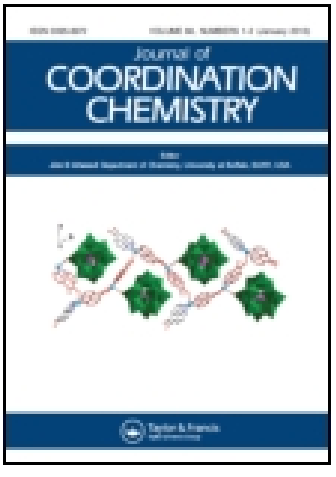

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Oxomolybdenum(VI) complexes with glycine bisphenol [O,N,O,O′] ligand: synthesis and catalytic studies

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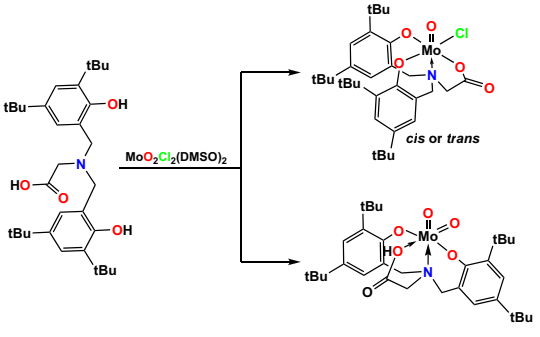

The oxomolybdenum(VI) complex [MoOCl(L)] with a tetradentate glycine bisphenol ligand (H_3L) was prepared by reaction of [$MoO_2Cl_2(DMSO)_2$] with a ligand precursor in hot toluene. The product was isolated in moderate yield as separable *cis* and *trans* isomers along with the third minor component, [$MoO_2(HL)$]. The solid-state structure of *trans*-[MoOCl(L)] was determined by X-ray diffraction. The ligand has tetradentate coordination through three oxygens and one nitrogen, which is located *trans* to the terminal oxo whereas the sixth coordination site is occupied by a chloride. Both *cis* and *trans* isomers of [MoOCl(L)] are active catalysts for epoxidation of *cis*-cyclooctene and sulfoxidation of tolyl methyl sulfide. The *cis* isomer gave higher activity in epoxidation and sulfoxidation reactions at room temperature than the *trans* isomer but they performed identically at 50 °C.

Keywords: Molybdenum complex; Epoxidation; Sulfoxidation

1. Introduction

Coordination chemistry of molybdenum is often studied due to its active role in several biological oxidation and oxo-transfer reactions [1]. Synthetic approaches to model the active

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sites of molybdenum enzymes have been either biomimetic (structural modeling) or bio-inspired (functional modeling), and rather simple coordination compounds can be studied as models for sophisticated biological systems [2]. In general, active structures involve molybdenum ions in high-oxidation states; thus, the reactivity of many active species can be modeled with isolated oxomolybdenum species which are stabilized by biologically relevant hard donors, for instance amine, carboxylate, and aryloxido ligands. Multidentate phenolic ligands are generally used to make such model compounds. For example, the reactions of MoO_2Cl_2 derivatives with tetrapodal amine trisphenols or aminoalcohol bisphenols are known to lead to neutral mononuclear oxochloromolybdenum(VI) complexes which can catalyze a number of oxidations including sulfoxidation, epoxidation, and haloperoxidation reactions [3, 4]. Similarly, sterically demanding tetradentate diamino bisphenols form active dioxomolybdenum(VI) complexes [5–7].

Although metal complexes with different aminobisphenol ligands are generally well known, the chemistry of such ligands with a carboxylate acid side-arm is scantly studied. There are several reports on iron, cobalt, and vanadium complexes with glycine bisphenols [8–13]. These ligands carry two phenol groups, a carboxylic acid functionality and amino nitrogen, so they mimic nicely many biomolecules for example, tyrosine. In the present article, we describe the synthesis, structure, and catalytic applications of oxochloromolybdenum(VI) complexes with N,N-bis(3,5-di-tert-butyl-2-hydroxybenzyl)aminoacetic acid (H_3L).

