , (17) tetrapyrimidine Mo, (10) tetra O7 |
| 128 | (22) τ CS, (11) τ CO |
| 135 | (40) τ CS |
| 142 | (26) τ CS, (17) tetrapyrimidine Mo, (13) N10 umbrella |
| 152 | (18) tetra O7, (12) tetra C24, (11) tetra N10 |
| 166 | (74) τ CC |
| 169 | (13) τ NN, (11) τ _{ring} , (10) tetrapyrimidine Mo, (10) rock CCl |
| 180 | (26) tetrapyrimidine |
| 194 | (55) tetrapyrimidine |
| 210 | (12) τ _{ring} , (11) tetrapyrimidine Mo, (10) rock CCl |
| 217 | (22) tetrapyrimidine, (16) ν (NMo), (13) δ (CCS), (12) tetra C26 |
| 222 | (23) tetrapyrimidine, (11) τ _{ring} , (10) τ CC |
| 230 | (25) tetrapyrimidine, (21) tetra C18, (13) τ _{ring} |
| 250 | (26) τ _{ring} , (14) δ (CCS), (12) tetra N10, (12) tetra C24 |
| 260 | (16) τ _{ring} , (14) tetrapyrimidine Mo, (11) tetra C17 |
| 266 | (53) tetrapyrimidine Mo, (12) τ _{ring} , (11) δ (CCS) |
| 290 | (14) τ _{ring} , (11) rock CCl, (11) tetrapyrimidine, (10) δ (CCS) |
| 307 | (10) δ (CCS), (10) ν (C-C), (10) ν (C-Cl) |
| 320 | (38) δ (CCC), (16) δ (OCC), (12) ν (OMo) |
| 333 | (19) tetrapyrimidine, (15) τ _{ring} , (10) rock CCl |
| 349 | (72) tetrapyrimidine |
| 368 | (17) τ _{ring} , (16) δ (MoCO), (14) tetrapyrimidine |
| 405 | (22) τ _{ring} , (15) N8 umbrella, (14) τ CN |
| 414 | (74) τ _{ring} , (25) γ (CH) _{ring} |
| 423 | (22) tetrapyrimidine Mo, (20) ν (NMo), (13) δ (CCS) |
| 432 | (17) ν (CCl), (10) τ _{ring} |
| 435 | (11) ν (CCl), (10) δ _{ring} |
| 462 | (24) tetra C26, (13) τ _{ring} |
| 488 | (24) τ _{ring} , (11) C12 umbrella, (10) N8 umbrella |
| 497 | (21) ν (CS), (10) tetra C11 |
| 510 | (23) τ _{ring} , (14) C26 umbrella |
| 525 | (22) O7 umbrella, (17) tetra O7, (15) δ (MoOH), (11) γ (CH) _{ring} |
| 531 | (13) τ _{ring} , (11) δ (MoCO), (10) ν (OMo) |
| 548 | (14) δ _{ring} , (11) τ _{ring} |
| 560 | (37) CCl wag, (23) τ _{ring} , (11) C11 umbrella |

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| 591 | (35) $\gamma(\text{CH})_{\text{ring}}$, (20) CH_2 twist, (19) τ_{CC} , (12) CH_2 rock |
| 621 | (38) $\delta(\text{OCC})$, (26) $\delta(\text{CCC})$, (12) CH_2 rock |
| 628 | (53) δ_{ring} |
| 629 | (41) δ_{ring} |
| 633 | (84) δ_{ring} |
| 646 | (36) C_{24} umbrella, (19) δ_{ring} , (11) τ_{NN} |
| 657 | (79) $\nu(\text{C-S})$ |
| 671 | (42) δ_{ring} , (10) ν_{ring} |
| 683 | (32) δ_{ring} , (11)tetra C11 |
| 697 | (26) τ_{ring} , (18) C_{17} umbrella |
| 709 | (21) τ_{ring} , (12) δ_{ring} |
| 723 | (44) $\gamma(\text{CH})_{\text{ring}}$, (36) τ_{ring} |
| 729 | (50) $\gamma(\text{CH})_{\text{ring}}$, (29) τ_{ring} |
| 751 | (20) δ_{ring} , (11) ν_{ring} , (10) $\nu(\text{CCl})$, (10) $\nu(\text{C-S})$ |
| 772 | (26) τ_{ring} , (19) C_{12} umbrella, (17) C_{11} umbrella, (13) C_{17} umbrella |
| 790 | (36) $\gamma(\text{CH})_{\text{ring}}$, (16) τ_{ring} |
| 805 | (37) $\gamma(\text{CH})_{\text{ring}}$, (19) τ_{ring} |
| 835 | (13) ν_{ring} , (11) $\rho(\text{CH})_{\text{ring}}$, (11) δ_{ring} |
| 863 | (76) $\gamma(\text{CH})_{\text{ring}}$ (12) τ_{ring} |
| 876 | (30) $\gamma(\text{CH})_{\text{ring}}$ (19) ν_{ring} , (12) δ_{ring} , (11) τ_{ring} |
| 879 | (48) $\gamma(\text{CH})_{\text{ring}}$, (17) τ_{ring} , (11) ν_{ring} |
| 889 | (74) $\gamma(\text{CH})_{\text{ring}}$, (25) τ_{ring} |
| 893 | (49) $\nu(\text{CC})$, (25) $\nu(\text{C-O})$ |
| 936 | (71) $\gamma(\text{CH})_{\text{ring}}$, (16) τ_{ring} |
| 940 | (54) $\nu(\text{OMo})$ |
| 947 | (41) $\nu(\text{OMo})$, (16) δ_{ring} , (11) ν_{ring} |
| 960 | (49) $\gamma(\text{CH})_{\text{ring}}$, (28) $\nu(\text{OMo})$, (13) τ_{ring} |
| 964 | (46) $\nu(\text{OMo})$, (41) $\gamma(\text{CH})_{\text{ring}}$, (10) τ_{ring} |
| 965 | (50) $\gamma(\text{CH})_{\text{ring}}$, (22) $\nu(\text{OMo})$, (12) τ_{ring} |
| 984 | (39) CH_2 rock, (30) CH_2 wag, (17) $\nu(\text{C-O})$ |
| 998 | (63) $\gamma(\text{CH})_{\text{ring}}$, (24) τ_{ring} |
| 999 | (19) CH_2 rock, (17) $\nu(\text{C-O})$, (17) CH_2 wag |
| 1000 | (42) ν_{ring} , (10) CH_2 rock, (10) $\nu(\text{C-O})$ |
| 1007 | (97) $\delta(\text{CH}_3)$ |
| 1014 | (37) CH_2 wag, (27) CH_2 rock, (16) CH_2 twist, (16) τ_{CC} |
| 1015 | (40) ν_{ring} , (38) δ_{ring} , (10)tetra C18 |
| 1015 | (37) δ_{ring} , (21) ν_{ring} , (12) $\gamma(\text{CH})_{\text{ring}}$ |
| 1019 | (57) $\gamma(\text{CH})_{\text{ring}}$, (20) τ_{ring} |
| 1021 | (67) $\gamma(\text{CH})_{\text{ring}}$, (23) τ_{ring} |
| 1028 | (56) $\delta(\text{CH}_3)$, (11) δ_{ring} |
| 1038 | (57) $\gamma(\text{CH})_{\text{ring}}$, (23) τ_{ring} |
| 1039 | (33) $\gamma(\text{CH})_{\text{ring}}$, (27) CH_2 twist, (27) τ_{CC} |
| 1040 | (29) $\gamma(\text{CH})_{\text{ring}}$, (17) τ_{CC} , (17) CH_2 twist, (10) $\nu(\text{NN})$ |
| 1042 | (63) $\gamma(\text{CH})_{\text{ring}}$, (25) τ_{ring} |
| 1049 | (44) ν_{ring} , (29) δ_{ring} , (23) $\delta(\text{CH})_{\text{ring}}$ |
| 1057 | (32) ν_{ring} , (22) δ_{ring} , (18) $\delta(\text{CH})_{\text{ring}}$, (13) $\nu(\text{NN})$ |
| 1104 | (42) $\delta(\text{CH})_{\text{ring}}$, (38) ν_{ring} , (17) δ_{ring} |
| 1109 | (39) ν_{ring} , (38) $\delta(\text{CH})_{\text{ring}}$, (18) δ_{ring} |
| 1113 | (43) ν_{ring} , (29) $\delta(\text{CH})_{\text{ring}}$, (10) $\nu(\text{CCl})$ |

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| 1126 | (36)CH ₂ rock, (19)v(CO), (14)v(CC), (12) δ (CH) _{ring} |
| 1148 | (40) δ (CH) _{ring} (23)v _{ring} , (19) δ _{ring} |
| 1196 | (25) δ (CH) _{ring} , (16)v _{ring} , (13)CH ₂ twist, (10)v(CC) |
| 1198 | (43)CH ₂ twist, (12)tetra O7, (10) δ (COH) |
| 1204 | (86) δ (CH) _{ring} , (14)v _{ring} |
| 1206 | (34) δ (CH) _{ring} , (15)v _{ring} , (11)v(CN), (11)tetra C24 |
| 1207 | (86) δ (CH) _{ring} , (14)v _{ring} |
| 1215 | (54) δ (CH) _{ring} , (22)v _{ring} |
| 1224 | (77) δ (CH) _{ring} , (22)v _{ring} |
| 1269 | (39)v(CO), (26)v _{ring} , (18) δ (CH) _{ring} |
| 1300 | (59) δ (CH) _{ring} , (18)v _{ring} |
| 1315 | (18) δ (CH) _{ring} , (14)v(CN), (12)v(CN4), (11)v(CC), (10)v(CN2) |
| 1324 | (58) δ (CH) _{ring} , (14)CH ₂ rock, (11)v(C=C) |
| 1326 | (20)v _{ring} , (20) δ (CH) _{ring} , (16)v(CC), (12)v(CN4), (11)v(CN) |
| 1341 | (33)CH ₂ twist, (21)tetra O7, (18) δ (COH) |
| 1349 | (52) δ (CH) _{ring} , (37)v _{ring} |
| 1352 | (54)v _{ring} , (38) δ (CH) _{ring} |
| 1374 | (61)v _{ring} , (39) δ (CH) _{ring} |
| 1375 | (54) δ (CH) _{ring} , (45)v _{ring} |
| 1382 | (67)v _{ring} , (12)v(CC) |
| 1390 | (97) δ (CH ₃) |
| 1404 | (85)CH ₂ wag |
| 1419 | (32)v _{ring} , (25) δ (CH) _{ring} |
| 1468 | (81)CH ₂ scis |
| 1471 | (60) δ (CH) _{ring} , (25)v _{ring} , (10) δ _{ring} |
| 1477 | (56) δ (CH) _{ring} , (24)v _{ring} , (11) δ _{ring} |
| 1479 | (98) δ (CH ₃) |
| 1481 | (23)v(CN2), (17) δ (CH) _{ring} , (12)v(CN1) |
| 1490 | (27) δ (CH) _{ring} , (23) δ (CH ₃), (13)v _{ring} , (11)v(CN2) |
| 1498 | (70) δ (CH ₃) |
| 1515 | (99)CH ₂ scis |
| 1518 | (60) δ (CH) _{ring} (22)v _{ring} |
| 1523 | (53) δ (CH) _{ring} , (19)v _{ring} |
| 1547 | (35)v(CN1)(17)v _{ring} , (16) δ (CH) _{ring} |
| 1596 | (61)v _{ring} , (10)v(CN1) |
| 1625 | (71)v _{ring} , (18) δ (CH) _{ring} |
| 1628 | (73)v _{ring} , (16) δ (CH) _{ring} |
| 1636 | (72)v _{ring} , (14) δ (CH) _{ring} |
| 1644 | (70)v _{ring} , (19) δ (CH) _{ring} |
| 1650 | (68)v _{ring} , (20) δ (CH) _{ring} |
| 1707 | (69)v(C=C), (14)CH ₂ scis |
| 3055 | (100)v(CH ₂) |
| 3091 | (100)v(CH ₃) |
| 3121 | (100)v(CH ₂) |
| 3161 | (54)v(CH) _{ring} , (46)v(CH ₂) |
| 3178 | (55)v(CH ₂), (44)v(CH) _{ring} |
| 3192 | (100)v(CH) _{ring} |

