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Diastereoselective synthesis and catalytic activity of two chiral *cis*-dioxido molybdenum(VI) complexes

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Abstract: Two enantiomerically pure chiral molybdenum(VI) dioxido complexes (**1** and **2**) of the type [MoO_2**L**] (**L**= dianionic, tetradentate *ONNO*-ligand) were synthesized and investigated in enantioselective oxidation reactions. The solid state structures of complex **1** and **2**, determined via single-crystal X-ray diffraction analysis revealed two fundamentally different coordination geometries: a *C*1-symmetric *cis*-β isomer (Λ-**1**), and a *C*2-symmetric *cis*-α isomer (Δ-**2**). In both cases, only one of the two possible helical enantiomers (Λ- or Δ-helix) was formed. The complexes were examined as precatalysts in the epoxidation of the challenging prochiral substrate *trans*-stilbene, using either *tert*-butylhydroperoxide (TBHP) or cumylhydroperoxide (CHP) as oxidants. The asymmetric *cis*-β complex **1** was found to be significantly more active in the epoxidation than its *cis*-α counterpart **2**, asymmetric induction was, however, negligible for both complexes. The complexes were also tested in catalytic enantioselective sulfoxidation reactions where chiral induction could be achieved, albeit small. The observed putative molybdenum oxido-peroxido intermediate **1-O_2** could be identified as an important pre-complex before formation of the active catalyst in sulfoxidation.

Introduction

The synthesis and characterization of chiral metal complexes is undeniably one of the abiding interests in synthetic inorganic chemistry. Much of this interest is inspired by the prospective practical application of such chiral complexes in asymmetric catalysis. A broad range of asymmetric reactions can be catalyzed efficiently by a variety of chiral transition metal complexes to give products in high enantioselectivity. The chirality in these complexes can be located either on the ligand or at the metal center, or on both. In "chiral-at-metal" complexes, the metal ion itself inherits the chiral information which subsequently is transferred to the products in stereoselective metal-catalyzed reactions.[1] In comparison to traditional chiral complexes, where the chiral information is intrinsic to the ligand framework (chiral-at-ligand), chiral-at-metal complexes gained much less attention until recently. However, nowadays chiral-at-metal catalysts are successfully applied in several important enantioselective transformations.[2,3]

Among methods for the synthesis of chiral-at-metal coordination compounds, induction of chiral information from ligand to the metal center is the most efficient and rational way.[4] This chiral induction, which is also known as predetermination of chirality at the metal center, has been previously reported for various transition metal complexes,[5] underlining the potential of such complexes for the application in asymmetric catalysis. Kol and co-workers showed that predetermination of chirality around a metal center strongly depends on the design of the chiral ligand.[6] Thus, there is a great interest in investigating new combinations of chiral ligands and metal cores in order to prepare enantiopure chiral-at-metal complexes. Herein, we report on the synthesis of two molybdenum(VI) dioxido complexes with enantiopure tetradentate *ONNO*-ligands. In addition, we re-investigated the capability of these two chiral molybdenum(VI) complexes **1** and **2** as catalysts for epoxidation and sulfoxidation reactions focusing on the influence of the coordination motif.[7,8]

Results and Discussion

Synthesis of chiral ligands. The salen-type ligand $\mathbf{H_2L^1}$ has been synthesized via Schiff base condensation of (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate with 2-hydroxy-1-naphthaldehyde in excellent yield (Figure 1).[9,10] The obtained ligand exhibited >98% enantiomeric excess determined by HPLC analysis using a chiral column. Synthesis and analytical data for ligand $\mathbf{H_2L^1}$ have been previously published.[11–13]

The subsequent reduction of the imine moiety of $\mathbf{H_2L^1}$ with $NaBH_4$ in MeOH gave the salan-type ligand $\mathbf{H_4L^2}$ with 98% ee in fair yield after recrystallization. The ^{1}H NMR spectrum of the free salen ligand $\mathbf{H_2L^1}$ shows a peak at 8.78 ppm ($CDCl_3$) that is assigned to the C-H protons of the imine groups. Reduction of $\mathbf{H_2L^1}$ led to the disappearance of this signal, but new signals appeared at 4.22-4.50 and 3.70 ppm ($CDCl_3$). These signals were ascribed to be -CH_2- and NH protons, respectively, consistent with the reduction of both imine moieties on the ligand to amine groups. Ligand $\mathbf{H_4L^2}$ was further characterized by FT-IR spectroscopy and elemental analysis.

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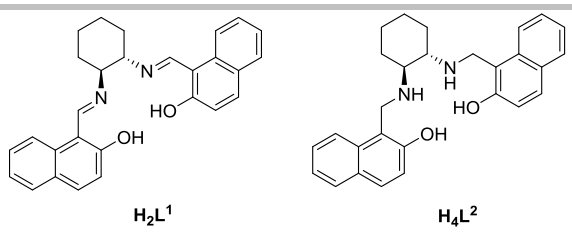
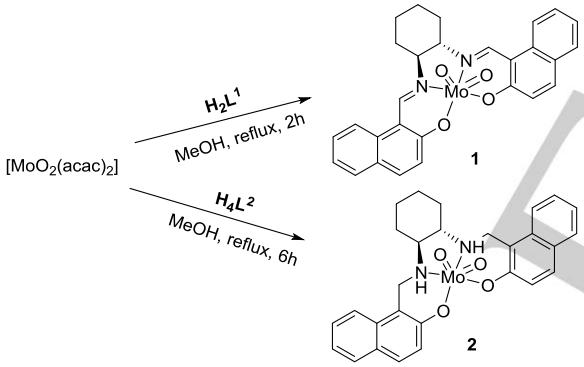


Figure 1. Ligands $\mathbf{H_2L^1}$ (salen-type) and $\mathbf{H_4L^2}$ (salan-type) employed in this study.

