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ARTICLE

Hydrazone-Based Ligand with Pyrrolidine Donor and Its Molybdenum(VI) Complex: Synthesis, Structure, and Reactivity

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Dedicated to Professor Dr. Peter Klüfers on the Occasion of his 70th Birthday

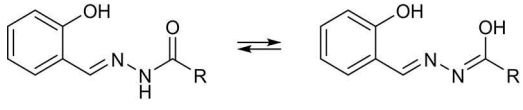
The Schiff-base condensation of salicylaldehyde and 4-aminobutanehydrazide hydrochloride leads to the hydrazone-based ligand H_2salhyab containing an amino side chain. The reaction of H_2salhyab·HCl with bis(acetylacetonato)dioxidomolybdenum leads to the formation of [MoO_2(salhycab)(MeOH)] (H_2salhycab = 2-((pyrrolidine-2-ylidenehydrazineylidene)methyl) phenol), whereby the amino side chain reacted with the hydrazide carbonyl group to form a cyclic amidine with a pyrrolidine ring leading a new type of tridentate hydrazone ligand with [NNO] donor set. X-ray crystallography revealed the additional coordination of a methanol molecule at the molybdenum(VI) center which leads to the formation of hydrogen-bonded dimers of the neutral complex in the crystal structure. The complex [MoO_2(salhycab)(MeOH)] was found to be an efficient catalyst for the peroxidic oxidation of phenyl methyl sulfide.

Introduction

Molybdenum has been reported as an important metal in biological systems and, numerous molybdenum containing enzymes are known.[1] In particular, the existence of molybdenum in oxotransferase enzymes has sparked interest in reactivity and coordination chemistry of *cis*-dioxidomolybdenum(VI) complexes.[2] Various molybdenum(VI) complexes have been reported as efficient catalysts for epoxidation and hydroxylation of olefins,[3] oxidation of sulfides[4] as well as alcohols,[5] and as catalysts of oxygen transfer reaction.[6] Among these applications sulfoxides are of specific interest due to their relevance for pharmaceutical industry and academia.[7] Although sulfoxidation activity has been reported for different molybdenum-based catalysts ranging from simple salts[8] and composite metal oxides[9] to heterogeneous materials.[10] However, the number of documented *cis*-dioxomolybdenum(VI) complexes catalyzing the peroxidic oxidation of sulfides is still rather limited.[11]

Hydrazones are widely used ligand systems due to their potential in various fields including analytical, sensing, switching, and biological applications.[12] A specific subgroup of interest in medicinal and coordination chemistry are the acylhydrazones,[13] which in the case of their salicylidene derivatives are tridentate chelate ligands.[14] Such *N*-salicylidene hydrazides with pendant functionalized side chains (see Scheme 1) have been introduced as versatility tridentate ligand systems with [ONO] donor set capable of supporting different protonation states and various types of transition metal complexes.[14] These ligands specifically enable the variation of possible aggregation modes and supramolecular assemblies.[15]

For molybdenum(VI) complexes with *N*-salicylidene hydrazides that contain an ω-hydroxy side chain, this leads to intermolecular interactions of the side chain oxygen donor either as an additional ligand at the molybdenum(VI) center or via hydrogen bonding.[16] This is in contrast to vanadium(V) complexes, for which intramolecular hydrogen bonding interactions of the side chain donor with the oxido groups of the vanadium(V) center were observed.[17] For an ω-amino functionalized *N*-salicylidene hydrazide ligand with a long side chain (R=$(CH_2)_5NH_2$, see Scheme 1), however, only intermolecular hydrogen bonding interactions for the vanadium(V) complex are found.[18] With this concept, we were also able to generate a β-amino acid functionalized molybdenum(VI) complex that efficiently catalyzes the peroxidic oxidation of sulfides.[19]



Scheme 1. Representation of *N*-salicylidene hydrazide ligands with functionalized side chain and their tautomeric forms.