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|------|----------------------------------|
| 3193 | (100) ν (CH) _{ring} |
| 3199 | (100) ν (CH) _{ring} |
| 3203 | (100) ν (CH) _{ring} |
| 3209 | (100) ν (CH ₃) |
| 3210 | (100) ν (CH) _{ring} |
| 3216 | (100) ν (CH) _{ring} |
| 3221 | (99) ν (CH) _{ring} |
| 3225 | (99) ν (CH) _{ring} |
| 3226 | (100) ν (CH ₃) |
| 3228 | (100) ν (CH) _{ring} |
| 3234 | (99) ν (CH) _{ring} |
| 3235 | (99) ν (CH) _{ring} |
| 3247 | (99) ν (CH) _{ring} |
| 3255 | (100) ν (CH) _{ring} |
| 3274 | (99) ν (CH ₂) |
| 3664 | (94) ν (OH) |

Table S4. Experimental and calculated wavelengths (nm) and oscillator strengths (f) of complex **5**.

| Experimental | Calculated | | |
|-----------------|-------------------------------------|---------------------|---|
| wavelength (nm) | Wavelength (nm) (scaled by 0.82) | Oscillator strength | Major contributions ($\geq 10\%$) |
| 435 | 443 | 0.0406 | HOMO -> LUMO (90%) |
| 310 | 314 | 0.0731 | H-2 -> L+1 (56%), H-1 -> L+1 (32%) |
| 251 240 | 261 | 0.1846 | HOMO -> L+3 (37%), H-3 -> LUMO (23%), H-4 -> LUMO (13%) |
| | 235 | 0.1438 | H-4 -> LUMO (51%), HOMO -> L+3 (14%) |

Table S5. Quantum chemical descriptors based on DFT calculations used for SAR studies.

| | L | 1 | 2 | 3 | 4 | 5 |
|------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Total energy (a.u.) | -1074.045 | -1407.395 | -1447.373 | -1485.942 | -1525.902 | -1485.438 |
| E _{HOMO} (eV) | -6.211 | -6.424 | -6.204 | -5.897 | -6.195 | -6.181 |
| E _{LUMO} (eV) | -3.571 | -3.144 | -3.163 | -3.150 | -3.147 | -3.113 |

| | | | | | | |
|--|-----------|-----------|-----------|-----------|-----------|-----------|
| ΔE_{gap} (eV) | 2.640 | 3.280 | 3.042 | 2.748 | 3.048 | 3.069 |
| Total dipole moment (D) | 3.175 | 6.791 | 8.076 | 8.4084 | 8.123 | 7.214 |
| Chemical potential (eV) | -4.891 | -4.647 | -4.684 | -4.524 | -4.671 | -4.647 |
| Ionization energy (I) | 5.741 | 8.272 | 7.836 | 6.585 | 5.551 | 7.755 |
| Electron affinity (A) | 3.619 | 2.340 | 0.870 | 2.122 | 3.157 | 1.034 |
| Mulliken electronegativity (χ) (eV) | 4.891 | 4.647 | 4.684 | 4.524 | 4.671 | 4.647 |
| Softness (S) (eV) | 0.379 | 0.305 | 0.329 | 0.364 | 0.328 | 0.326 |
| Hardness (η) (eV) | 1.320 | 1.64 | 1.521 | 1.374 | 1.524 | 1.535 |
| Electrophilicity index (ω) (eV) | 9.061 | 6.584 | 7.212 | 7.448 | 7.158 | 7.034 |
| E+ | -1073.834 | -1407.091 | -1447.085 | -1485.700 | -1525.698 | -1485.153 |
| E- | -1074.178 | -1407.481 | -1447.405 | -1486.020 | -1526.018 | -1485.476 |

| Table S6. Main delocalization energy (in kJ/mol) for Ligand (L) | |
|--|---------------|
| Delocalization | |
| BD(2) O 3 - C 7 → BD*(2) C 11 - C 12 | 13.45 |
| BD(2) N 4 - C 13 → LP (2) N 5 | 52.80 |
| BD(2) N 4 - C 13 → BD*(2) N 4 - C 13 | 0.89 |
| BD(2) N 4 - C 13 → BD*(2) C 14 - C 19 | 1.37 |
| BD(2) N 6 - C 20 → LP (2) N 5 | 57.98 |
| BD(2) N 6 - C 20 → BD*(2) C 22 - C 23 | 2.77 |
| BD(2) C 9 - C 10 → BD*(2) C 11 - C 12 | 17.72 |
| BD(2) C 11 - C 12 → BD*(2) O 3 - C 7 | 29.18 |
| BD(2) C 11 - C 12 → BD*(2) C 9 - C 10 | 20.63 |
| BD(2) C 14 - C 19 → BD*(2) N 4 - C 13 | 2.85 |
| BD(2) C 14 - C 19 → BD*(2) C 15 - C 16 | 20.06 |
| BD(2) C 14 - C 19 → BD*(2) C 17 - C 18 | 20.78 |
| BD(2) C 15 - C 16 → LP (2) N 5 | 0.68 |
| BD(2) C 15 - C 16 → BD*(2) C 14 - C 19 | 21.93 |
| BD(2) C 15 - C 16 → BD*(2) C 17 - C 18 | 21.46 |
| BD(2) C 17 - C 18 → BD*(2) C 14 - C 19 | 21.77 |
| BD(2) C 17 - C 18 → BD*(2) C 15 - C 16 | 20.44 |
| BD(2) C 22 - C 23 → BD*(2) N 6 - C 20 | 3.50 |
| BD(2) C 22 - C 23 → BD*(2) C 24 - C 25 | 21.29 |
| BD(2) C 22 - C 23 → BD*(2) C 26 - C 27 | 19.41 |
| BD(2) C 24 - C 25 → BD*(2) C 22 - C 23 | 21.05 |
| BD(2) C 24 - C 25 → BD*(2) C 26 - C 27 | 21.34 |
| BD(2) C 26 - C 27 → BD*(2) C 22 - C 23 | 22.02 |
| BD(2) C 26 - C 27 → BD*(2) C 24 - C 25 | 20.55 |
| $\Delta E_{\text{T}} \pi \rightarrow \pi^*$ | 455.92 |

| | | | | | | |
|---|---|---|-----------|--------|----|-------|
| LP (2)Cl | 1 | → | BD* (1) C | 9 - C | 10 | 3.74 |
| LP (2)Cl | 1 | → | BD* (1) C | 10 - C | 11 | 3.61 |
| LP (3)Cl | 1 | → | BD* (2) C | 9 - C | 10 | 10.75 |
| LP (2) S | 2 | → | LP (2) N | 5 | | 3.14 |
| LP (2) S | 2 | → | BD* (2) N | 6 - C | 20 | 25.23 |
| LP (2) S | 2 | → | BD* (1) C | 21 - H | 37 | 3.09 |
| LP (2) S | 2 | → | BD* (1) C | 21 - H | 38 | 3.18 |
| LP (1) O | 3 | → | BD* (1) C | 7 - C | 8 | 2.81 |
| LP (2) O | 3 | → | BD* (1) C | 7 - C | 8 | 10.85 |
| LP (2) O | 3 | → | BD* (1) C | 7 - C | 12 | 8.76 |
| LP (1) N | 4 | → | BD* (1) C | 13 - C | 14 | 11.62 |
| LP (1) N | 5 | → | BD* (1) N | 6 - C | 20 | 10.13 |
| LP (2) N | 5 | → | BD* (2) N | 4 - C | 13 | 29.28 |
| LP (2) N | 5 | → | BD* (2) N | 6 - C | 20 | 64.89 |
| LP (1) N | 6 | → | BD* (1) S | 2 - C | 20 | 15.67 |
| LP (1) N | 6 | → | BD* (1) N | 5 - C | 20 | 2.41 |
| LP (1) N | 6 | → | BD* (2) C | 22 - C | 23 | 9.51 |
| LP (1) N | 6 | → | BD* (1) C | 22 - C | 27 | 3.40 |
| LP = Lone pair; BD and BD* = bond and antibond, respectively, | | | | | | |

| Table S7. Main delocalization energy (in kJ/mol) for [MoO₂(L)MeOH] (1). | | | | | | | |
|---|--------|----|---|------------|--------|-------|-------|
| Delocalization | | | | | | | |
| BD (2) N | 7 - N | 8 | → | LP* (1) C | 16 | 22.19 | |
| BD (2) N | 7 - N | 8 | → | BD* (2) N | 9 - C | 23 | 20.33 |
| BD (2) C | 11 - C | 12 | → | LP (1) C | 10 | 29.75 | |
| BD (2) C | 11 - C | 12 | → | LP* (1) C | 16 | 26.12 | |
| BD (2) C | 11 - C | 12 | → | BD* (2) C | 13 - C | 14 | 10.16 |
| BD (2) C | 13 - C | 14 | → | BD* (2) C | 11 - C | 12 | 12.68 |
| BD (2) C | 17 - C | 18 | → | BD* (2) C | 19 - C | 20 | 10.42 |
| BD (2) C | 17 - C | 18 | → | BD* (2) C | 21 - C | 22 | 10.65 |
| BD (2) C | 19 - C | 20 | → | BD* (2) C | 17 - C | 18 | 11.33 |
| BD (2) C | 19 - C | 20 | → | BD* (2) C | 21 - C | 22 | 10.47 |
| BD (2) C | 21 - C | 22 | → | BD* (2) C | 17 - C | 18 | 10.78 |
| BD (2) C | 21 - C | 22 | → | BD* (2) C | 19 - C | 20 | 10.83 |
| BD (2) C | 25 - C | 26 | → | BD* (2) C | 27 - C | 28 | 10.03 |
| BD (2) C | 25 - C | 26 | → | BD* (2) C | 29 - C | 30 | 10.40 |
| BD (2) C | 27 - C | 28 | → | BD* (2) C | 25 - C | 26 | 11.29 |
| BD (2) C | 27 - C | 28 | → | BD* (2) C | 29 - C | 30 | 10.63 |
| BD (2) C | 29 - C | 30 | → | BD* (2) C | 25 - C | 26 | 11.14 |
| BD (2) C | 29 - C | 30 | → | BD* (2) C | 27 - C | 28 | 10.60 |
| $\Delta E_{\pi \rightarrow \pi^*}$ | | | | | | 249.8 | |
| LP (2) S | 3 | | → | BD* (2) N | 9 - C | 23 | 14.39 |
| LP (1) O | 4 | | → | LP* (2) Mo | 1 | | 22.84 |
| LP (2) O | 4 | | → | LP (1) C | 10 | | 24.82 |
| LP (3) O | 4 | | → | LP* (2) Mo | 1 | | 47.40 |

| | | | |
|---|---|---------------------|-------|
| LP (1) O 5 | → | LP* (1) Mo 1 | 15.12 |
| LP (1) O 6 | → | LP* (1) Mo 1 | 11.85 |
| LP (2) O 6 | → | BD* (2) Mo 1 - O 5 | 27.50 |
| LP (1) N 7 | → | LP* (1) Mo 1 | 24.76 |
| LP (1) N 7 | → | LP* (3) Mo 1 | 13.71 |
| LP (1) N 7 | → | BD* (1) Mo 1 - O 6 | 17.97 |
| LP (1) C 10 | → | BD* (2) C 11 - C 12 | 32.43 |
| LP (1) C 15 | → | BD* (2) C 13 - C 14 | 45.21 |
| LP (3) O 51 | → | LP* (3) Mo 1 | 13.79 |
| LP (3) O 51 | → | BD* (1) Mo 1 - O 5 | 17.52 |
| LP (2) O 51 | → | BD* (1) C 47 - H 49 | 16.85 |
| LP = Lone pair; BD and BD* = bond and antibond, respectively. | | | |