Synthesis of chiral molybdenum(VI) complexes. The synthesis of complex **1** has been previously published, albeit the racemic version derived from *rac*-$\mathbf{H_2L1}$ and without crystal structure.[14,15] The so obtained complex *rac*-**1** was tested in the epoxidation of cyclohexene and 1-octene under TBHP-limiting conditions.[14] The chiral molybdenum(VI) complexes [MoO_2($\mathbf{L^1}$)] (**1**) and [MoO_2($\mathbf{H_2L^2}$)] (**2**) were obtained by adding [MoO_2(acac)$_2$] to one equivalent of the corresponding ligand in refluxing methanol (Scheme 1). Upon cooling both **1** and **2** precipitated and were isolated as yellow to brown solids in analytically pure form in 60 and 55% yield, respectively. They are highly soluble in CH_2Cl_2 and $CHCl_3$, moderately soluble in methanol, and insoluble in diethyl ether and aliphatic solvents. Proton NMR experiments revealed that these complexes were stable at ambient conditions in solid as well as in solution for several weeks.



Scheme 1. Synthetic procedure for the preparation of complexes **1** and **2**.

For tetradentate *ONNO*-ligands coordinated at a $[MoO_2]^{2+}$ core, three geometrical isomers may in principle be formed (Figure 2). At present, the *trans* structure has not been reported in literature because of the unfavorable trans arrangement of the two oxido ligands and is thus unlikely. In the *cis*-α isomer, the ligand phenolate oxygen atoms coordinate *trans* to each other, which results in a higher overall symmetry (*C*2). In the case of the lower symmetry *cis*-β isomer, there is no symmetry axis (*C*1) as the phenolate oxygen atoms of the ligand coordinate *cis* to each other.

Both *C*2-symmetric *cis*-α and *C*1-symmetric *cis*-β configurations for dioxido molybdenum(VI) complexes have been previously reported, dependent on the employed ligand.[8,16,17–21] The ^{1}H and ^{13}C NMR spectra of complex **1** showed distinct signals for both ligand half-units, in accordance with the asymmetric *cis*-β configuration. This is exemplified by the distinct chemical shifts of the imine protons (9.51 and 8.86 ppm), arising from the asymmetric coordination of the salen ligand to the metal center. NMR spectroscopy also found no evidence for the formation of another isomer in the reaction solution.

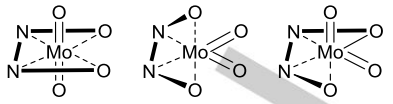


Figure 2. Possible geometric isomers for the coordination of a symmetric tetradentate *ONNO*-ligand at a molybdenum(VI) dioxido metal center.

Complex **1** was further characterized by IR spectroscopy, elemental analysis, and mass spectrometry. The solid state structure of complex **1** was additionally confirmed by single-crystal X-ray diffraction analysis (CCDC 1028614). The molecular structure of complex **1** is depicted in Figure 3, details on crystallographic data and structure refinement are listed in Table S1, selected bond lengths and angles are provided in Table 1. The solid state structure of complex **1** confirms the formation of a Λ-Mo complex with *cis*-β configuration. The complex features a six coordinate Mo atom with distorted octahedral geometry in which the two oxygen atoms of the naphtholate rings are in a *cis* configuration with an O-Mo-O angle of 84.04(6)°. The Mo-O and Mo-N bonds *trans* to the oxido ligands (Mo1-O12 2.1342(12) Å, Mo1-N2 2.2963(14) Å) are distinctly longer than *trans* to imine nitrogen (Mo1-O22 1.9366(11) Å, Mo1-N1 2.1088(14) Å), reflecting the stronger *trans* influence of the oxido groups. The $[MoO_2]^{2+}$ fragment has the expected *cis* configuration (O1-Mo1-O2 104.04(6)°) and Mo=O bond lengths (Mo1-O2 1.7062(11) Å, Mo1-O1 1.7141(13) Å) are in the expected range.[22] Furthermore, the (*R*,*R*)-chirality of the ligand backbone and the left-handed Λ-chirality around the Mo atom can be seen in the X-ray crystal structure of the complex.