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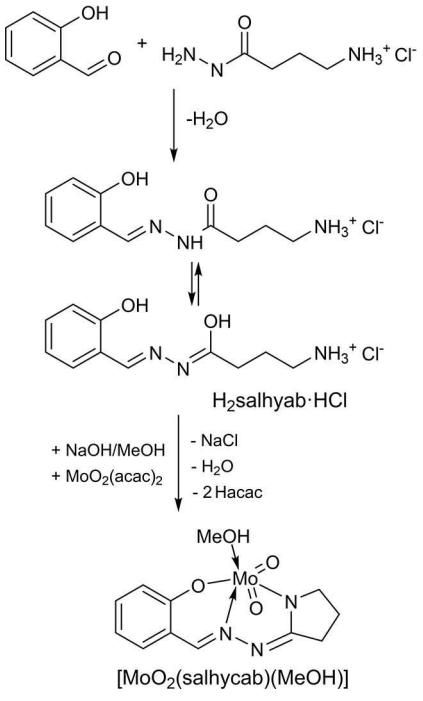
In this work, we present the synthesis and characterization of an ω-amino *N*-salicylidene hydrazide ligand with a shortened side chain (R=$(CH_2)_3NH_2$, see Scheme 1) and its complexation reaction to form a *cis*-dioxidomolybdenum(VI) complex that leads to the formation of a cyclic amidine with a pyrrolidine ring, resulting in a new type of tridentate hydrazone-based ligand with [ONN] donor set.

Results and Discussion

Synthesis and Characterization

The amino side chain functionalized Schiff base 4-amino-*N*′-[(2-hydroxyphenyl)methylidene]butanohydrazide (H_2salhyab) was synthesized in a two step reaction. First, the carbonic acid hydrazide was synthesized by reaction of the corresponding ester with hydrazine hydrate under reflux and continuous stirring for 12 h.[20] Subsequently, the Schiff base was obtained by condensation of the carbonic acid hydrazide with salicylaldehyde in ethanol and isolated as monohydrochloride salt H_2salhyab·HCl, as depicted in Scheme 2 (for details see Experimental Section).

Such carbonic acid hydrazides are known as tridentate chelate ligands with [ONO] donor set and, due to their tautomeric forms, possess a variable protonation state at the amide function, which allows them to act as mono- or dianionic chelates.[21] The reaction of the hydrochloride salt H_2salhyab·HCl with bis(acetylacetonato)dioxidomolybdenum(VI) in methanol solution in the presence of one equivalent sodium hydroxide



Scheme 2. Synthesis of H_2salhyab and the complex [MoO_2(salhycab)(MeOH)].

leads to the formation of a neutral complex, which could be isolated as orange crystalline material. This complex contains the cyclized amidine derivative H_2salhycab (2-((pyrrolidine-2-ylidene-hydrazineylidene)methyl)phenol) of the employed ligand with a pyrrolidine ring leading to a new type of tridentate hydrazone-based ligand with [ONN] donor set. The formation of the cyclic amidine seems to be favored by the lengths of the amino side chain leading to a five membered pyrrolidine ring as such a cyclization was not observed for derivatives with longer amino side chain.[18] This ligand cyclization is supported by elemental analysis, NMR spectroscopy, and X-ray crystallography which also revealed the presence of an additional methanol molecule coordinated at the molybdenum (VI) center leading to the neutral complex [MoO_2(salhycab)(MeOH)].

The ^{1}H NMR data confirms the formation of the complex and the coordination mode of the cyclized hydrazone-based pyrrolidine ligand. In particular, the twofold deprotonation of the ligand is confirmed by the absence of the characteristic NH and OH resonances in the ^{1}H NMR spectra of the complex. The cyclization as well as the coordination of the pyrrolidine donor at the molybdenum(VI) center is consistent with the observed downfield shift of the resonance corresponding to the relevant methylene group from about 2.8 ppm in the hydrochloride of the open chain ligand H_2salhyab·HCl ($CH_2NH_3^+$) to about 3.8 ppm in the complex with the coordinated cyclic amidine ligand salhycab^{2-} (CH_2N–Mo). This is also supported by the absence of the NH resonance of the ammonium group at 8.04 ppm (NH_3^+). Moreover, for the open chain ligand H_2salhyab the azomethine proton (CH=N) gives rise to two resonances at 8.28 and 8.42 ppm attributed to E–Z isomerism,[22] whereas for the coordinated cyclized H_2salhycab ligand only one resonance is observed at 8.47 ppm. Interestingly, a much more pronounced coordination induced shift[23] is observed for comparable molybdenum(VI) and vanadium(V) complexes with carbonic acid hydrazide ligands that provide an [ONO] donor set.[16,22,24] The presence of the coordinated methanol molecule is confirmed by the specific resonances of the methyl and OH protons at 3.16 ppm and 4.08 ppm, respectively, as well as the ^{13}C resonance at 48.6 ppm.