2. Experimental

2.1. *Materials and methods*

The starting materials $[MoO_2Cl_2(DMSO)_2]$ [14], $[MoO_2(acac)_2]$ [15], and H_3L [11] were prepared according to literature procedures. tBuOOH was purified by vacuum distillation prior to use. Other chemicals and solvents were obtained from commercial sources and were used as purchased. All syntheses were carried out under ambient atmosphere. IR spectra were measured in compressed KBr pellets using a Nexus 870 FT-IR spectrometer. NMR spectra were recorded at 25 °C with a Bruker Avance 500 spectrometer equipped with a broadband observe probe (BBO-5 mm-Zgrad). The samples were dissolved in $CDCl_3$ or DMSO-d_6 with TMS as an internal chemical shift reference (0 ppm for both nuclei). UV–VIS spectra were measured in $CHCl_3$ solutions.

2.2. *Syntheses*

The stirred suspension of finely ground $[MoO_2Cl_2(DMSO)_2]$ (356 mg, 1.00 mM) in 60 mL of toluene was treated with H_3L (498 mg, 0.98 mM). The reaction mixture turned dark blue upon heating and was stirred under reflux for 16 h, filtered, and evaporated in vacuum. The isomeric mixture was chromatographed over silica using CH_2Cl_2 as an eluent to obtain two separated blue fractions, which were identified as [*trans*-MoOCl(L)] (*trans*-**1**, the phenolate moieties are at *trans* positions) and [*cis*-MoOCl(L)] (*cis*-**1**, the phenolate moieties at *cis* positions). A yellow fraction (**2**) was collected as a trace quantity by adding gradually 10% of acetonitrile to the eluent.

trans-**1**: IR: 1240 vs 1203 s, 1170 vs 1126 w, 1101 w, 1025 w, 958 vs 933 m, 914 vs 892 m, 863 s, 808 w, 761 m, 721 w, 694 w, 655 w, 597 m, 580 s, 559 m. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (2 H, d, $J = 2.0$ Hz), 7.14 (2 H, d, $J = 2.0$ Hz), 4.69 (2 H, d, $J = 13.0$

Hz), 3.65 (2 H, d, $J = 13.5$ Hz), 3.42 (2 H, s), 1.56 (18 H, s), 1.35 (18 H, s) ppm.^{13}C NMR (101 MHz, $CDCl_3$): δ 171.55, 160.68, 152.16, 140.92, 128.38, 126.21, 124.56, 62.92, 55.65, 35.65, 35.20, 31.43, 30.17 ppm. UV–VIS ($CHCl_3$): λ_{max}, nm (ε) 678 (10,703). Yield 177 mg (27%).

cis-**1**: IR: 1238 vs 1203 s, 1170 vs 1128 w, 1027 w, 978 w, 956 s, 931 m, 915 vs 871 m, 848 m, 808 w, 759 m, 721 m, 701 m, 653 m, 605 m, 578 s, 566 s. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (1 H, d, $J = 1.9$ Hz), 7.44 (1 H, d, $J = 1.9$ Hz), 7.24 (1 H, d, $J = 1.7$ Hz), 7.18 (1 H, d, $J = 1.6$ Hz), 5.01 (1 H, d, $J = 13.9$ Hz), 3.87 (1 H, d, $J = 16.3$ Hz), 3.76 (1 H, d, $J = 11.0$ Hz), 3.73 (1 H, d, $J = 11.0$ Hz), 3.47 (1 H, d, $J = 16.4$ Hz), 3.40 (1 H, d, $J = 13.0$ Hz), 1.55 (9 H, s), 1.49 (9 H, s), 1.33 (9 H, s), 1.31 (9 H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.33, 162.74, 157.01, 151.48, 150.06, 140.86, 140.51, 129.38, 128.73, 125.29, 125.10, 124.76, 124.16, 62.79, 61.74, 59.56, 35.86, 35.14, 34.49 (two overlapping signals), 31.48, 31.32, 30.43, 29.88 ppm. UV–VIS ($CHCl_3$): λ_{max}, nm (ε) 693 (10,573). Yield 70 mg (11%).

Complex **2** was also prepared independently by the reaction of $[MoO_2(acac)_2]$ (165 mg, 0.50 mM) and H_3L (255 mg, 0.50 mM) in 15 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 3 h to give a dark solution. The solution was filtered through a short pad of silica and the yellow product was collected by adding methanol to the solvent. The brownish yellow filtrate was evaporated to obtain 190 mg (60%) of yellow solid. IR and NMR spectra of this product were identical with those measured for the yellow product obtained in the reaction of $[MoO_2Cl_2(DMSO)_2]$ with H_3L.