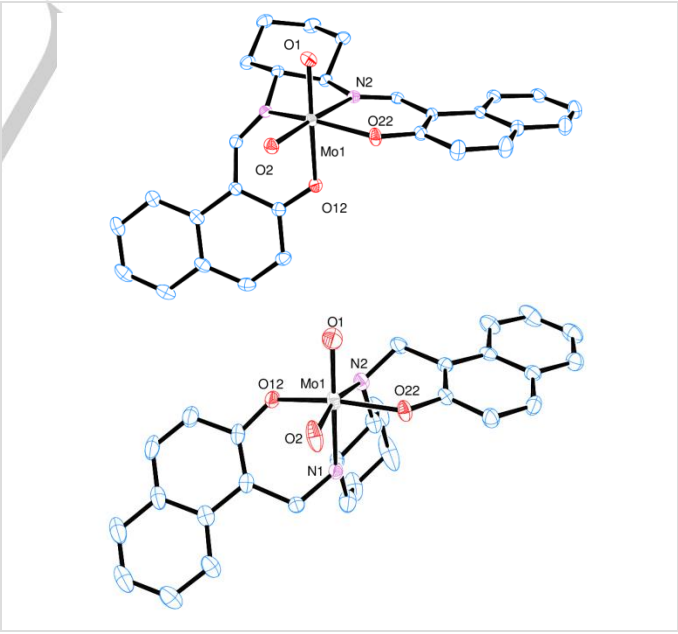


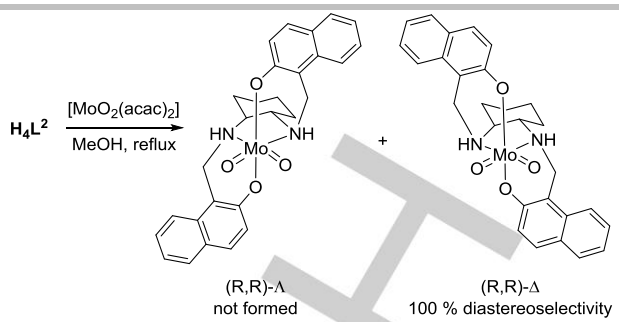
Figure 3. Molecular view (50% probability level) of complexes Λ-**1** (top) and Δ-**2** (bottom). H atoms and solvent molecules are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) of complexes **1** and **2**.

	1	2
Mo1-O2	1.7062(11)	1.697(2)
Mo1-O1	1.7141(13)	1.712(2)
Mo1-O12	2.1342(12)	1.9662(17)
Mo1-O22	1.9366(11)	1.9450(17)
Mo1-N1	2.1088(14)	2.3180(9)
Mo1-N2	2.2963(14)	2.3051(7)
O1-Mo1-O12	164.33(5)	95.50(9)
O1-Mo1-N1	91.17(6)	163.42(9)
O1-Mo1-N2	84.59(6)	91.15(9)
O1-Mo1-O22	101.90(6)	97.65(9)
O1-Mo1-O2	104.04(6)	108.76(12)
O2-Mo1-N2	167.61(6)	160.05(9)
O2-Mo1-N1	97.92(6)	87.03(8)
O2-Mo1-O12	164.33(5)	98.22(8)
O2-Mo1-O22	104.94(5)	97.34(8)
N1-Mo1-O22	149.82(6)	84.90(6)
N1-Mo1-N2	72.71(5)	73.27(3)
N1-Mo1-O12	77.20(5)	76.74(5)
O12-Mo1-O22	84.04(6)	155.18(8)
O12-Mo1-N2	81.96(5)	80.61(6)

In the case of complex **2**, chelation of the salan ligand **H_4L^2** to the $[MoO_2]^{2+}$ core generates two additional stereogenic centers at the amine nitrogen atoms, resulting in the possible formation of two diastereomers. If non-chiral salan ligands are employed, in general a racemic mixture of complexes is obtained.[23] However, when a chiral non-racemic ligand like **H_4L^2** is used, one diastereomer may be formed preferentially, a phenomenon which has been termed predetermination of chirality-at-metal.[2] According to the NMR spectra, complex $[MoO_2(\mathbf{H_2L^2})]$ (**2**) was obtained by reaction of the **H_4L^2** ligand with $[MoO_2(acac)_2]$ precursor as a single diastereomer of C_2-symmetry. Complex **2** displayed a single set of signals for the ligand in the ^{1}H NMR spectrum, in which only 6 signals for 12 aromatic hydrogen atoms were observed. In addition, the ^{13}C NMR spectrum revealed three resonances at 24.24, 29.96 and 45.61 ppm for the six cyclohexyl carbon atoms, consistent with a C_2-symmetric *cis*-α structure. Most importantly, there was no indication for the formation of the other possible diastereomers in the recorded NMR spectra. Single-crystal X-ray diffraction analysis also confirmed this conclusion (CCDC 1028615).

The solid state structure of complex **2** exhibits the symmetric cis-α configuration, in contrast to complex **1**. The molecular structure of complex **2** is depicted in Figure 3, details on crystallographic data and structure refinement are listed in Table S1, selected bond lengths and angles are provided in Table 1. The structure reveals a six-coordinate Mo atom in a distorted octahedral geometry, in which the oxido ligands are trans to the amine nitrogens. The Mo-N bonds in complex **2** (Mo1-N1 2.3180(1) Å, Mo1-N2 2.3051(1) Å) are significantly longer than those found in the complex **1** (Mo1-N1 2.1088(1) Å, Mo1-N2 2.2963(1) Å). However, the Mo=O bonds lengths are essentially similar in both complexes. The solid state structure clearly shows the (R,R)-chirality of the cyclohexyl backbone and (S,S)-configuration of the nitrogen atoms. This kind of chelation leads to an overall Δ-wrapping of the salan ligand around the molybdenum center, consistent with chiral induction from ligand to metal (Scheme 2). Such high diastereoselectivities were also observed for other (R,R)-enantiopure salan ligands like **H_4L^2**, leading to the Δ-configuration at the molybdenum atom.[17–20] Kol and co-workers reported similar behavior for titanium(IV) complexes, and could also show that the (S,S)-configured cyclohexyldiamine ligand gives the opposite Λ-configuration at the metal atom.[6,24,25]



Scheme 2. High diastereoselectivity of the coordination of **H_4L^2** to the $[MoO_2]$ core.