The formation of the cyclic amidine upon coordination at the molybdenum(VI) center is also evident from the changes observed for the relevant ^{13}C NMR resonances. In particular, the resonance related to the methylene group next to the terminal ammonium group of H_2salhyab·HCl ($CH_2NH_3^+$) at 38.2 ppm is found at 58.3 ppm for the corresponding methylene group of the pyrrolidine ring. In addition, this significant downfield shift is also consistent with the coordination of the pyrrolidine N donor at the molybdenum(VI) center. A similar, although less pronounced, coordination induced shift is observed for the resonance of the azomethine carbon atom (140.8 and 146.3 ppm, E–Z isomers) of the uncoordinated open chain ligand, which is found at 151.5 ppm in the complex with the cyclic amidine ligand.[25]

The IR spectrum of the complex [MoO_2(salhycab)(MeOH)] contains strong bands at 909 and 930 cm^{-1}, corresponding to the stretching vibrations of the *cis*-MoO_2 group. This is in good agreement with examples reported in literature that also

contain a coordinated alcoholic oxygen donor in *trans* position to one of the oxido donors at the molybdenum(VI) center.[16,19,26] The strong band assigned to the stretching vibration of the CH=N–N=C group, commonly observed in the range from 1600 to 1625 cm^{-1} for dianionic carbonic acid hydrazides coordinated to metal centers,[18,22,27] is found well within this range for [MoO_2(salhycab)(MeOH)] at 1606 cm^{-1}, although in this case an amidine is part of the functional group. The presence of a coordinated methanol molecule is evident from a broad band at 3436 cm^{-1}.

Structure Description

The neutral complex [MoO_2(salhycab)(MeOH)] crystallizes in the monoclinic space group $P2_1/c$ (see Experimental Section for crystallographic details). The molecular structure of the complex is depicted in Figure 1. Selected bond length and angles for the first coordination sphere of the molybdenum(VI) center of [MoO_2(salhycab)(MeOH)] are summarized in Table 1. The structure shows that the employed ω-amino *N*-salicylidene hydrazide ligand H_2salhyab was transformed to the cyclic amidine ligand H_2salhycab upon complexation leading to a pyrrolidine ring in the newly formed hydrazone-based ligand.

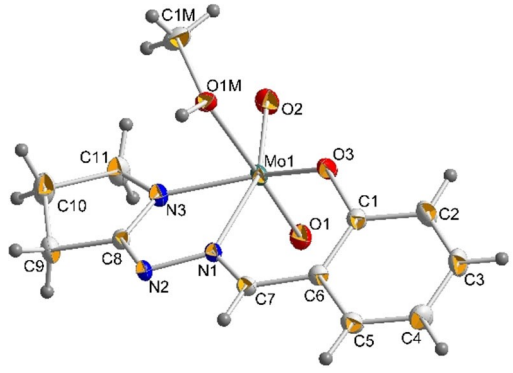


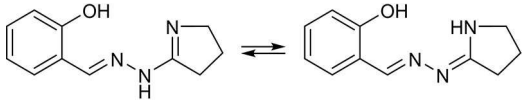
Figure 1. Molecular structure of the complex [MoO_2(salhycab)(MeOH)] together with the atom labeling. Thermal ellipsoids are drawn at 50 % probability level.

Table 1. Selected bond lengths (in pm) and angles (in °) for [MoO_2(salhycab)(MeOH)].