Table S8. Main delocalization energy (in kJ/mol) for [MoO₂(L)EtOH] (2).

| Delocalization | | | |
|--------------------------------------|---|---------------------|---------------|
| BD (2) N 9 - C 24 | → | BD* (2) N 8 - C 17 | 14.39 |
| BD (2) N 10 - C 26 | → | BD* (3) Mo 1 - O 5 | 16.52 |
| BD (2) N 10 - C 26 | → | BD* (2) N 9 - C 24 | 75.39 |
| BD (2) C 11 - C 16 | → | BD* (2) C 12 - C 13 | 19.10 |
| BD (2) C 11 - C 16 | → | BD* (2) C 14 - C 15 | 26.77 |
| BD (2) C 12 - C 13 | → | BD* (2) N 8 - C 17 | 27.34 |
| BD (2) C 12 - C 13 | → | BD* (2) C 11 - C 16 | 23.77 |
| BD (2) C 12 - C 13 | → | BD* (2) C 14 - C 15 | 20.19 |
| BD (2) C 14 - C 15 | → | BD* (2) C 11 - C 16 | 17.50 |
| BD (2) C 14 - C 15 | → | BD* (2) C 12 - C 13 | 25.45 |
| BD (2) C 18 - C 23 | → | BD* (2) C 19 - C 20 | 20.08 |
| BD (2) C 18 - C 23 | → | BD* (2) C 21 - C 22 | 20.72 |
| BD (2) C 19 - C 20 | → | BD* (2) C 18 - C 23 | 21.79 |
| BD (2) C 19 - C 20 | → | BD* (2) C 21 - C 22 | 21.91 |
| BD (2) C 21 - C 22 | → | BD* (2) C 18 - C 23 | 21.94 |
| BD (2) C 21 - C 22 | → | BD* (2) C 19 - C 20 | 19.93 |
| BD (2) C 26 - C 31 | → | BD* (2) C 27 - C 28 | 20.29 |
| BD (2) C 26 - C 31 | → | BD* (2) C 29 - C 30 | 20.70 |
| BD (2) C 27 - C 28 | → | BD* (2) C 26 - C 31 | 22.28 |
| BD (2) C 27 - C 28 | → | BD* (2) C 29 - C 30 | 21.77 |
| BD (2) C 29 - C 30 | → | BD* (2) C 26 - C 31 | 22.01 |
| BD (2) C 29 - C 30 | → | BD* (2) C 27 - C 28 | 20.74 |
| ΔE_T $\pi \rightarrow \pi^*$ | | | 520.58 |

| | | | |
|---|---|--------------------|-------|
| LP (2) S 3 | → | BD*(2) N 9 - C 2 | 24.68 |
| LP (1) O 4 | → | LP*(2)Mo 1 | 44.91 |
| LP (2) O 4 | → | BD*(2) C 11 - C 16 | 23.88 |
| LP (3) O 4 | → | LP*(2)Mo 1 | 96.29 |
| LP (3) O 4 | → | LP*(3)Mo 1 | 21.03 |
| LP (3) O 4 | → | BD*(2)Mo 1 - O 6 | 15.38 |
| LP (3) O 4 | → | BD*(1)Mo 1 - N 10 | 18.96 |
| LP (1) O 5 | → | LP*(1)Mo 1 | 30.62 |
| LP (1) O 5 | → | LP*(2)Mo 1 | 10.83 |
| LP (1) O 5 | → | LP*(3)Mo 1 | 20.55 |
| LP (1) O 6 | → | LP*(1)Mo 1 | 22.92 |
| LP (2) O 6 | → | BD*(2)Mo 1 - O 5 | 53.19 |
| LP (1) N 8 | → | LP*(1)Mo 1 | 52.44 |
| LP (1) N 8 | → | LP*(3)Mo 1 | 28.62 |
| LP (1) N 8 | → | BD*(1)Mo 1 - O | 34.92 |
| LP (1) N 9 | → | BD*(1) N 10 - C 24 | 11.80 |
| LP (2) O 7 | → | LP*(3)Mo 1 | 36.04 |
| LP (2) O 7 | → | BD*(1)Mo 1 - O 5 | 39.08 |
| LP = Lone pair; BD and BD* = bond and antibond, respectively. | | | |

| Table S9. Main delocalization energy (in kJ/mol) for [MoO ₂ (L)PrOH] (3). | | | |
|--|---|--------------------|-------|
| Delocalization | | | |
| BD (2)Mo 1 - O 5 | → | BD*(1)Mo 1 - O 6 | 11.66 |
| BD (2) N 8 - N 9 | → | LP (1) C 17 | 22.17 |
| BD (2) N 8 - N 9 | → | BD*(2) N 10 - C 24 | 19.84 |
| BD (2) C 11 - C 16 | → | BD*(2) C 12 - C 13 | 9.54 |
| BD (2) C 11 - C 16 | → | BD*(2) C 14 - C 15 | 13.34 |
| BD (2) C 12 - C 13 | → | LP (1) C 17 | 25.98 |
| BD (2) C 12 - C 13 | → | BD*(2) C 11 - C 16 | 11.89 |
| BD (2) C 12 - C 13 | → | BD*(2) C 14 - C 15 | 10.11 |
| BD (2) C 14 - C 15 | → | BD*(2) C 11 - C 16 | 8.77 |
| BD (2) C 14 - C 15 | → | BD*(2) C 12 - C 13 | 12.71 |
| BD (2) C 18 - C 19 | → | BD*(2) C 20 - C 21 | 10.46 |
| BD (2) C 18 - C 19 | → | BD*(2) C 22 - C 23 | 10.72 |
| BD (2) C 20 - C 21 | → | BD*(2) C 18 - C 19 | 11.29 |
| BD (2) C 20 - C 21 | → | BD*(2) C 22 - C 23 | 10.57 |
| BD (2) C 22 - C 23 | → | BD*(2) C 18 - C 19 | 10.74 |
| BD (2) C 22 - C 23 | → | BD*(2) C 20 - C 21 | 10.76 |
| BD (2) C 26 - C 27 | → | BD*(2) C 28 - C 29 | 10.11 |
| BD (2) C 26 - C 27 | → | BD*(2) C 30 - C 31 | 10.37 |
| BD (2) C 28 - C 29 | → | BD*(2) C 26 - C 27 | 11.20 |
| BD (2) C 28 - C 29 | → | BD*(2) C 30 - C 31 | 10.56 |
| BD (2) C 30 - C 31 | → | BD*(2) C 26 - C 27 | 11.12 |

| | | |
|---|---------------------|---------------|
| BD (2) C 30 - C 31 → | BD* (2) C 28 - C 29 | 10.68 |
| ΔET π→π* | | 274.59 |
| LP (2) S 3 → | BD* (2) N 10 - C 24 | 14.12 |
| LP (1) O 4 → | LP* (2) Mo 1 | 22.37 |
| LP (2) O 4 → | BD* (2) C 11 - C 16 | 11.93 |
| LP (3) O 4 → | LP* (2) Mo 1 | 48.26 |
| LP (3) O 4 → | LP* (3) Mo 1 | 10.62 |
| LP (1) O 5 → | LP* (1) Mo 1 | 15.31 |
| LP (1) O 5 → | LP* (3) Mo 1 | 10.28 |
| LP (1) O 6 → | LP* (1) Mo 1 | 11.34 |
| LP (2) O 6 → | BD* (2) Mo 1 - O 5 | 26.02 |
| LP (1) N 8 → | LP* (1) Mo 1 | 26.46 |
| LP (1) N 8 → | LP* (3) Mo 1 | 14.30 |
| LP (1) N 8 → | BD* (1) Mo 1 - O 6 | 17.46 |
| LP (1) C 17 → | BD* (2) N 8 - N 9 | 376.10 |
| LP (1) C 17 → | BD* (2) C 12 - C 13 | 22.05 |
| LP (2) O 7 → | LP* (3) Mo 1 | 17.86 |
| LP (2) O 7 → | BD* (1) Mo 1 - O 5 | 19.34 |
| LP (1) C 33 → | BD* (1) C 55 - H 56 | 11.75 |
| LP = Lone pair; BD and BD* = bond and antibond, respectively. | | |

| Table S10. Main delocalization energy (in kJ/mol) for [MoO₂(L)BuOH] (4). | | |
|--|---------------------|-------|
| Delocalization | | |
| BD (2) N 9 - C 24 → | BD* (2) N 8 - C 17 | 14.43 |
| BD (2) N 10 - C 26 → | BD* (3) Mo 1 - O 5 | 16.53 |
| BD (2) N 10 - C 26 → | BD* (2) N 9 - C 24 | 75.84 |
| BD (2) C 11 - C 16 → | BD* (2) C 12 - C 13 | 19.10 |
| BD (2) C 11 - C 16 → | BD* (2) C 14 - C 15 | 26.75 |
| BD (2) C 12 - C 13 → | BD* (2) N 8 - C 17 | 27.34 |
| BD (2) C 12 - C 13 → | BD* (2) C 11 - C 16 | 23.78 |
| BD (2) C 12 - C 13 → | BD* (2) C 14 - C 15 | 20.21 |
| BD (2) C 14 - C 15 → | BD* (2) C 11 - C 16 | 17.50 |
| BD (2) C 14 - C 15 → | BD* (2) C 12 - C 13 | 25.42 |
| BD (2) C 18 - C 23 → | BD* (2) C 19 - C 20 | 20.16 |
| BD (2) C 18 - C 23 → | BD* (2) C 21 - C 22 | 20.71 |
| BD (2) C 19 - C 20 → | BD* (2) C 18 - C 23 | 21.71 |
| BD (2) C 19 - C 20 → | BD* (2) C 21 - C 22 | 21.93 |
| BD (2) C 21 - C 22 → | BD* (2) C 18 - C 23 | 21.96 |
| BD (2) C 21 - C 22 → | BD* (2) C 19 - C 20 | 19.92 |
| BD (2) C 26 - C 31 → | BD* (2) C 27 - C 28 | 20.39 |
| BD (2) C 26 - C 31 → | BD* (2) C 29 - C 30 | 20.68 |
| BD (2) C 27 - C 28 → | BD* (2) C 26 - C 31 | 22.20 |
| BD (2) C 27 - C 28 → | BD* (2) C 29 - C 30 | 21.76 |

| | | | |
|---|---|---------------------|---------------|
| BD (2) C 29 - C 30 | → | BD* (2) C 26 - C 31 | 22.04 |
| BD (2) C 29 - C 30 | → | BD* (2) C 27 - C 28 | 20.75 |
| $\Delta E_T \pi \rightarrow \pi^*$ | | | 521.11 |
| LP (2) S 3 | → | BD* (2) N 9 - C 24 | 24.90 |
| LP (1) O 4 | → | LP* (2) Mo 1 | 44.84 |
| LP (2) O 4 | → | BD* (2) C 11 - C 16 | 23.88 |
| LP (3) O 4 | → | LP* (2) Mo 1 | 96.46 |
| LP (3) O 4 | → | LP* (3) Mo 1 | 21.44 |
| LP (3) O 4 | → | BD* (2) Mo 1 - O 6 | 15.42 |
| LP (3) O 4 | → | BD* (1) Mo 1 - N 10 | 19.01 |
| LP (1) O 5 | → | LP* (1) Mo 1 | 30.65 |
| LP (1) O 5 | → | LP* (2) Mo 1 | 10.88 |
| LP (1) O 5 | → | LP* (3) Mo 1 | 20.57 |
| LP (1) O 6 | → | LP* (1) Mo 1 | 22.75 |
| LP (2) O 6 | → | BD* (2) Mo 1 - O 5 | 52.80 |
| LP (1) N 8 | → | LP* (1) Mo 1 | 52.89 |
| LP (1) N 8 | → | LP* (3) Mo 1 | 28.72 |
| LP (1) N 8 | → | BD* (1) Mo 1 - O 6 | 34.92 |
| LP (1) N 9 | → | BD* (1) N 10 - C 24 | 11.82 |
| LP (2) O 7 | → | LP* (3) Mo 1 | 35.62 |
| LP (2) O 7 | → | BD* (1) Mo 1 - O 5 | 38.69 |
| LP = Lone pair; BD and BD* = bond and antibond, respectively. | | | |