We observed the same diastereoselectivity with an (S,S)-configured bispyrolidine salan ligand, that resulted exclusively in the Λ-configured Mo complex.[21] However, in some cases the formation of both diastereomers of Zn and Ti complexes were observed, even if enantiopure salan ligands were used.[6,23,24] Furthermore, a molybdenum(VI) complex was reported, that gave a 1:1 mixture of diastereomers when a chiral salalen ligand (only one imine moiety reduced to the corresponding amine) was used.[20]

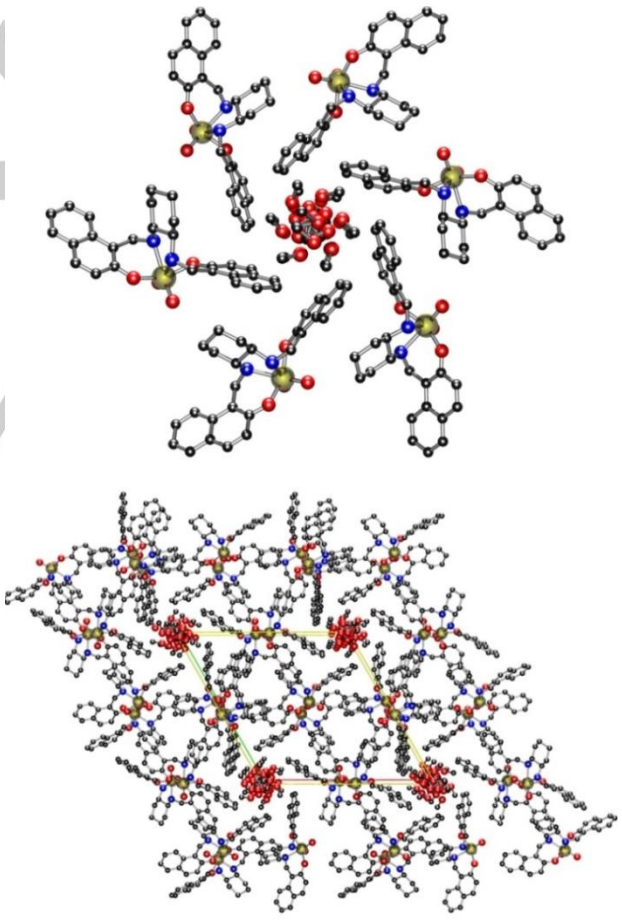


Figure 4. Perspective view of the single-stranded helix along the 6_5 screw axis (top); the molecules of **2** are helically arranged around the 6_5 screw axes forming tubes parallel to the c-axes. These tubes are filled with disordered methanol solvent molecules.

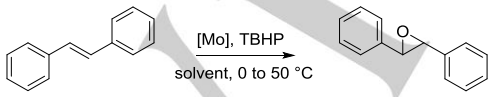
Complex **2** was further characterized by elemental analysis, mass spectrometry as well as by IR spectroscopy. This chiral complex crystallized from methanol as the solvent adduct **2**·CH_3OH in the rare enantiomorphic hexagonal space group $P6_5$

(Figure 4). Single-crystal structural analysis indicates that complex **2**·CH_3OH exhibits an infinite cylindrical single-stranded helical structure with *M* (left-handed) helicity. The molecules are helically arranged around 6_5 screw axes forming tubes parallel to the *c*-axes. These tubes are filled with disordered methanol solvent molecules turning their methyl groups towards the naphthalene rings. Obviously, a sufficient homochiral helicating element in the complex introduces only one type of helicity within the crystal.[26] Thus, in total, three different types of chirality have been identified in the crystal structure of complex **2**: configurational chirality on the cyclohexyl backbone, conformational chirality on the molybdenum center, and supramolecular chirality in the crystalline state.

Finally, UV-Vis and Circular Dichroism (CD) spectra were recorded for complexes **1** and **2** in CH_2Cl_2 (see Figure S5). The UV-Vis spectrum for **1** had previously been reported.[14] Complex **2** shows two resolved transitions in the UV-Vis spectrum. A lower energy ligand-to-metal charge transfer centered at 386 nm and a higher energy intra-ligand π-π* transition at 337 nm.[27] The same features were reported for **1** at 434 and 322 nm.[14] Literature on CD spectra of chiral Mo(VI) complexes is scarce.[27,28] The CD spectra of **1** and **2** differ quite a bit, with especially complex **2** giving a more complex spectrum because of having more chiral centers. Similar to the observed absorptions in the visible region of the UV-Vis spectrum, the CD spectra show the strongest absorptions between 330 and 405 nm. Both complexes show a distinct peak of opposite sign in their respective CD spectra. For complex **1**, a peak of negative sign at 366 nm can be observed ($\Delta\varepsilon$ = -3.7 M^{-1} cm^{-1}), for complex **2** a positive peak at 350 nm (($\Delta\varepsilon$ = 6.5 M^{-1} cm^{-1}) (see Figure S5). Form these spectra we can conclude that no racemization of complexes **1** or **2** in solution occurs, thereby not explaining the lack of chiral induction observed in catalytic reactions.