Mo1–O1	169.85(15)	Mo1–N1	227.67(15)
Mo1–O2	170.29(15)	Mo1–N3	206.08(18)
Mo1–O3	195.38(15)	C8–N2	131.0(3)
Mo1–O1M	231.39(14)	C8–N3	134.0(3)
O1–Mo1–O2	105.19(7)	O2–Mo1–O3	106.46(7)
O1–Mo1–O3	96.24(7)	O2–Mo1–O1M	83.19(6)
O1–Mo1–O1M	170.80(7)	O3–Mo1–O1M	77.46(6)
O1–Mo1–N1	93.43(6)	O2–Mo1–N1	159.02(7)
O1–Mo1–N3	100.45(7)	O2–Mo1–N3	95.94(7)
O3–Mo1–N1	80.48(6)	O3–Mo1–N3	147.40(7)
N1–Mo1–O1M	79.01(5)	N3–Mo1–O1M	82.14(6)
N1–Mo1–N3	70.79(6)		

From the molecular structure it is evident that the molybdenum atom is found in a distorted octahedral geometry, with the [ONN] donor set of the hydrazone ligand, the methanol oxygen donor, and the two oxido groups of the *cis*-MoO_2^{2+} moiety forming the coordination sphere. The Mo=O bond lengths (Mo–O1 and Mo–O2) are found in the typical range of 169–170 pm and also the O–Mo–O bond angle with 105.19(7)° in the expected range.[26b,28] Due to the *cis* configuration of the oxido groups, O1 is in an axial position with respect to the equatorial plane defined by the tridentate ligand (O3, N1, and N3), while the second oxido group O2 located in the equatorial plane is in *trans* position to the imine donor N1 at a distance of 227.67(15) pm. The dianionic tridentate ligand salhycab^{2-} coordinates in a meridional fashion leading to a five- and six-membered chelate ring with bite angles of 70.8° and 80.5°, respectively. The two formally anionic donor atoms O3 and N3 of the ligand are in *trans* position with an angle O3–Mo–N3 of 147.40(7)° and a Mo–O3 bond length of 195.38(15) pm, which is somewhat elongated with respect to the corresponding molybdenum(VI) complexes with *N*-salicylidene hydrazide ligands (phenolate Mo–O 193 pm).[16,19] Moreover, the Mo–N3 bond length is found at 206.08(18) pm, which is consistent with the anionic nature of amidate nitrogen donor. This is supported by the bond lengths for the amidine carbon atom C8 with 131 and 134 pm for C8–N2 and C8–N3, respectively, which show that the deprotonated ligand in the complex corresponds to the tautomeric form with the C=N double bond of the amidate is in conjugation with the imine C=N bond of the hydrazone (see Scheme 3). Although a comparison with coordinated hydrazine amidinate ligands from literature is not possible, this is supported by the equivalent observation in the case of the related *N*-salicylidene hydrazide ligands, where the corresponding enolate form of the amide group shows similar bond lengths (C–N 131 pm and C–O 130 pm),[22,29] whereas for complexes with coordinated keto form a pronounced difference for the bond lengths is observed (C–N 133 pm and C–O 127 pm).[29]

The octahedral coordination sphere of the molybdenum atom is completed by a methanol molecule, which is coordinated in *trans* position to the oxido group O1 and weakly bounded at the molybdenum(VI) center (Mo–O1M 231.36(14) pm) due to the *trans* influence of the oxido group.[30] In the crystal structure the OH group of the coordinated methanol is involved in hydrogen bonding to a neighboring complex molecule leading to a dimer of neutral complexes as depicted in Figure 2.



Scheme 3. Tautomeric forms of the protonated ligand H_2salhycab.

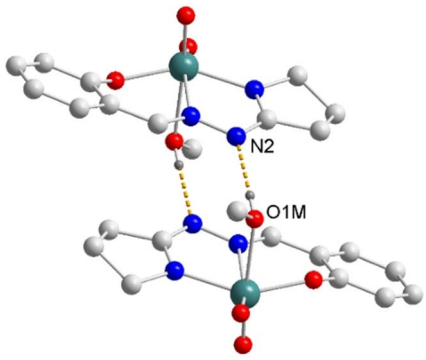
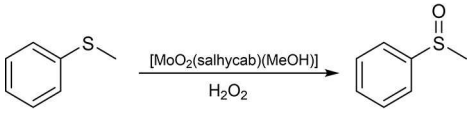


Figure 2. Hydrogen bonded dimer of $[MoO_2(salhycab)(MeOH)]$ with an O1M···N2 Distance of 268.8(2) pm (O1M–H···N3 179(3)°). Hydrogen atoms not involved in hydrogen binding are omitted for clarity.