2: IR: 1238 vs 1203 m, 1168 s, 1126 m, 1106 w, 1074 w, 1029 w, 977 m, 933 s, 914 vs 894 vs 846 vs 808 m, 775 w, 759 s, 698 w, 673 w, 649 w, 607 m, 559 s. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.11 (2 H, d, $J = 2.5$ Hz), 6.97 (2 H, d, $J = 2.5$ Hz), 4.44 (2 H, d, $J = 13.0$ Hz), 3.62 (2 H, d, $J = 13.0$ Hz), 2.96 (2 H, s), 1.32 (18 H, s), 1.25 (18 H, s) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ 173.03, 160.68, 140.24, 136.88, 124.67, 123.42, 122.45, 61.71, 57.78, 49.07, 35.02, 34.29, 32.05, 30.26 ppm.

2.3. *X-ray structure determination*

Single crystals of *trans*-**1** were grown from hot acetonitrile as an acetonitrile solvate. The X-ray data were collected on a Bruker–Nonius Kappa CCD diffractometer equipped with an APEXII detector, with Mo Kα radiation ($\lambda = 0.71073$ Å) at 123(2) K. Empirical absorption corrections using SADABS 2008 were applied [16]. The structure was solved by direct methods using SIR97 [17] program and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97 program [18]. Figures 1 and S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.928287) were drawn with ORTEP3 for Windows [19] and S2 with Mercury [20]. All non-hydrogen atoms were refined first isotropically and then anisotropically. All hydrogens were placed in their calculated positions with fixed isotropic thermal parameters and refined as a riding model. Crystallographic data for *trans*-**1**: formula $C_{32}H_{46}ClMoNO_5{\cdot}C_2H_3$ N, $M_r = 697.14$, orthorhombic, space group *Pcab*, $a = 10.3960(2)$, $b = 21.4576(4)$, $c = 31.7701(7)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 8$, $V = 7087.1(2)$ Å^3, $T = 123(2)$ K, $\rho_c = 1.307$ g cm^{-3}, $F(0\,0\,0) = 2928$, μ(Mo–K$_\alpha$) = 0.486 mm^{-1}, 21,272 data, 7709 unique ($R_{int} = 0.0351$), 432 parameters, final $R_1(I > 2\sigma\ (I)) = 0.0338$, $wR_2 = 0.0795$, GOF = 1.038. CCDC 956,883 contains the supplementary crystallographic data for *trans*-**1**.

Table 1. Catalytic activities of *cis*-**1** and *trans*-**1**.

Entry	Catalyst	% Cat	T (°C)	$t_{1/2}$ (min)[a]	Conversion (%)[b]	TON	TOF (h^{-1})[c]
Epoxidation of cis-cyclooctene							
1	*cis*-**1**	5	25	23	74	14.7	46
2	*trans*-**1**	5	25	–	18	3.6	6
3	*cis*-**1**	5	40	4	84	16.8	73
4	*trans*-**1**	5	40	13	83	16.6	54
5	*cis*-**1**	2,5	40	7	85	34.0	132
6	*trans*-**1**	2,5	40	22	84	33.6	91
7	*cis*-**1**	5	50	4	81	16.2	62
8	*trans*-**1**	5	50	7	84	16.8	70
9	*cis*-**1**	2,5	50	4	80	32.0	154
10	*trans*-**1**	2,5	50	12	83	33.2	125
Sulfoxidation of tolyl methyl sulfide							
11	*cis*-**1**	5	25	20	84	16.8	76
12	*trans*-**1**	5	25	40	85	17.0	29
13	*cis*-**1**	5	40	8	84	16.8	66
14	*trans*-**1**	5	40	13	82	16.4	56
15	*cis*-**1**	2,5	40	12	82	32.8	120
16	*trans*-**1**	2,5	40	15	77	30.8	89
17	*cis*-**1**	5	50	7	87	17.4	84
18	*trans*-**1**	5	50	8	87	17.4	83
19	*cis*-**1**	2,5	50	5	84	33.6	151
20	*trans*-**1**	2,5	50	8	81	32.4	132

[a]Time required for a 50% decrease of the initial concentration of substrate.
[b]Yield of product measured by ^{1}H NMR after 24 h.
[c]TOF calculated at 10 min reaction as (mol product)·(mol catalyst)$^{-1}$·(t/h)$^{-1}$.