| Table S11. Main delocalization energy (in kJ/mol) for [MoO ₂ (L)allylOH] (5). | | | |
|--|---|---------------------|-------|
| Delocalization | | | |
| BD (2) N 9 - C 24 | → | BD* (2) N 8 - C 17 | 14.40 |
| BD (2) N 10 - C 26 | → | BD* (3) Mo 1 - O 5 | 16.40 |
| BD (2) N 10 - C 26 | → | BD* (2) N 9 - C 24 | 74.95 |
| BD (2) C 11 - C 16 | → | BD* (2) C 12 - C 13 | 19.08 |
| BD (2) C 11 - C 16 | → | BD* (2) C 14 - C 15 | 26.68 |
| BD (2) C 12 - C 13 | → | BD* (2) N 8 - C 17 | 27.32 |
| BD (2) C 12 - C 13 | → | BD* (2) C 11 - C 16 | 23.80 |
| BD (2) C 12 - C 13 | → | BD* (2) C 14 - C 15 | 20.20 |
| BD (2) C 14 - C 15 | → | BD* (2) C 11 - C 16 | 17.54 |
| BD (2) C 14 - C 15 | → | BD* (2) C 12 - C 13 | 25.45 |
| BD (2) C 18 - C 23 | → | BD* (2) C 19 - C 20 | 20.13 |
| BD (2) C 18 - C 23 | → | BD* (2) C 21 - C 22 | 20.71 |
| BD (2) C 19 - C 20 | → | BD* (2) C 18 - C 23 | 21.74 |
| BD (2) C 19 - C 20 | → | BD* (2) C 21 - C 22 | 21.90 |
| BD (2) C 21 - C 22 | → | BD* (2) C 18 - C 23 | 21.96 |
| BD (2) C 21 - C 22 | → | BD* (2) C 19 - C 20 | 19.95 |

| | | |
|---|--------------------|---------------|
| BD(2) C 26 - C 31 → | BD*(2) C 27 - C 28 | 20.22 |
| BD(2) C 26 - C 31 → | BD*(2) C 29 - C 30 | 20.73 |
| BD(2) C 27 - C 28 → | BD*(2) C 26 - C 31 | 22.33 |
| BD(2) C 27 - C 28 → | BD*(2) C 29 - C 30 | 21.75 |
| BD(2) C 29 - C 30 → | BD*(2) C 26 - C 31 | 21.98 |
| BD(2) C 29 - C 30 → | BD*(2) C 27 - C 28 | 20.74 |
| $\Delta E_{\pi \rightarrow \pi^*}$ | | 519.96 |
| LP(2) S 3 → | BD*(2) N 9 - C 24 | 24.59 |
| LP(1) O 4 → | LP*(2) Mo 1 | 44.87 |
| LP(2) O 4 → | BD*(2) C 11 - C 16 | 23.85 |
| LP(3) O 4 → | LP*(2) Mo 1 | 96.61 |
| LP(3) O 4 → | LP*(3) Mo 1 | 21.04 |
| LP(3) O 4 → | BD*(2) Mo 1 - O 6 | 15.32 |
| LP(3) O 4 → | BD*(1) Mo 1 - N 10 | 18.98 |
| LP(1) O 5 → | LP*(1) Mo 1 | 30.54 |
| LP(1) O 5 → | LP*(2) Mo 1 | 10.81 |
| LP(1) O 5 → | LP*(3) Mo 1 | 20.78 |
| LP(1) O 6 → | LP*(1) Mo 1 | 22.66 |
| LP(2) O 6 → | BD*(2) Mo 1 - O 5 | 51.64 |
| LP(1) N 8 → | LP*(1) Mo 1 | 53.03 |
| LP(1) N 8 → | LP*(3) Mo 1 | 28.55 |
| LP(1) N 8 → | BD*(1) Mo 1 - O 6 | 34.81 |
| LP(1) N 9 → | BD*(1) N 10 - C 24 | 11.86 |
| LP(2) O 7 → | LP*(3) Mo 1 | 35.81 |
| LP(2) O 7 → | BD*(1) Mo 1 - O 5 | 38.60 |
| LP = Lone pair; BD and BD* = bond and antibond, respectively. | | |

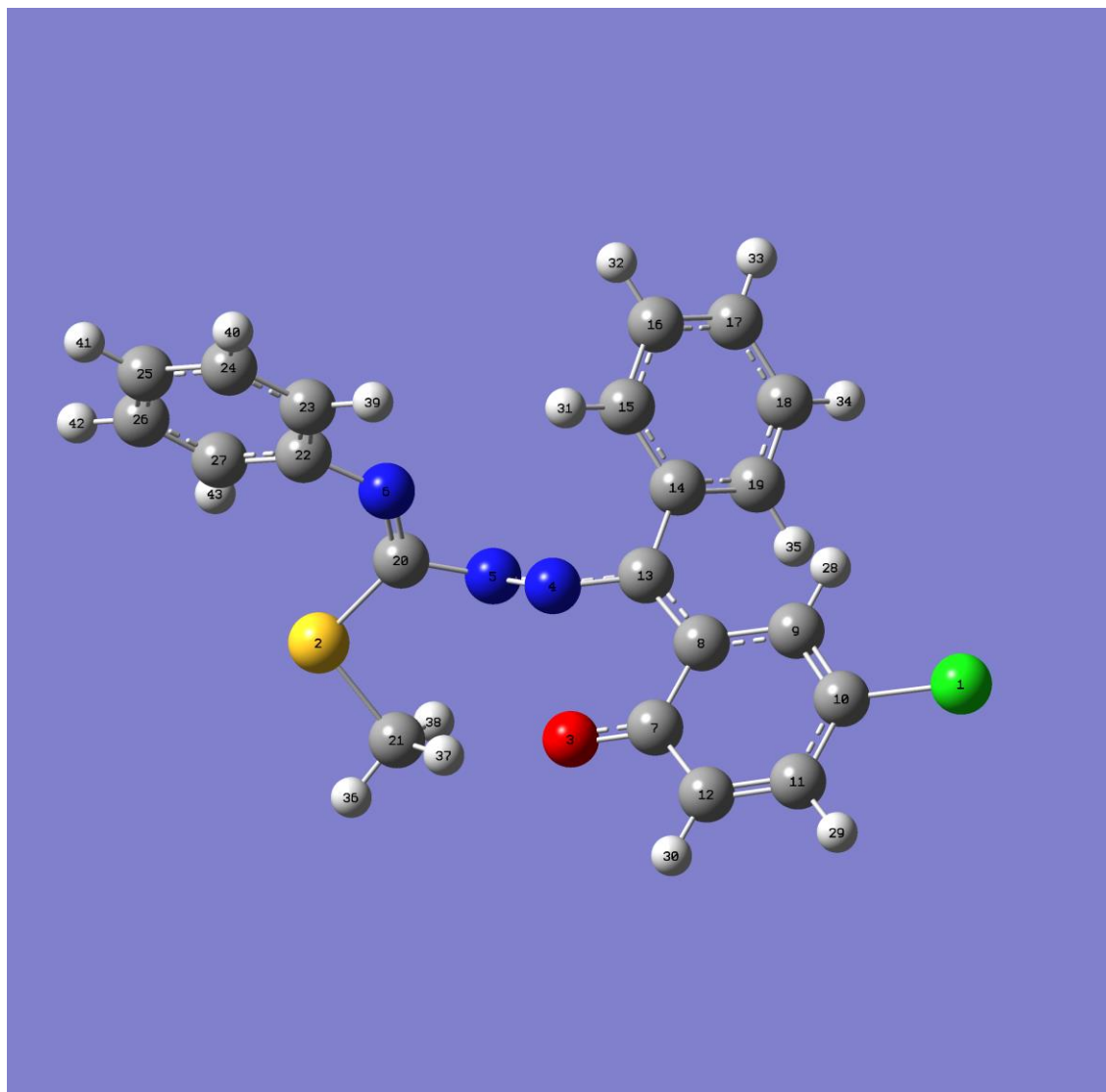


Figure S1. Atom numbering scheme of the ligand (L).

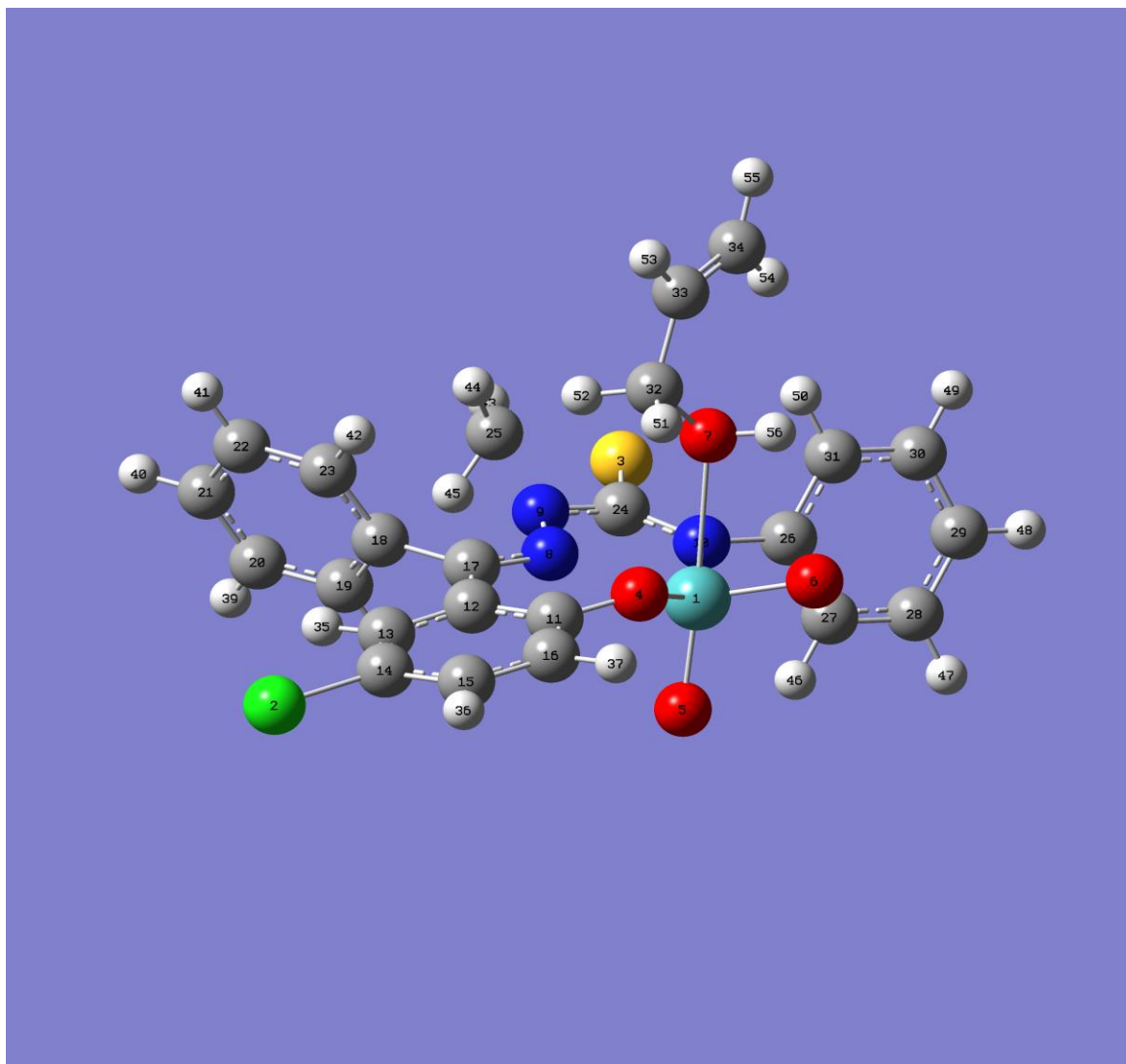


Figure S2. Atom numbering scheme of [MoO₂(L)allylOH] (**5**).