Catalytic oxidations. Complexes **1** and **2** have been tested as catalysts (0.5 mol% catalyst loading) in the epoxidation of prochiral *trans*-stilbene using *tert*-butylhydroperoxide (TBHP, 1.5 equiv.) as oxidant. Using complex **1,** the corresponding epoxide was obtained as the sole product with 65% yield after 24h (Table 2, entry 2). Under identical conditions, complex **2** only reached 19% yield of *trans*-stilbene oxide (Table 2, entry 6). Under all tested reaction conditions complex **1**, with the Schiff base imine backbone and *cis*-β configuration, was consistently more active than complex **2** with the reduced amine backbone and *cis*-α configuration (Figure 5).

Table 2. Epoxidation of *trans*-stilbene with complexes **1** and **2**.



	Cat.[a]	Solvent	T (°C)	time (h)	Yield (%)[b]	Sel. (%)[b]
1	**1**	CH_2Cl_2	rt	4	35	>99
2	**1**	CH_2Cl_2	rt	24	65	>99
3	**1**[c]	$CHCl_3$	50	4	96[c]	>99[d]
4	**2**	CH_2Cl_2	0	24	5	>99
5	**2**	CH_2Cl_2	rt	4	1	>99
6	**2**	CH_2Cl_2	rt	24	19	>99

[a] Reaction conditions: 0.5 mol% catalyst, 0.5 mmol *trans*-stilbene (1 equiv.), 0.75 mmol (1.5 equiv.) TBHP, solvent (1 mL); [b] selectivities and yields were determined by HPLC;[c] 0.05 mol% catalyst was used; [d] selectivity and yield was also determined by GC-MS measurement.

Complexes **1** and **2** are similar in many respects, such as the first coordination sphere, the Mo=O bond lengths, steric bulk and solubility, even though they have different octahedral configurations and ligand backbones. Therefore, under the same reaction conditions, differences in the catalytic activity of these complexes may likely be related to their isomeric configuration. The higher catalytic activity of **1** may be attributed to a labilization of one Mo=O bond in the *cis*-β complex, where a negative naphtholate oxygen atom is *trans* to one oxido ligand, whereas in the *cis*-α case observed in **2**, neutral amine nitrogen atoms are trans to both oxido ligands. These results are in agreement with our previous report on the effect of the geometrical configuration on catalysis by molybdenum(VI) dioxido complexes. A *cis*-β complex was found to be a more efficient catalyst for oxygen atom transfer between DMSO and PMe_3 than its sterically similar *cis*-α counterpart.[8]

Complexes **1** and **2** did not show any enantioselectivity in the epoxidation of *trans*-stilbene. In contrast to a previous study on highly enantioselective epoxidations using Mo complexes by Yamamoto and coworkers, changing the oxidant to the more bulky cumylhydroperoxide (CHP) did not improve enantioselectivity in our system, but significantly decreased the conversion.[29] In addition, no enantiomeric excess (ee) was observed when the epoxidation of *trans*-stilbene was carried out at 0 or 50 °C respectively. However, the catalytic activity of **1** increased gradually with increasing the reaction temperature. Even when the catalyst loading was lowered to 0.05 mol% of **1**, *trans*-stilbene was converted almost quantitatively into the corresponding epoxide at 50 ºC after 4 h (Table 2, entry 3), which is a significant improvement compared to previously studied salan Mo complexes.[19,21]

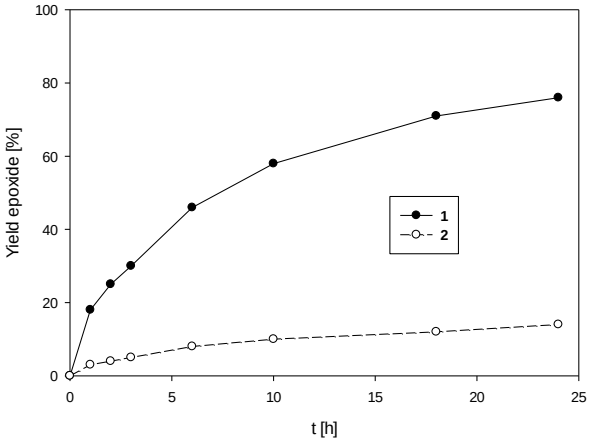
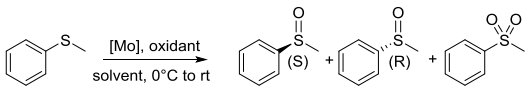


Figure 5. Comparison of conversion profiles for complexes **1** and **2** in the epoxidation of *trans*-stilbene; Conditions: 0.5 mol% catalyst, 1.5 equiv. TBHP, CH_2Cl_2, rt.