Sulfoxidation

The *cis*-dioxidomolybdenum complex $[MoO_2(salhycab)(MeOH)]$ was tested for its ability to catalyze the oxidation of sulfides under homogeneous conditions in solution using methyl phenyl sulfide (thioanisol) as model substrate (see Scheme 4). Hydrogen peroxide was used as oxidizing agent in a slight excess of 1.2 equivalents based on the sulfide substrate. The reaction was started by the addition of the oxidant to the solution (dichloromethane/methanol = 7:3) of the substrate, which was cooled to 0 °C. The reaction solution containing 1 mol% of catalyst based on the substrate was stirred at room temperature and monitored by gas chromatography. A control reaction under the same conditions without any complex present leads to less than 1% sulfide conversion. After the reaction the solvent was removed in vacuo and the products were separated by column chromatography.

The complex $[MoO_2(salhycab)(MeOH)]$ functions as an efficient catalyst for the sulfide oxidation. In the presence of 1 mol% of complex in a dichlormethane methanol solution mixture an overall yield of 83% was observed after a reaction time of 18 h, with the sulfoxide being the major product, which is well within the reported range observed for other molybdenum(VI) catalysts.[11,16,31] Unfortunately, the reaction also leads to an overoxidation resulting in the corresponding sulfone at an amount of 25% of the final product. Although this is a feature commonly observed for molybdenum(VI) catalysts, it is worth noting that no such overoxidation is observed for molybdenum(VI) and vanadium(V) catalysts with related *N*-salicylidene hydrazide ligands.[18–19,27b] For $[MoO_2(salhycab)(MeOH)]$ this overoxidation could be reduced by a stepwise addition of the hydrogen peroxide over a period 15 min in the initial phase of the reaction, which leads to the same overall yield, but the amount sulfone formed is reduced to 10%.



Scheme 4. Sulfoxidation of methyl phenyl sulphide with hydrogen peroxide and 1 mol% of $[MoO_2(salhycab)(MeOH)]$ as catalyst.

Conclusions

We report the synthesis of a new ω-amino *N*-salicylidene hydrazide ligand H_2salhyab with a short side chain of three methylene groups ($R=(CH_2)_3NH_2$, see Scheme 1). This potential ligand is employed in the synthesis of a molybdenum(VI) complex. However, this reaction leads to the formation of a cyclic amidine which is associated with an intramolecular condensation reaction of the terminal amino and the carbonyl group of the ligand. As revealed by the crystal structure, the obtained molybdenum(VI) complex $[MoO_2(salhycab)(MeOH)]$ contains the new and hitherto unprecedented tridentate hydrazone-based ligand H_2salhycab with a cyclic amidine as part of a pyrrolidine ring and an [ONN] donor set. This new ligand is coordinated in its dianionic form with the two formally negative donor groups the phenolate oxygen O3 and the amidinate nitrogen N3 in *trans* position at the molybdenum(VI) center. In the solid state the neutral complex molecules dimerize via hydrogen bonding between the coordinated methanol molecule and the non-coordinated amidinate nitrogen atom N2. The observed catalytic activity towards the peroxidic oxidation of sulfides is within the range for reported complexes with a corresponding *N*-salicylidene hydrazide backbone.

Experimental Section

Materials and Instrumentation: All reagents were used as received, without further purification. Abbreviations used throughout the manuscript: H_2salhyab = 4-amino-*N*′-[(2-hydroxyphenyl) methylidene]butanohydrazide and H_2salhycab = 2-((pyrrolidin-2-ylidenehydrazineylidene)methyl)phenol. Solution NMR spectra (^1H and ^{13}C) were recorded on Bruker Avance 200 and 400 spectrometers. Elemental analyses (C, H, N) were performed with a Leco CHNS-932 elemental analyzer. GC measurements were carried out on an SRI 8610D gas chromatograph using an MXT-1 Restek column. IR spectra were measured on a Bruker IFS55/Equinox spectrometer on samples prepared as KBr pellets.