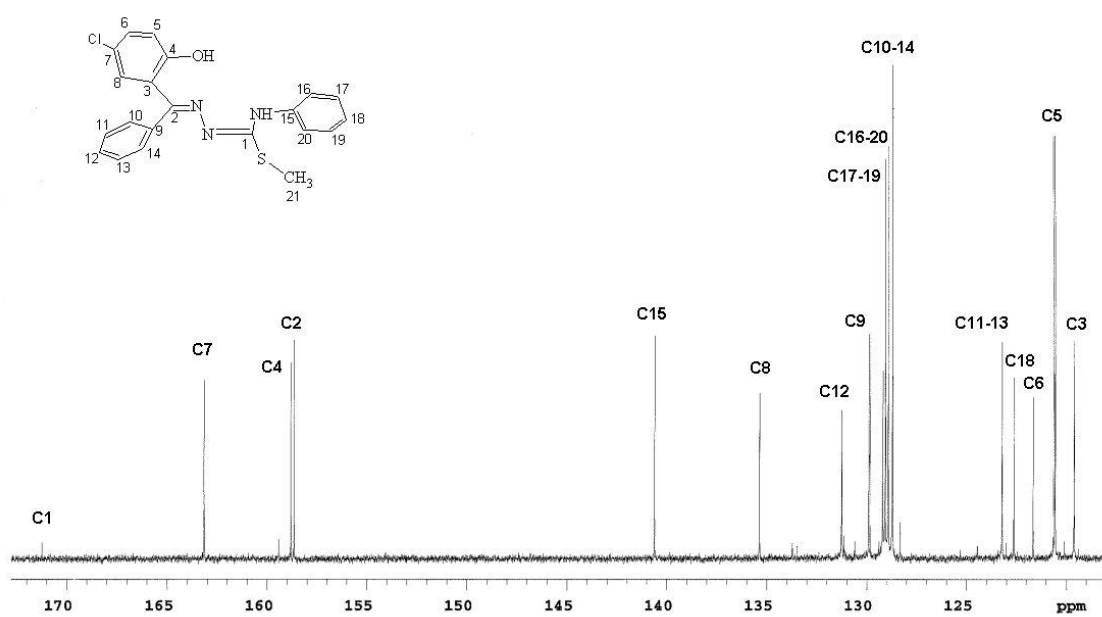
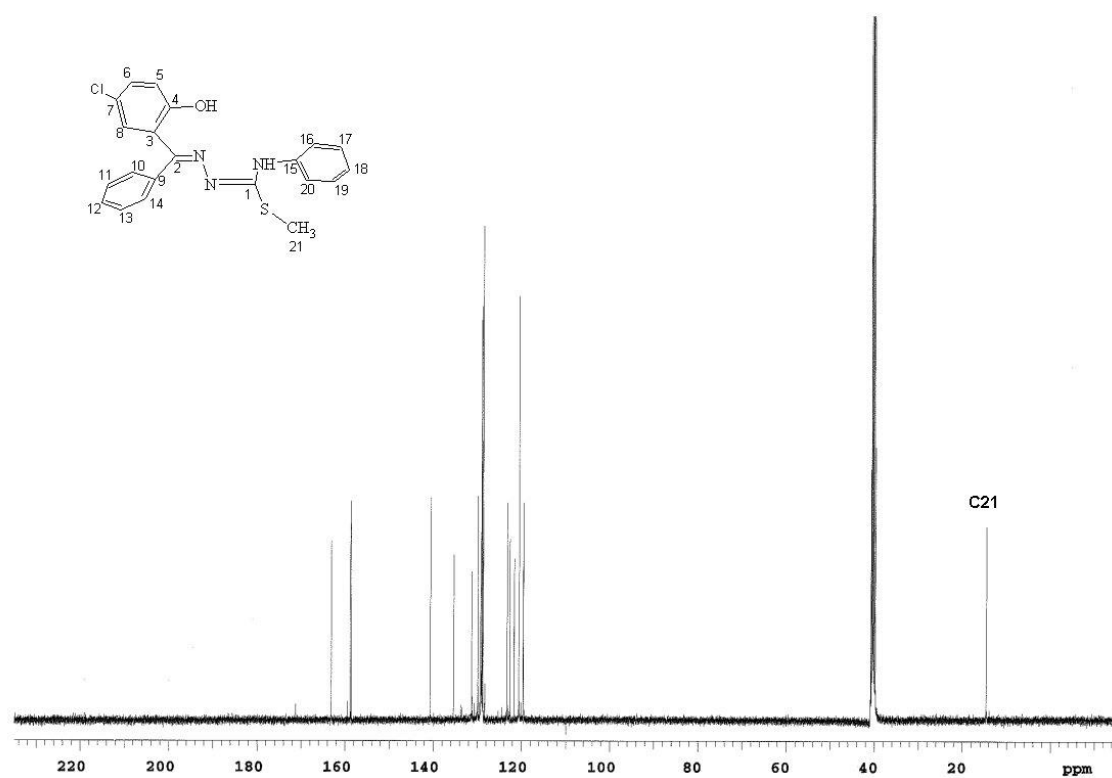


Figure S3. ¹³C NMR spectra of ligand **L** (top) and detailed assignment (bottom) (solvent: DMSO-d₆).

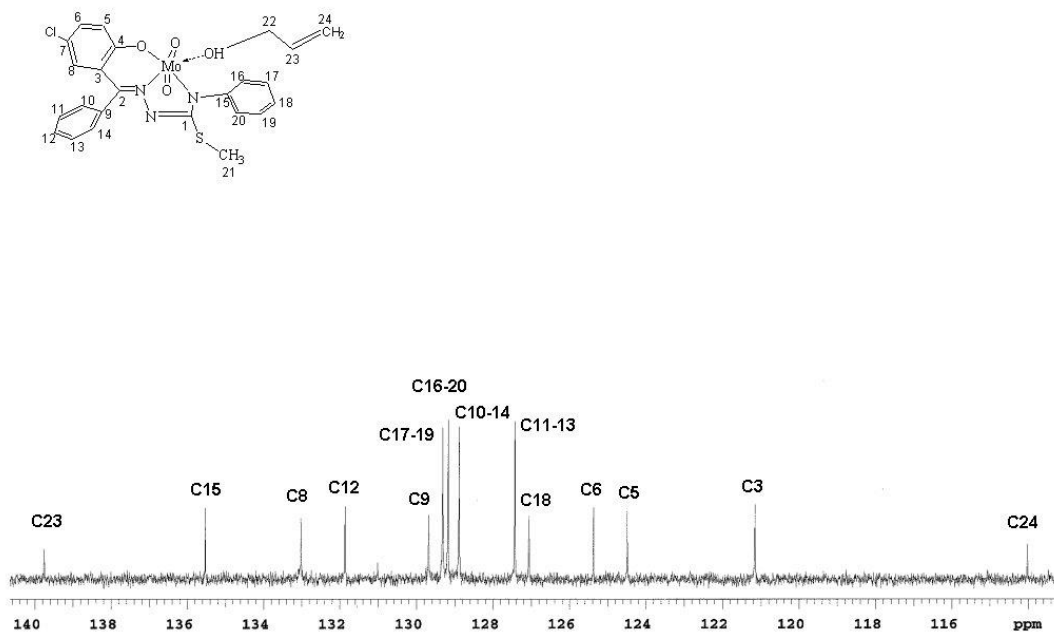
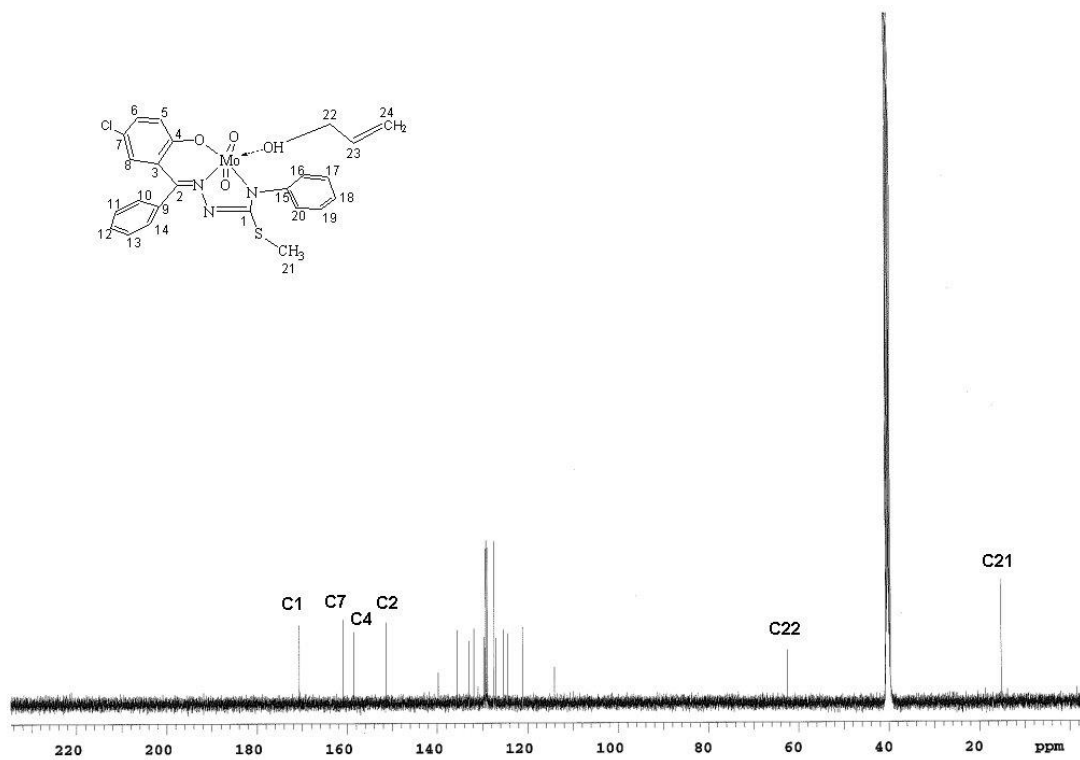


Figure S4. ¹³C NMR spectra of [MoO₂(L)Allyl alcohol] (5) complex (top) and assignment (bottom) (solvent: DMSO-d₆).