However, complex **1** shows some enantioselectivity in the oxidation of methylphenyl sulfide with hydrogen peroxide, as summarized in Table 3.

Table 3. Oxidation of methylphenyl sulfide with complexes **1** and **2**.



	Cat.[a]	Solvent	T (°C)	time (h)	Yield (%)[b]	Sel. (%)[b]	ee (%)
1	**1**[c]	CH_2Cl_2	rt	0.5	69	>99	0
2	**1**[c]	CH_2Cl_2	0	24	45	>99	0
3	**1**	$CHCl_3$	rt	4	98	91	1.4 (*S*)
4	**1**	$CHCl_3$	0	24	77	98	2.5 (*S*)
5	**1**	CH_3OH	0	24	99	95	9.4 (*S*)
6	**1**	CH_3CN	0	24	99	74	0.7 (*S*)
7	**2**	$CHCl_3$	0	24	99	98	1.3 (*R*)
8	**2**	CH_3OH	0	24	99	98	1.7 (*R*)

[a] Reaction conditions: 0.5 mol% catalyst, 0.5 mmol methylphenyl sulfide (1 equiv.), 0.75 mmol (1.5 equiv.) H_2O_2, solvent (1 mL); [b]selectivities to sulfoxide, yields and enantiomeric excesses were determined by HPLC. [c] 0.5 mmol (1 equiv.) of TBHP was used instead of H_2O_2.

It was found that enantioselectivity depends on the choice of solvent. In particular, catalytic sulfoxidation in methanol using complex **1** afforded (*S*)-methylphenyl sulfoxide in nearly quantitative yield, 95% selectivity with a slightly higher ee of 9.4% (Table 3, entry 5) compared to other solvents (in CH_2Cl_2 0% ee; in $CHCl_3$ 2.5% ee; in CH_3CN 0.7% ee). Noticeably, when TBHP was used as oxidant under the same reaction conditions, poor sulfoxide yield and essentially no enantioselectivity were observed (Table 3, entries 1 and 2).

Investigation of the enantioselectivity as a function of time (or conversion) revealed a slow and steady increase of ee reaching a maximum value after 24 h (Figure 6). This is in contrast to the results published by the groups of Kühn [30] and Gonçalves[31], in which enantioselectivities decrease as the reactions progress. Kinetic resolution of the formed sulfoxide by enantioselective oxidation to the sulfone was envisioned as a possible reason (Scheme 3).[32] There are numerous examples of titanium[33] and vanadium[34] catalyzed oxidative kinetic resolution of sulfoxides. However, here we ruled out this possibility by starting with racemic methylphenyl sulfoxide, which under the same reaction conditions led to the formation of methylphenyl sulfone in 26% overall yield with no enantiomeric enrichment (Scheme 3). As a result, we conclude that the observed enantioselectivity in the sulfoxidation is a result of the asymmetric oxidation of sulfide in the first step rather than an oxidative kinetic resolution of newly formed sulfoxide.

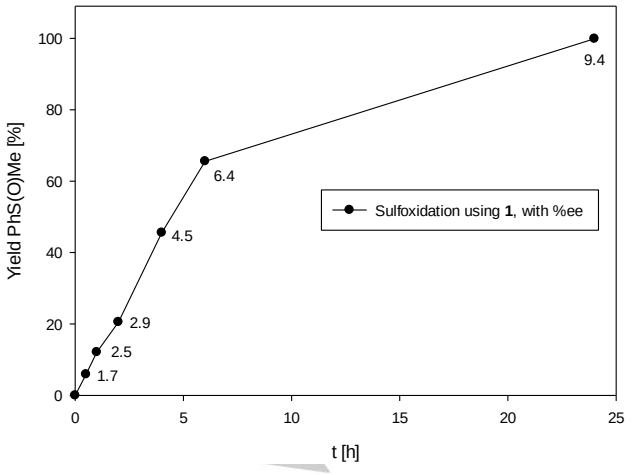
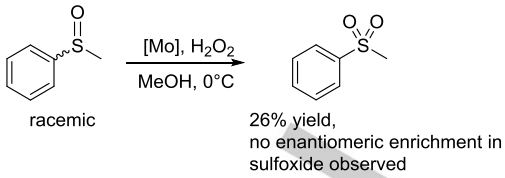


Figure 6. Time-conversion profile for the asymmetric oxidation of methylphenyl sulfide with catalyst **1** and %ee given for each sampling time; Conditions: 0.5 mol% **1**, 1.5 equiv. TBHP, MeOH, 0 °C.



Scheme 3. Oxidation of racemic sulfoxide by complex **1** showing no kinetic resolution.