2.4. *Catalytic studies*

Catalytic experiments were run in deuterated chloroform solutions while the reactions were monitored by ^{1}H NMR spectroscopy using a three-minute interval. Solutions of tBuOOH (0.3 mL, 0.2 M) and substrate (0.3 mL, 0.2 M of *cis*-cyclooctene or methyl-p-tolylsulfide +0.1 M of $C_2H_4Cl_2$ as an internal standard) were added in a 5 mm NMR tube. The catalyst solution (0.030 or 0.015 mL, 0.1 M) was added and the NMR tube was subsequently placed in the NMR probe. The reaction rates were estimated from integrated intensities of substrate and product spectra. In the epoxidation, the alkene multiplet at 5.6 ppm was turned to the epoxide multiplet at 2.9 ppm whereas in the sulfoxidation the sulfide methyl singlet at 2.45 was turned to the sulfoxide methyl singlet at 2.71 ppm. The results are shown in table 1.

3. Results and discussion

3.1. *Synthesis*

There are a handful of somewhat different methods for the synthesis of H_3L [8, 9, 11]. In our studies, we found the procedure reported by Weyhermüller *et al.* the most reliable, so H_3L was synthesized from glycine, 2,4-di-*tert*-butyl phenol, and paraformaldehyde in methanol under reflux [11].

The molybdenum(VI) oxo chloro complex **1** was synthesized applying a practice developed by us earlier for preparation of corresponding complexes with tetrapodal amine

trisphenols or aminoalcohol bisphenols (scheme 1) [4, 21]. Solid $[MoO_2Cl_2(DMSO)_2]$ was mixed with a stoichiometric amount of a ligand precursor in hot toluene and the resulting mixture was kept at reflux temperature to obtain an intense blue solution. Under such conditions, the reaction leads to a mixture of several compounds as seen by TLC. ^{1}H NMR spectrum of the evaporated mixture shows signals attributable to *cis* and *trans* isomers of **1** in *ca*. 1 : 1 ratio. The reaction was repeated several times and the isomeric mixtures were fractioned by silica column chromatography. In a typical experiment, *trans*-**1** was obtained in about 30% isolated yield whereas the yield for *cis*-**1** was just around 10% due to the partial decomposition upon separation and purification steps. Both compounds are readily soluble in common organic solvents. Isolated solid isomers are stable under ambient atmosphere but they slowly lose their color in solution. Generally, these carboxylate complexes, *cis*-**1** and *trans*-**1**, are less stable than corresponding aminoalkoxide bisphenolates [4, 21].

In our attempts to prepare aforesaid isomers, minor amounts of some yellow **2** were also isolated as a crystalline solid. The air-stable **2** is soluble in MeOH, MeCN, and DMSO although, it did not form single crystals suitable for XRD analyses. The molecular identity of **2** was studied by IR and NMR spectroscopy, which indicate that the compound is a dioxo complex of amine bisphenolate with a neutral carboxylic acid side-arm (see Section 3.2. Structure description). Complex **2** was also formed when $[MoO_2(acac)_2]$ was used as a starting material in reaction with H_3L in a dichloromethane solution at room temperature yielding an identical yellow product in a good yield.

3.2. *Structure description*

The ^{1}H NMR spectra of *cis*-**1** and *trans*-**1** show anticipated resonances for deprotonated ligands, which readily differentiate between the C_1 (*cis*-**1**) and C_s (*trans*-**1**) isomers. Especially, benzylic methylene protons in C_1 symmetric *cis*-**1** are seen as four separated one-proton doublets at 5.01, 3.87, 3.47, and 3.40 ppm whereas corresponding protons in *trans*-**1** are seen as two two-proton doublets at 4.69 and 3.65 ppm, respectively; these structures resemble those found for corresponding MoOCl complexes with aminoethanol bisphenols [21]. The IR spectra of isolated solids show a strong IR absorption at *ca*. 915 cm^{-1} which can be assigned as Mo = O stretch but they lack the typical doublets for the MoO_2 moiety, which indicates that the reaction includes also the removal of an oxo group.

The ^{1}H and ^{13}C NMR spectra of the yellow **2** are consistent with a C_s symmetric octahedral structure with a mirror plane passing through the two oxo groups and a side-arm oxygen donor. Upon complexation, the methylene protons adjacent to the phenolate group become diastereotopic. In the ^{1}H NMR spectrum of **2**, there are two doublets at 4.44 and 3.62, both with a geminal coupling constant $J = 13.0$ Hz.