Synthesis of 4-aminobutanehydrazide hydrochloride: To a solution of ethyl 4-aminobutanoate hydrochloride (7.68 g, 0.05 mmol) in ethanol (10 mL) hydrazine hydrate (2.50 g, 2.50 mL, 0.05 mmol) was added under continuous stirring, followed by addition of ethanol (40 mL) and water (5 mL). The resulting solution was heated to reflux under continuous stirring overnight. After cooling to room temperature, diethyl ether (50 mL) was added which caused a turbid solution. Stirring at room temperature for 12 h afforded a colorless precipitate. (Note: In the case an oily product is formed, the reaction mixture was dried in vacuo and subsequently extracted three times with hot ethanol and precipitated by stirring with diethyl ether (100 mL)). Yield: 6.45 g (0.04 mol; 84%). Elemental analysis for $C_4H_{12}N_3ClO$ ($M = 153.61\ g \cdot mol^{-1}$): calcd: C 31.28, H 7.87, N 27.36%; found: C 32.20, H 7.68, N 26.37%.

Synthesis of H_2salhyab·HCl: Salicylaldehyde (2.42 g, 0.02 mol, 2.07 mL) was added dropwise to a solution of 4-aminobutanehydrazide hydrochloride (3.20 g, 0.02 mol) in absolute ethanol (50 mL) heated to reflux. The resulting yellow solution was cooled down to room temperature and subsequently stirred overnight. The formed precipitate was filtered off and dried in vacuo. Additional material can be obtained by reducing the solution volume in vacuo to about half, followed by addition of diethyl ether (100 mL). Total yield: 4.12 g (0.016 mol; 80 %). Elemental analysis for $C_{11}H_{16}N_3ClO_2$ ($M = 257.72\ g\,mol^{-1}$): calcd: C 51.27, H 6.26, N 16.30 %; found: C 51.81, H 6.31, N 15.96 %. **^{1}H NMR** (400 MHz, dmso-d_6, ppm): $\delta = 1.80$–1.90 (m, 2H, CH_2), 2.36 and 2.70 (both t, $^3J = 7.2$ Hz, 2H total, CH_2CO), 2.79–2.85 (m, 2H, $CH_2NH_3^+$), 6.87–6.99 (m, 2H, arom. CH), 7.19–7.40 (m, 1H, arom. CH), 7.46–7.69 (m, 1H, arom. CH), 8.04 (br, 3H, NH_3^+), 8.28 and 8.42 (s, 1H total, CH=N), 10.16, 11.17, 11.29 and 12.02 (NH and OH, 2H total). **^{13}C{^{1}H} NMR** (50 MHz, dmso-d_6, ppm): $\delta = 21.8$, 22.8 (both CH_2), 29.0 and 30.6, (CH_2CO), 38.2 ($CH_2NH_3^+$), 116.1, 116.3, 118.6, 119.2, 120.0, 126.5, 130.6, 130.9, 131.1, 133.1 (all arom. CH and C), 140.8, 146.5 (both CH=N), 156.4, 157.3, 158.6, 162.5, 167.6 (arom. C), 172.9 (C=O). **IR** (KBr, selected data, cm^{-1}): $\tilde{\nu} = 3461$ (br, NH_3^+), 3169 (br, NH), 1689 (s; C=O), 1621 (s, C=N).