Compared to complex **1, 2** was expected to show a better chiral induction since in this complex two chiral centers at the nitrogen atoms are located in close proximity to the Mo center. But in contrast, with complex **2**, a generally lower and opposite enantioselectivity was achieved (Table 3, entries 7 and 8). These results could be explained by the observation that in **2**, because of the longer Mo-N bonds compared to **1** (**2**: Mo1-N1 2.3180(1) Å, Mo1-N2 2.3051(1) Å; **1**: Mo1-N1 2.1088(1) Å, Mo1-N2 2.2963(1) Å), the interaction between the metal and the chiral diamine centers is much weaker than in complex **1**. The weak interaction may result in partial dissociation of the chiral ligand (hemi-lability) from the molybdenum center during the catalytic process.[35,36] NMR studies of the catalytic reaction in $CDCl_3$ did not show any sign of hydrolysis of the ligand. However, the exchange between the coordinated and partially uncoordinated ligand can take place faster than the NMR timescale. Evidently, implementing chirality directly at the Mo center in complex **2** could not provide better enantioselectivity. We believe that in this case, the potentially weakly coordinated chiral diamine backbone is responsible for the loss of chiral induction.[35,36]

In order to further probe the mechanism of oxidation reactions, we attempted to synthesize the molybdenum(VI) oxido peroxido complex of **1, 1-O_2**, which is supposedly formed under catalysis conditions. Addition of TBHP or H_2O_2-urea adduct to complex **1** in various solvents (e.g. MeOH, $CHCl_3$, CH_2Cl_2) lead to a multitude of unidentifiable products, as observed by NMR and IR spectroscopy. By careful addition of aqueous hydrogen peroxide however, to a solution of **1** in MeOH and refluxing, a color change of the solution to bright red was observed. All attempts however to isolate this material in analytically pure form or to grow high quality single crystals were unsuccessful due to ligand hydrolysis or other decomposition reactions. A brief discussion of analytical data obtained for this putative oxido peroxido complex can be found in the Supporting Information.

Conclusions

Two chiral molybdenum(VI) complexes with enantiomerically pure tetradentate *ONNO*-ligands were prepared, featuring different ligand arrangements. With the salen-type ligand $\mathbf{H_2L^1}$ *cis*-β complex **1** was obtained, whereas the *cis*-α isomer **2** was obtained for the salan-type, diamine-based ligand $\mathbf{H_4L^2}$. The chiral induction from the ligands $\mathbf{H_2L^1}$ and $\mathbf{H_4L^2}$ to metal led to an efficient predetermination of chirality around the $[MoO_2]^{2+}$ core. In addition, a helical stacking of molecules for complex **2** caused the formation of supramolecular chirality in the crystals. Both complexes have been tested as catalysts in asymmetric epoxidation and sulfoxidation. The comparative catalytic study revealed the superiority of *cis*-β complex Λ-**1** over *cis*-α counterpart Δ-**2** in the catalytic epoxidation of *trans*-stilbene. However, no enantiomeric excess in the epoxide was obtained. On the other hand, using the same two complexes, the

sulfoxidation of prochiral methylphenyl sulfide provided with high yields of sulfoxide with some enantioselectivity.

Experimental Section

General Remarks. (*R*,*R*)-1,2-Diammoniumcyclohexane mono-(+)-tartrate was prepared according to literature procedures.[9] Synthesis of ligand **H_2L^1** has been previously described.[11,12] All other chemicals were used without purification as purchased from commercial sources. All NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer (25 °C) and mass spectrometry on an Agilent Technologies 5795C inert XL MSD. $CDCl_3$ was used as NMR solvent and chemical shifts are reported in ppm relative to the solvent residual peak. FT-IR spectra were obtained on a Bruker Alpha P Diamond FTIR spectrometer. GC-MS analyses were performed with an Agilent 7890A GC system with an Agilent 19091J-433 column coupled to a 5975C inert XL EI/CI mass selective detector (MSD). Helium was used as the mobile phase. HPLC with diode array detection (HPLC/DAD) analyses were carried out with an Agilent 1200 series instrument equipped with a chiral ASTEC Cellulose DMP column (5 µm, 25 cm x 4.6 mm) with heptane/isopropanol (90:10 v/v for epoxidation and 80:20 v/v for sulfoxidation) as the mobile phase. CD measurements were performed on a Jasco J-1500 CD Spectrometer. Diffraction measurements were performed on a SMART APEX II diffractometer equipped with a CCD detector using graphite monochromated Mo K_α (λ = 0.7107 Å) radiation. The structure was solved by direct methods (SHELXS-97)[27] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[28] Elemental analyses (C, H and N) were performed using a Heraeus Vario Elementar analyser (Department of Inorganic Chemistry, University of Technology Graz).

Synthesis of (*R*,*R*)-H_4L^2. The synthesis of **H_4L^2** was performed according to a literature procedure published for similar ligands.[15,37] 422 mg of **(*R*,*R*)-H_2L^1** (1 mmol) were dissolved in methanol (15 mL), cooled to 0 °C, and 152 mg (4 mmol) of $NaBH_4$ was added in one portion. The resulting mixture was stirred at rt for 1 h and then refluxed for 2 h. After cooling to ambient temperature, 5 mL distilled water was added cautiously. The resulting reddish solution was filtered and the precipitate recrystallized from water and methanol to give **H_4L^2** ligand. Yield: 170 mg (0.4 mmol, 40%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 11.88 (s, 2H), 6.80-8.00 (m, 12H), 4.22-4.63 (m, 4H), 3.69 (s, 2H), 2.57 (m, 2H), 1.28-2.20 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$,δ): 156.10, 132.18, 129.49, 128.88, 128.52, 126.64, 122.85, 121.06, 129.09, 111.27, 69.63, 51.71, 29.13, 24.18. FT-IR (ATR) (cm^{-1}): 3294 (w, N-H), 2950 (w), 2862 (w), 1605 (m), 1485 (m), 1368 (m) , 1230 (m), 875 (m). Anal. Calc. for $C_{28}H_{30}N_2O_2$ (MW 426.56) (%): C, 78.84; H, 7.09; N, 6.57. Found: C, 78.94; H, 7.30; N, 6.50.