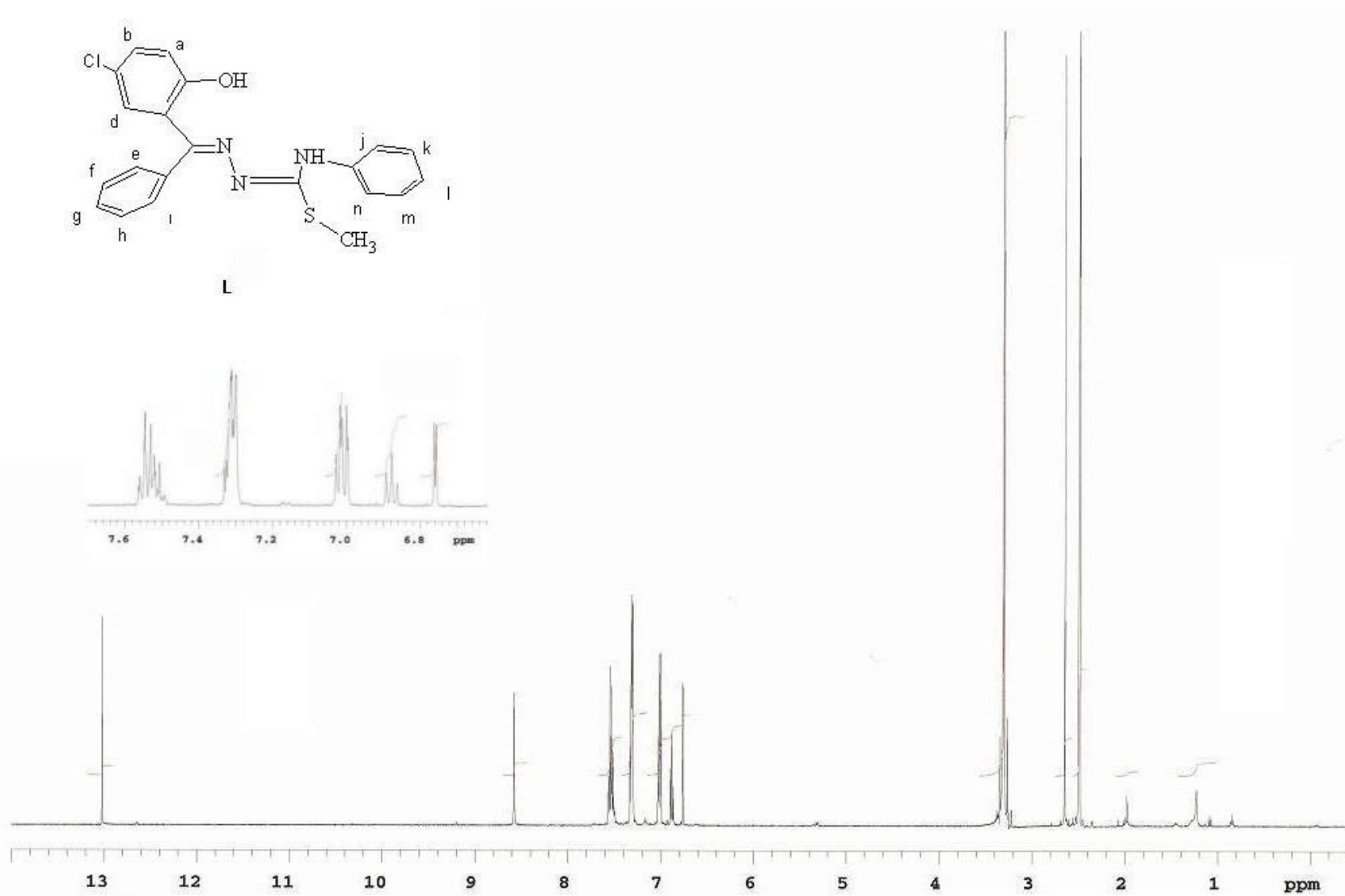


Figure S5. ¹H NMR spectrum of the ligand (**L**) and aromatic group peaks an inset (solvent: DMSO-d₆, reference: TMS).

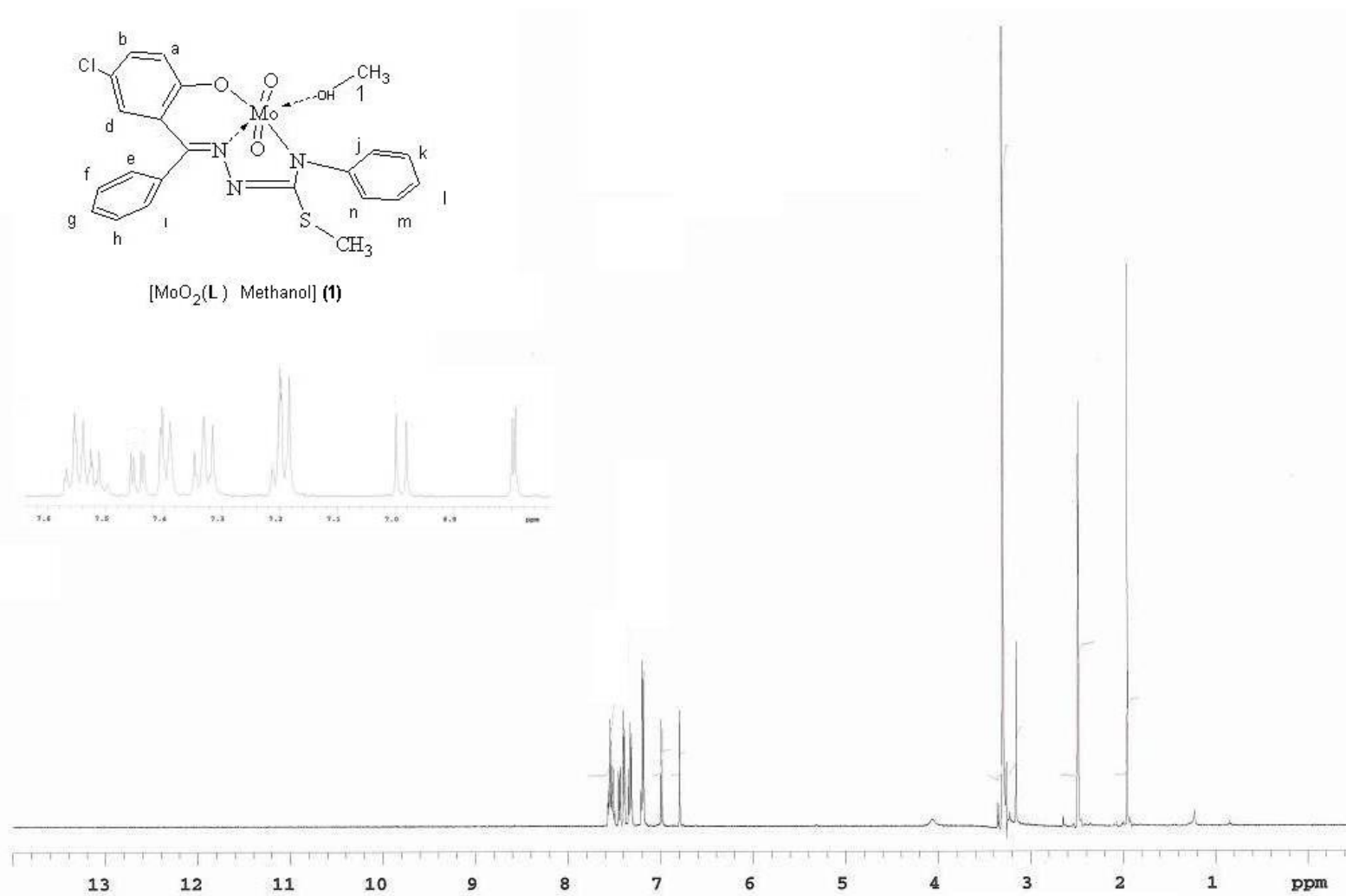


Figure S6. ^1H NMR spectrum of $[\text{MoO}_2(\text{L})\text{methanol}]$ (**1**) complex and aromatic group peaks as inset (solvent: DMSO-d_6 , reference: TMS).

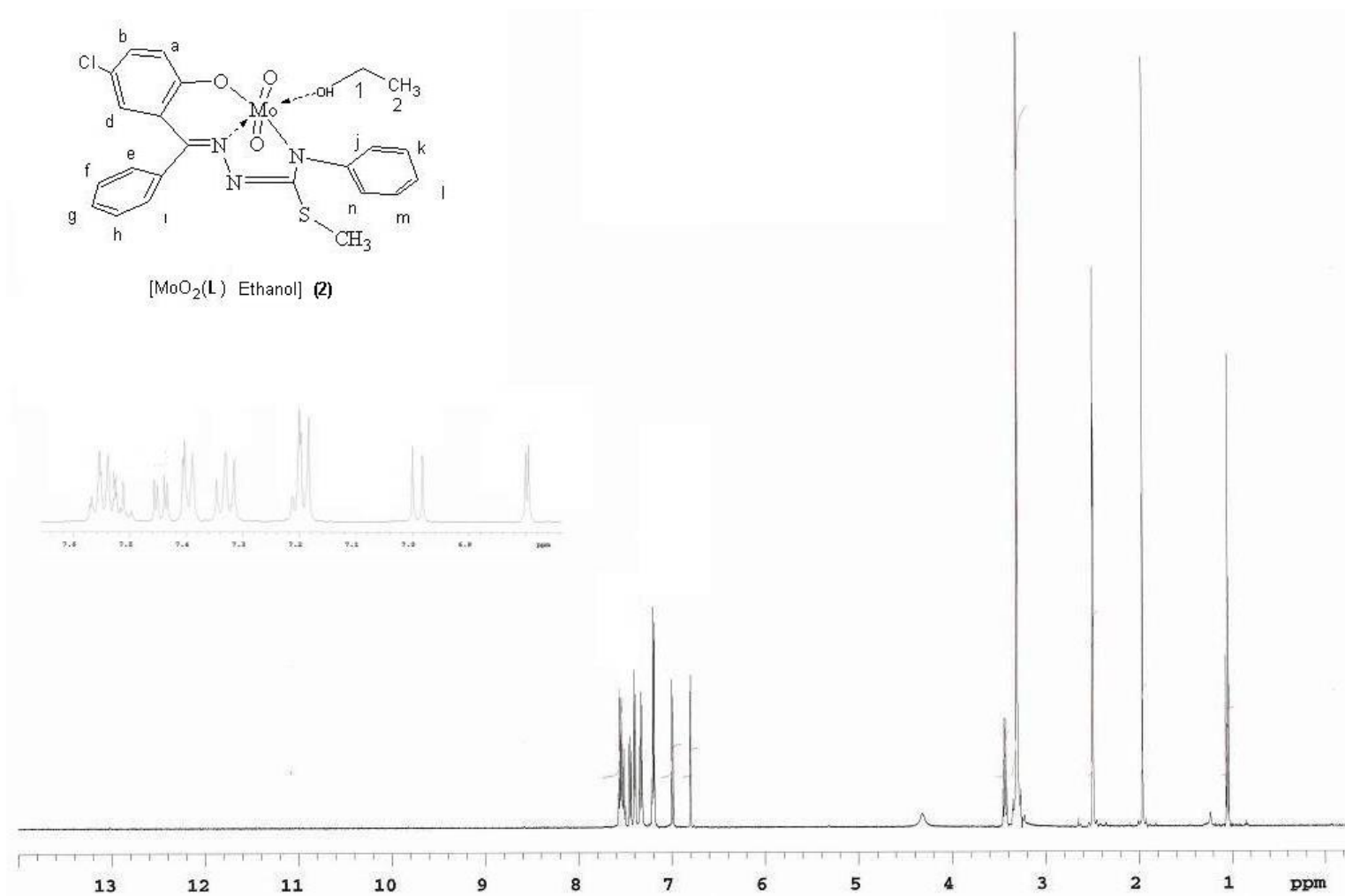


Figure S7. ^1H NMR spectrum of $[\text{MoO}_2(\text{L})\text{ethanol}]$ (2) complex and aromatic group peaks as inset (solvent: DMSO-d_6 , reference: TMS).