There are few reports on structurally well-characterized dioxomolybdenum complexes with tripodal tetradentate aminobisphenolate ligands [6, 7, 22–24]. These compounds present typically a couple of medium to strong IR absorptions at 850–950 cm^{-1}. The strong absorptions at 886–905 and 908–944 cm^{-1} are assigned as asymmetric and symmetric M = O stretches, respectively, while these two absorptions show generally a difference of *ca*. 20–35 cm^{-1}. Complex **2** shows four strong IR-absorptions in the range of 846–933 cm^{-1}. The strongest absorption maxima are at 894 and 914 cm^{-1}, which is characteristic for octahedral complexes of MoO_2.

Crystallization of *trans*-**1** from acetonitrile leads to formation of a solvate *trans*-**1**•MeCN. In solid state, it forms monomeric molecules in which the glycine bisphenolate has

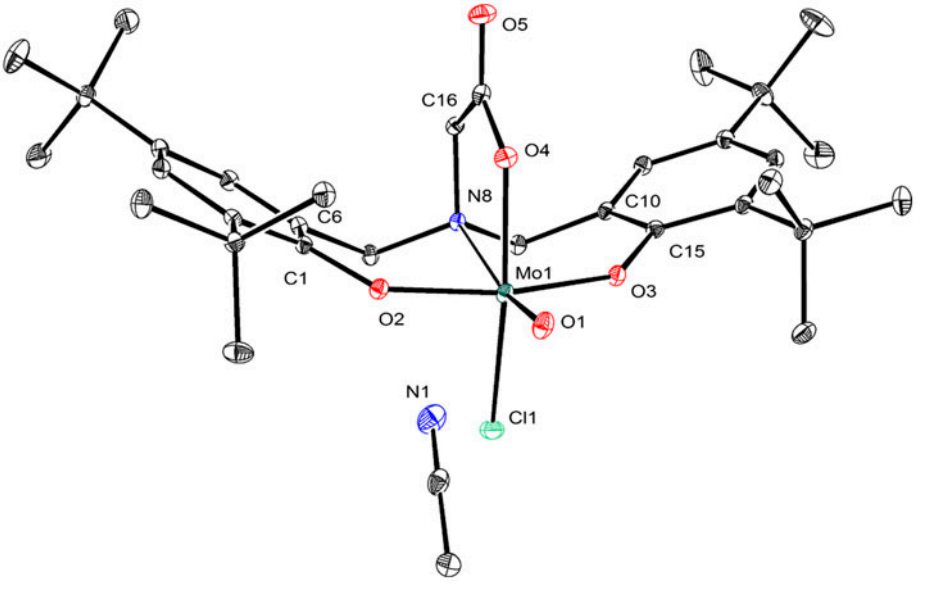
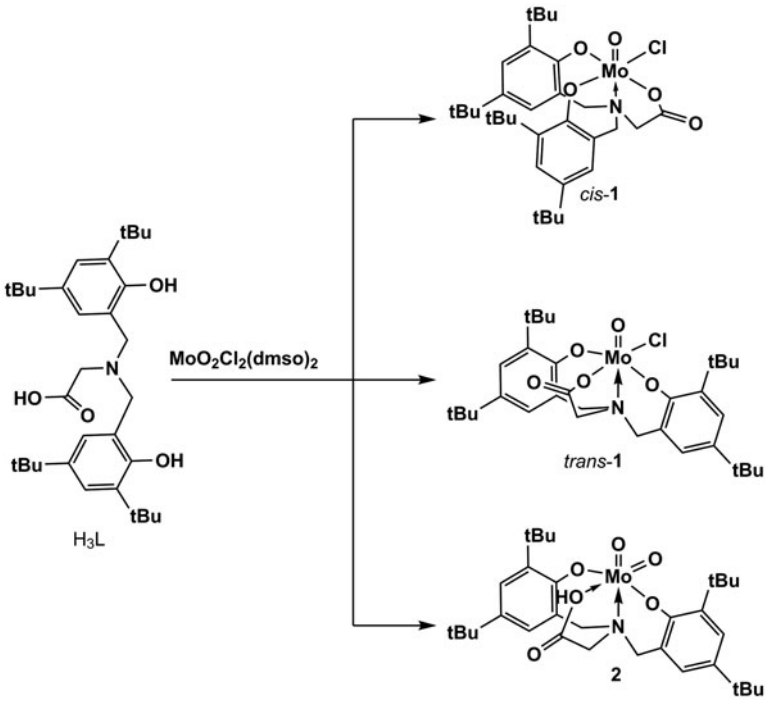