Synthesis of [MoO_2(salhycab)(MeOH)]: To a stirred solution of H_2salhyab·HCl (0.80 g, 3.10 mmol) in methanol (60 mL) was added NaOH (0.12 g, 3.10 mmol), followed by the addition of $MoO_2(acac)_2$ (1.00 g, 3.10 mmol). The resulting red solution was heated under reflux with continuous stirring for one hour. Subsequently the volume of the solution was reduced to about half under reduce pressure and left at room temperature while an orange-reddish precipitate was formed. The resulting precipitate was filtered off and the filtrate kept in an open flask at room temperature. Upon slow evaporation of the solvent suitable orange crystals for X-ray measurement could be isolated. Total yield: 0.72 g (1.99 mmol; 64 %). Elemental analysis for $C_{12}H_{15}N_3MoO_4$ ($M = 361.20\ g\,mol^{-1}$): calcd: C 39.90, H 4.19, N 11.63 %; found: C 40.20, H 4.16, N 11.55 %. **^{1}H NMR** (400 MHz, dmso-d_6, ppm): $\delta = 2.06$–2.14 (m, 2H, CH_2), 2.48–2.50 (m, CH_2C=N, overlap with the solvent signal), 3.16 (d, $^3J = 5.2$ Hz, 3H, CH_3OH), 3.82–3.86 (m, 2H, CH_2–N–Mo), 4.08 (q, $^3J = 5.2$ Hz, 1H, CH_3OH), 6.79–6.98 (m, 2H, arom. CH), 7.36–7.40 (m, 1H, arom. CH), 7.53–7.55 (m, 1H, arom. CH), 8.47 (s, 1H, CH=N). **^{13}C{^{1}H} NMR** (100 MHz, dmso-d_6, ppm): $\delta = 25.4$ (CH_2), 26.3 (CH_2C=N), 48.6 (CH_3OH), 58.3 (CH_2N–Mo), 118.1, 120.3, 120.8, 133.3, 133.6 (all arom.CH and C), 151.5 (CH=N), 160.2 (arom. C–O–Mo), 176.5 (C=N) ppm. **IR** (KBr, selected data, cm^{-1}): $\tilde{\nu} = 3436$ (br, OH), 1606 (s, –C=N–N=C–), 930 and 909 (s, MoO_2).

Sulfoxidation: The molybdenum complex [MoO_2(salhycab)(MeOH)] (0.025 mmol) was dissolved at room temperature in a mixture of CH_2Cl_2 and CH_3OH (7:3, 25 mL) and phenyl methyl sulfide (0.29 ml, 2.5 mmol) was added. The resulting solution was cooled to 0 °C and a slight excess of an aqueous solution of H_2O_2 26 % (1.2 equiv., 0.35 mL, 3 mmol) was dropwise added to start the reaction. This addition was either performed with the total amount at once or in a stepwise manner over the first 15 min of the reaction. Subsequently the reaction solution was stirred at room temperature (283 K) in a capped flask and monitored by gas chromatography. After the reaction the solvent was removed in vacuo and the products were separated by column chromatography on silica gel using a diethyl ether/pentane mixture (9:1) as eluent for the unreacted sulfide and ethyl acetate as eluent for the corresponding sulfoxide.

X-ray Crystallography: Crystals of [MoO_2(salhycab)(MeOH)] suitable for X-ray crystallography were obtained directly from the mother liquor. The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo–K_α radiation. Data were corrected for Lorentz and polarization effects and absorption was taken into account on a semi-empirical basis using multiple-scans (SADABS 2016/2).[32] The structure was solved by direct methods (SHELXT)[33] and refined by full-matrix least squares techniques against F^2 (SHELXL-2018).[34] All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically. A summary of crystallographic and structure refinement data is given in Table 2. Crystallographic data (excluding structure factors) for [MoO_2(salhycab)(MeOH)] has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. A copy of the data can be obtained free of charge on quoting the depository number CCDC-2047182 (E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Table 2. Crystallographic data for [MoO_2(salhycab)(MeOH)].

empirical formula	$C_{12}H_{15}MoN_3O_4$
formula weight/g mol^{-1}	361.21
crystal system	Monoclinic
space group	$P2_1/c$ (No. 14)
a/pm	1021.06(3)
b/pm	1282.03(4)
c/pm	1091.66(2)
α/°	90.0
β/°	110.274(2)
δ/°	90.0
V/nm^3	1.34048(6)
T/°C	−90
Z	4
μ(Mo K_α)/mm^{-1}	0.996
measured reflections	9330
Data with $I > 2\sigma(I)$	2762
unique reflections (R_{int})	3055 (0.0235)
goodness-of-fit on F^2	1.050
Final R indices [all data]	$R_1 = 0.0284$, $\omega R_2 = 0.0635$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0239$, $\omega R_2 = 0.0610$

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