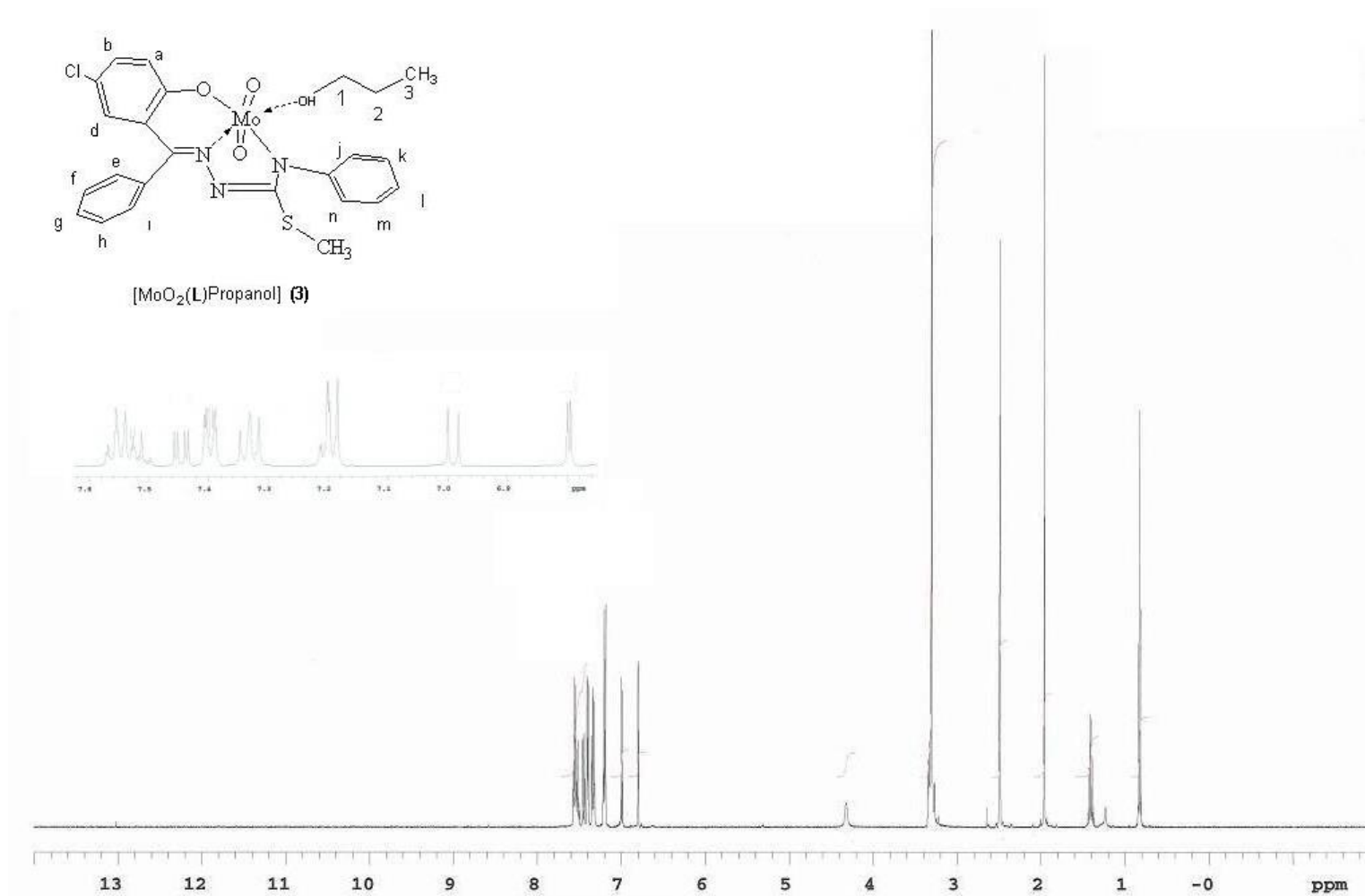


Figure S8. ^1H NMR spectra of $[\text{MoO}_2(\text{L})\text{propanol}]$ (**3**) complex and aromatic group peaks as inset (solvent: DMSO-d_6 , reference: TMS).

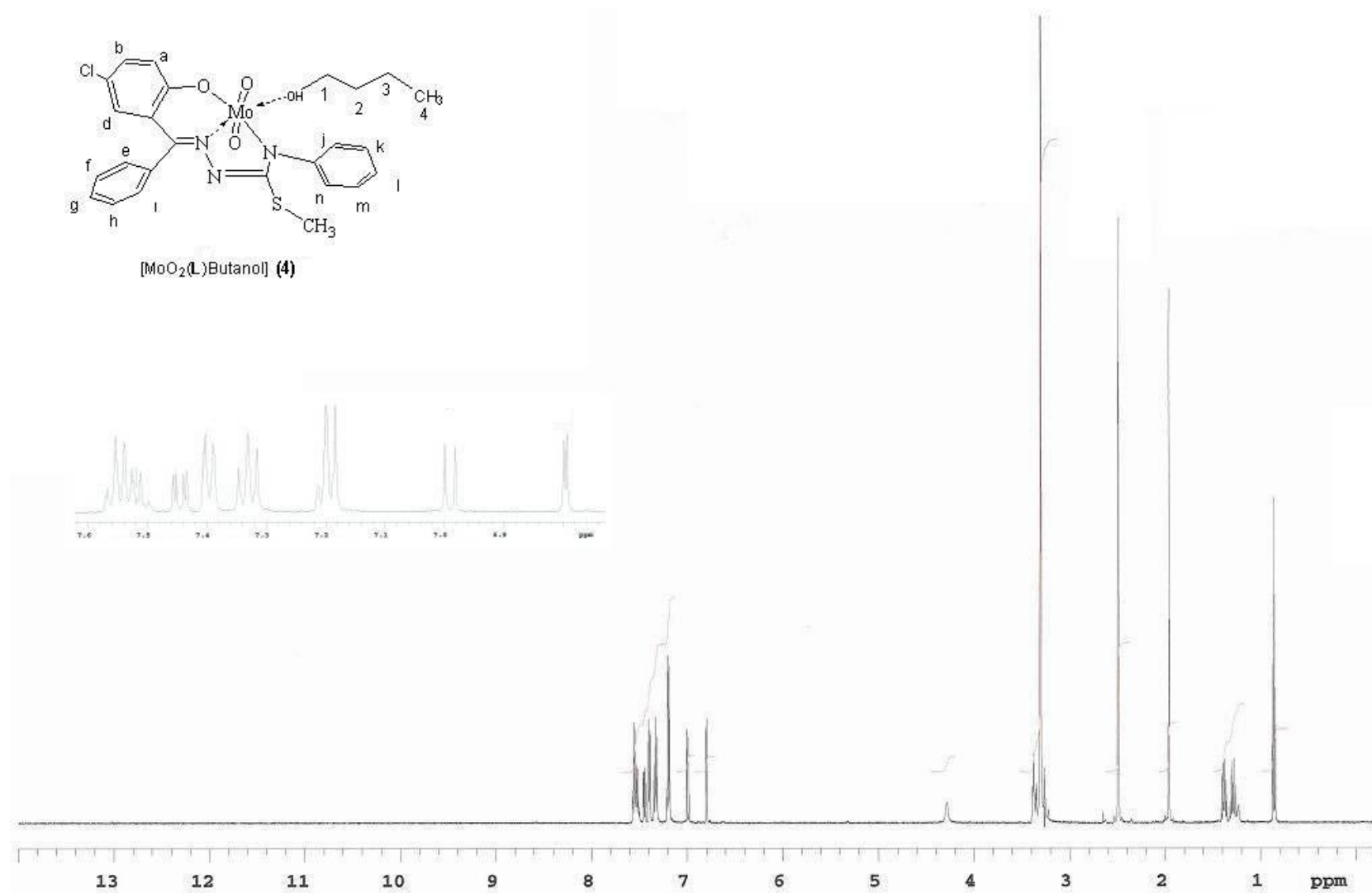


Figure S9. ¹H NMR spectra of [MoO₂(L)butanol] (4) complex and aromatic group peaks as inset (solvent: DMSO-d₆, reference: TMS).

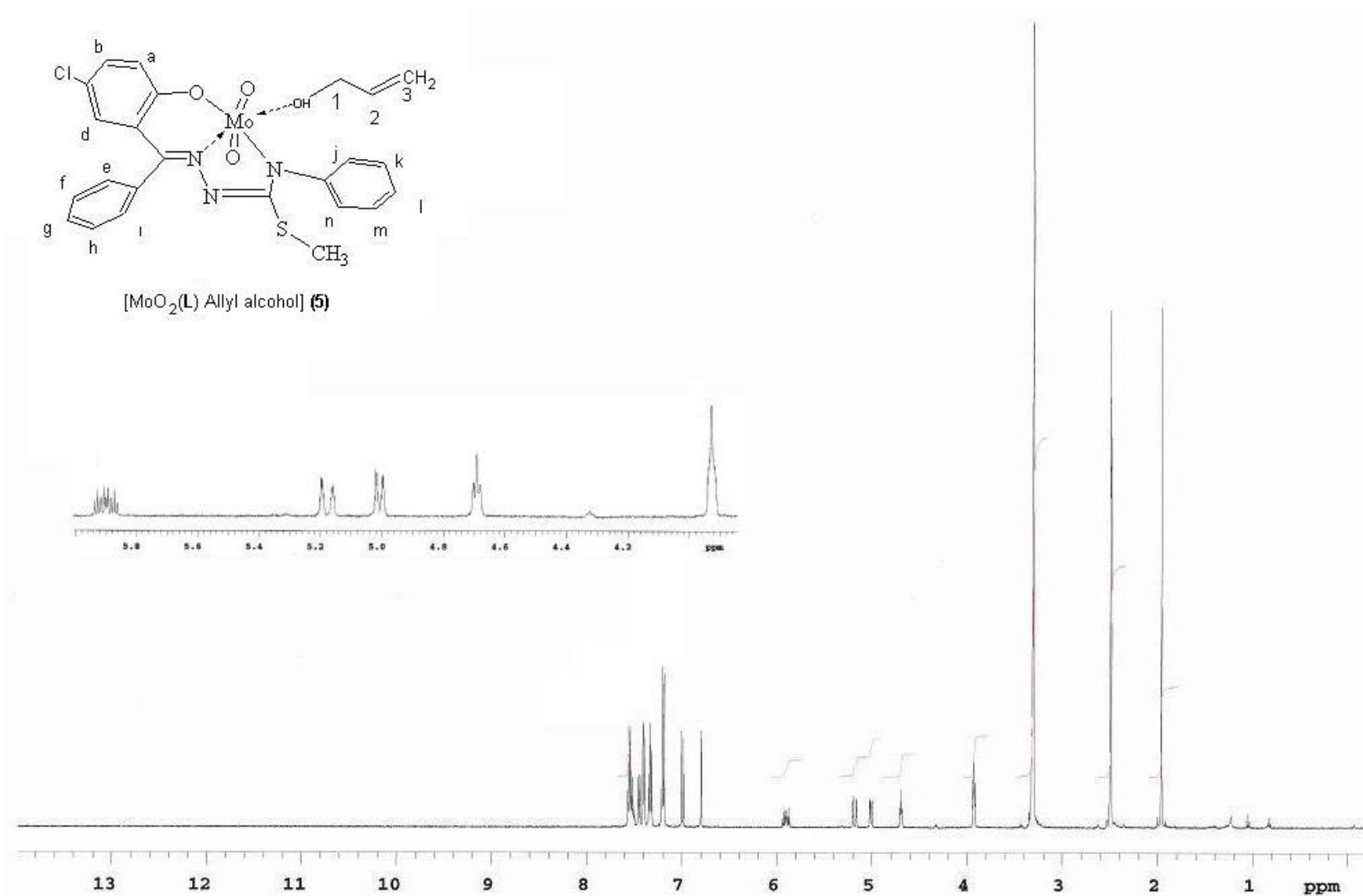


Figure S10. ^1H NMR spectra of $[\text{MoO}_2(\text{L})\text{allyl alcohol}]$ (**5**) complex and aromatic group peaks as inset (solvent: DMSO-d_6 , reference: TMS).