Synthesis of (*R*,*R*)-Λ-[$MoO_2(L^1)$] (1). Synthesis of complex *rac*-**1** has been previously described.[14][15] For convenience to the reader, the NMR data in $CDCl_3$ is presented here (DMSO-d_6 was used in the published literature).[14] Other analytical data is consistent to published data. Yield of **1**: 329 mg (0.6 mmol, 60%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.51 (s, 1H), 8.86 (s, 1H), 8.19-7.05 (m, 12H), 4.28 (m, 1H), 2.87 (m, 1H), 2.73-1.26 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 170.42, 160.98, 156.61, 156.49, 139.06, 136.68, 136.17, 133.77, 133.65, 129.54, 129.43, 129.18, 128.76, 128.20, 124.32, 124.13, 123.76, 121.89, 121.69, 120.00, 117.31, 111.86, 77.93, 71.90, 30.80, 29.02, 24.86, 24.16. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of CH_2Cl_2/toluene solution of the complex.

Synthesis of (*R*,*R*)-Δ-[$MoO_2(H_2L^2)$] (2). Ligand **H_4L^2** (1 mmol) was dissolved in methanol (10 mL) and was added to a methanol solution (10 mL) of [$MoO_2(acac)_2$] (1 mmol). The suspension was heated under reflux for 6 hours. After cooling, the orange powder was filtered off and washed with cold methanol. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a methanol solution of the complex. Yield: 304 mg (0.55 mmol, 55%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.84-7.13 (m, 12H), 5.23 (m, 4H), 2.94 (m, 2H), 2.44 (m, 4H), 1.69 (m, 4H), 1.03 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.07, 132.80, 129.42, 128.78, 128.53, 126.65, 123.34, 121.48, 121.27, 111.24, 58.47, 45.61, 29.96 , 24.24. EI-MS (70 eV) m/z: 554 (7) M^+. FT-IR (ATR) (cm^{-1}): 3245 (w, N-H), 3061 (w), 2932 (w), 2858 (w), 1615 (m), 1596 (m), 1464 (m), 1428 (m), 1396 (m), 1271 (m), 1235 (s), 1029 (w), 916 and 894 (vs, Mo=O), 810 (m), 774 (s), 745 (s), 568 (s). Anal. Calc. for $C_{28}H_{28}MoN_2O_4$ (MW 552.50) (%): C, 60.87; H, 5.11; N, 5.07. Found: C, 60.53; H, 5.07; N, 5.37.

Catalytic reaction. Typical catalytic reactions (epoxidation and sulfoxidation) were performed by stirring a solution of catalyst (0.5 mol%) and the corresponding substrate (0.5 mmol, 1 equiv) in 1 mL of solvent. After stirring the mixture for 5 min, with the addition of oxidant (0.75 mmol, 1.5 equiv) the reaction was started. The reaction mixture was stirred at the desired temperature and the reaction progress was monitored by GC-MS and HPLC. For GC-MS analyses, samples were taken and the reaction was quenched by addition of a small amount of MnO_2 to decompose excess oxidant. After centrifugation, sample aliquots were diluted with ethyl acetate and injected into the GC column. For HPLC analyses, samples were taken, dried, diluted with heptane/isopropanol (90:10 v/v), and treated with a catalytic amount MnO_2 to quench the excess of peroxide. The resulting slurry was filtered through a pad of Celite and the filtrate injected into a chiral HPLC column.

Supporting information (see footnote on the first page of this article): IR spectrum of **H_2L1** (Figure S1), EI-MS spectra for **1** and **1-O_2** (Figure S2) are shown; full details of crystallographic data collection and refinement as well as bond lengths and angles for **1** and **2** are given.

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Keywords: molybdenum • coordination modes • oxido ligands • chirality • epoxidation

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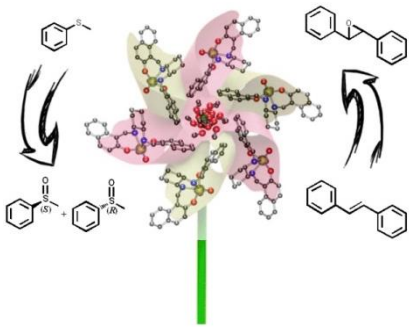
Entry for the Table of Contents
Layout 1:

FULL PAPER

The synthesis of two chiral *cis*-dioxido Mo(VI) complexes bearing enantiopure, tetradendate ligands is described. For complex **2**, exclusive formation of the Δ-helix due to predetermination of chirality leads to a highly diastereoselective synthesis of this complex. Chiral induction, however, in asymmetric oxidation reactions was low.



Chiral complexes*

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Diastereoselective synthesis and catalytic activity of two chiral *cis*-dioxido molybdenum(VI) complexes