Table S12. Chemical shift values of ligand (**L**) and complexes (**1–5**), ¹H NMR (δ: ppm, d₆-DMSO, reference: TMS).

| Compound | 2-OH | NH-Ph | Alcohol-OH | S-CH ₃ | 1 | 2 | 3 | 4 | 5 |
|--|----------------------|--------------------|--|---------------------|--|-----------------------------------|--|-----------------------------------|----------|
| L | 13.02 (s) (1H) | 8.6 (s) (1H) | - | 2.65 (s) (3H) | - | - | - | - | - |
| [MoO ₂ (L)methanol] (1) | - | - | 4.12 (s) (1H) | 1.95 (s) (3H) | 3.16 (s) (3H) | - | - | - | - |
| [MoO ₂ (L)ethanol] (2) | - | - | 4.32 (s) (1H) | 1.95 (s) (3H) | 3.41–3.45 (m) (2H) | 1.05 (t) (J = 6.83) (2H) | - | - | - |
| [MoO ₂ (L)propanol] (3) | - | - | 4.32 (s) (1H) | 1.95 (s) (3H) | 3.32–3.34 (m) (2H) | 1.38–1.42 (m) (2H) | 0.82 (t) (J = 7.32) (3H) | - | - |
| [MoO ₂ (L)butanol] (4) | - | - | 4.29 (s) (1H) | 1.95 (s) (3H) | 3.34–3.38 (m) (2H) | 1.36–1.39 (m) (2H) | 1.27–1.30 (m) (2H) | 0.85 (t) (J = 7.32) (3H) | - |
| [MoO ₂ (L^H)allyl alcohol] (5) | - | - | 4.69 (t) (J = 5.37– 5.85) (1H) | 1.96 (s) (3H) | 3.92 (t) (J = 4.88–5.37) (2H) | 5.87–5.97 (m) (1H) | 5.01 (d-d) (J = 1.96–2.44) (2H) | - | - |

Table S13. ¹H NMR chemical shift values of aromatic hydrogens of ligand (**L**) and complexes (**1–5**) (δ : ppm, d₆-DMSO, Reference: TMS).

| Compound | a | b | d | e | f | g | h | i | j | k | l | m | n |
|--|-----------------------------------|-------------------------------------|-----------------------------------|-----------------------------------|--------------------------|--------------------------|--------------------------|-----------------------------------|--|-----------------------------------|-----------------------------------|-----------------------------------|--|
| L | 6.76 (d) (J = 2.92) (1H) | 7.33 (d) (J = 2.44) (1H) | 6.88 (t) (J = 7.32) (1H) | 7.31 (d) (4H) | 7.51–7.56 (m) (3H) | 7.51–7.56 (m) (3H) | 7.51–7.56 (m) (3H) | 7.31 (d) (4H) | 7.31 (d) (4H) | 7.02 (t) (J = 7.32) (3H) | 7.02 (t) (J = 7.32) (3H) | 7.02 (t) (J = 7.32) (3H) | 7.31 (d) (4H) |
| [MoO ₂ (L)methanol] (1) | 6.79 (d) (J = 2.44) (1H) | 7.45 (d-d) (J = 2.44) (1H) | 6.99 (d) (J = 8.79) (1H) | 7.40 (d) (J = 6.83) (2H) | 7.51–7.56 (m) (3H) | 7.51–7.56 (m) (3H) | 7.51–7.56 (m) (3H) | 7.40 (d) (J = 6.83) (2H) | 7.33 (t) (J = 7.32–8.3) (2H) | 7.21 (t) (J = 7.32) (3H) | 7.21 (t) (J = 7.32) (3H) | 7.21 (t) (J = 7.32) (3H) | 7.33 (t) (J = 7.32–8.3) (2H) |
| [MoO ₂ (L)ethanol] (2) | 6.80 (d) (J = 2.93) (1H) | 7.45 (d-d) (J = 2.93) (1H) | 6.99 (d) (J = 8.79) (1H) | 7.40 (d) (J = 6.83) (2H) | 7.51–7.57 (m) (3H) | 7.51–7.57 (m) (3H) | 7.51–7.57 (m) (3H) | 7.40 (d) (J = 6.83) (2H) | 7.33 (t) (J = 7.81) (2H) | 7.21 (t) (J = 7.32) (3H) | 7.21 (t) (J = 7.32) (3H) | 7.21 (t) (J = 7.32) (3H) | 7.33 (t) (J = 7.81) (2H) |
| [MoO ₂ (L)propanol] (3) | 6.79 (d) (J = 2.44) (1H) | 7.45 (d-d) (J = 2.93) (1H) | 6.99 (d) (J = 8.79) (1H) | 7.40 (d) (J = 6.83) (2H) | 7.51–7.57 (m) (3H) | 7.51–7.57 (m) (3H) | 7.51–7.57 (m) (3H) | 7.40 (d) (J = 6.83) (2H) | 7.33 (t) (J = 7.81) (2H) | 7.21 (t) (J = 7.32) (3H) | 7.21 (t) (J = 7.32) (3H) | 7.21 (t) (J = 7.32) (3H) | 7.33 (t) (J = 7.81) (2H) |
| [MoO ₂ (L ^H)butanol] (4) | 6.79 (d) (J = 2.93) (1H) | 7.45 (d-d) (J = 2.44) (1H) | 6.99 (d) (J = 8.79) (1H) | 7.40 (d) (J = 6.83) (2H) | 7.51–7.57 (m) (3H) | 7.51–7.57 (m) (3H) | 7.51–7.57 (m) (3H) | 7.40 (d) (J = 6.83) (2H) | 7.33 (t) (J = 7.32–8.3) (2H) | 7.21 (t) (J = 7.32) (3H) | 7.21 (t) (J = 7.32) (3H) | 7.21 (t) (J = 7.32) (3H) | 7.33 (t) (J = 7.32–8.3) (2H) |
| [MoO ₂ (L ^H)allyl- alcohol] (5) | 6.79 (d) (J = 2.92) (1H) | 7.45 (d-d) (J = 2.93) (1H) | 6.99 (d) (J = 8.79) (1H) | 7.40 (d) (J = 6.83) (2H) | 7.50–7.57 (m) (3H) | 7.50–7.57 (m) (3H) | 7.50–7.57 (m) (3H) | 7.40 (d) (J = 6.83) (2H) | 7.33 (t) (J = 7.32– 8.30) (2H) | 7.20 (t) (J = 7.81) (3H) | 7.20 (t) (J = 7.81) (3H) | 7.20 (t) (J = 7.81) (3H) | 7.33 (t) (J = 7.32– 8.30) (2H) |

Table S14. The molybdenum-centered bond distances and angles of complex **5**. ⁽¹⁾ indicates axis angles of the octahedron, ⁽²⁾ angles between allyl alcohol oxygen (O4) and the atoms in the meridional positions.

| Experimental | Theoretical | | | | | | Ligand |
|--------------|--------------|--------------|----------|---------|---------|----------|---------|
| | Allylalcohol | Allylalcohol | Methanol | Ethanol | Butanol | Propanol | |
| | Distance (Å) | Distance (Å) | | | | | |
| Mo1- O1 | 1.934(2) | 1.965 | 1.939 | 1.96527 | 1.96490 | 1.96592 | - |
| Mo1-O2 | 1.684(2) | 1.735 | 1.740 | 1.73531 | 1.73528 | 1.73547 | - |
| Mo1-O3 | 1.711(2) | 1.745 | 1.742 | 1.74506 | 1.74501 | 1.74419 | - |
| Mo1-O4 | 2.380(2) | 2.529 | 2.271 | 2.50326 | 2.49665 | 2.49703 | - |
| Mo1-N1 | 2.245(2) | 2.284 | 2.294 | 2.28565 | 2.28444 | 2.28651 | - |
| Mo1-N3 | 2.059(2) | 2.076 | 2.147 | 2.07768 | 2.07809 | 2.07769 | - |
| N3-C14 | 1.346(3) | 1.36814 | 1.38311 | 1.36719 | 1.36627 | 1.36673 | 1.28350 |
| N2-C14 | 1.308(3) | 1.32701 | 1.31948 | 1.32730 | 1.32776 | 1.32759 | 1.45186 |
| N2-N1 | 1.393(3) | 1.40845 | 1.40639 | 1.40874 | 1.40957 | 1.40883 | 1.26602 |

| | | | | | | | |
|-------|----------|---------|---------|---------|---------|---------|---------|
| N1-C7 | 1.309(3) | 1.32900 | 1.32506 | 1.32872 | 1.32872 | 1.32843 | 1.37859 |
| C2-C7 | 1.466(3) | 1.47235 | 1.47132 | 1.47266 | 1.47253 | 1.47273 | 1.48455 |
| C7-C8 | 1.486(3) | 1.42840 | 1.43038 | 1.42857 | 1.42867 | 1.42858 | 1.47047 |
| C1-O1 | 1.338(3) | 1.36281 | 1.35948 | 1.36224 | 1.36210 | 1.36225 | 1.28946 |

Angle (degrees)

| | | | | | | | |
|----------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| O4-Mo1-O2 ⁽¹⁾ | 171.31(9) | 176.94 | 160.59954 | 176.49365 | 176.25159 | 176.17149 | - |
| O3-Mo1-N1 ⁽¹⁾ | 157.66(8) | 154.37 | 160.66326 | 154.70289 | 154.41245 | 154.83469 | - |
| O1-Mo1-N3 ⁽¹⁾ | 146.79(8) | 146.05 | 147.67587 | 146.36964 | 146.50959 | 146.32844 | - |
| O4-Mo1-O1 ⁽²⁾ | 77.26(7) | 100.45 | 95.83609 | 100.07757 | 99.98523 | 78.12956 | - |
| O4-Mo1-O3 ⁽²⁾ | 82.69(9) | 107.31 | 102.43118 | 107.19686 | 107.23806 | 76.60676 | - |
| O4-Mo1-N1 ⁽²⁾ | 78.06(8) | 97.18 | 95.42376 | 96.89878 | 97.13103 | 79.60262 | - |
| O4-Mo1-N3 ⁽²⁾ | 79.08(8) | 101.18 | 102.43118 | 100.93044 | 100.79348 | 79.26179 | - |
| Mo1-N3 ⁽²⁾ -C14 | 118.1(1) | 117.96795 | 115.50812 | 117.92013 | 117.94188 | 117.92652 | - |
| N3 ⁽²⁾ -C14-N2 | 124.0(2) | 123.13662 | 123.39468 | 123.21361 | 123.19433 | 123.24865 | 118.16024 |
| C14-N2-N1 | 109.1(2) | 111.13637 | 113.18457 | 111.12199 | 111.06999 | 111.09972 | 115.43981 |
| N2-N1-C7 | 115.1(2) | 115.98808 | 115.33104 | 116.04114 | 109.11436 | 116.05020 | 128.38413 |

| | | | | | | | |
|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| C8-C7-C2 | 117.7(2) | 122.80182 | 121.54697 | 122.81917 | 122.80204 | 122.82209 | 115.66864 |
| C2-C1-O1 | 122.1(2) | 121.78294 | 122.46368 | 121.83497 | 121.83847 | 121.84497 | 119.60861 |
| C1-O1-Mo1 | 129.7(2) | 133.38912 | 138.22807 | 133.43659 | 121.83847 | 133.42098 | - |
| N2-N1-Mo1 | 117.0(1) | 115.06485 | 114.58699 | 115.03026 | 122.43151 | 115.01676 | - |
| Mo1-N1-C7 | 127.9(2) | 128.86315 | 130.02732 | 128.85626 | 128.14588 | 128.85740 | - |