Figure 1. The molecular structure of *trans*-**1**•MeCN. The hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°) are: Mo–O1, 1.6766(15); Mo–O2, 1.8724(14); Mo–O3, 1.8811(14); Mo–O4, 2.0149 (14); Mo1-N8, 2.4266(17); Mo1-Cl1, 2.3513(5); O1-Mo1-N8, 168.80(7); O2-Mo1-O3 162.11(6); O4-Mo1-Cl1, 162.15(4).

coordinated as a tetradentate trianionic ligand through three oxygen donors and one nitrogen donor (figure 1). The nitrogen donor is located *trans* to the terminal oxo, which is typical for oxomolybdenum aminophenolates [3–7, 21–24]. The Mo–N bond is relatively long (*ca.* 2.43 Å) due to the strong structural *trans* effect of a multiple bonded oxo ligand [25]. The chloride is *trans* to the carboxylate oxygen. A mean plane defined by the chelate ring atoms Mo1, O4, C17, C16, and N8 as well as terminal ligands O1 and Cl1 divides the molecule of *trans*-**1** into two similar, although not crystallographically identical halves.

The carboxylate Mo–O4 bond length of 2.015 is *ca.* 0.11 Å longer than Mo–O alkoxide (1.897–1.903 Å) [4, 21] or aryloxide (1.873–1.903 Å) [3, 25] bonds in structurally related aminoalcoholate bisphenolates or amine trisphenolates. Otherwise, the bonding parameters between the metal center and the trianionic aminocarboxylate bisphenolate ligand are in accord with previous studies on oxomolybdenum(VI) complexes with tripodal aminoalcohol bisphenolates and amine trisphenolates [3, 4, 21, 26]. In general, *trans*-**1** has a structure very similar to [MoOCl((tBuPhO)$_3$ N)] ((tBuPhO)$_3$ N = 6,6′,6″-(nitrilotris(methylene))tris (2-(tert-butyl)phenolate), which is an efficient epoxidation and sulfoxidation catalyst [3]. *Trans*-**1** crystallizes as distinct molecules without any strong hydrogen bonds (only weak H bonds with CH•••O distances from 2.359 to 2.697 Å are found, see figure S1) or other non-covalent interactions between complex units, which also explains the high solubility of the complex. Bulky tBu substituents in the phenolate groups obviously prevent any strong stacking interactions; therefore, the shortest distances between the aromatic rings from adjacent molecules are 5.208 Å which indicates that there is no π-stacking as seen in figure S2. The solvate acetonitrile molecules are located in the cavities of the structure with C35H···O5 distance of 2.359 E (figure S1) and with the N···H distances of 2.881 and

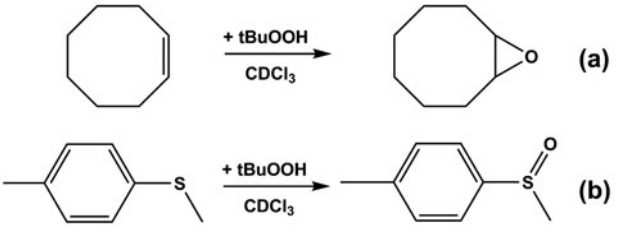


Scheme 1. Reaction of glycine bisphenol H3L with MoO2Cl2(DMSO)2].

3.100 E to the nearest benzylic hydrogens of the organic ligand. Otherwise the structure is stabilized by van der Waals forces to have a 3-D close packing of molecules in the lattice.

3.3. *Catalytic activity*

Dioxomolybdenum complexes with different organic ligands are frequently used as catalysts for oxygen transfer reactions, *e.g.* oxidation reactions of alkenes and sulfides with H_2O_2 or tBuOOH [7, 27–34]. However, the use of corresponding mono-oxo chloro complexes is not extensively studied [3, 4]. In our experiments, the oxo chloro complexes *cis*-**1** and *trans*-**1** were tested as catalysts for epoxidation of *cis*-cyclooctene and sulfoxidation of methyl-p-tolylsulfide with one equivalent of *tert*-butyl hydroperoxide as an oxidant (scheme 2). The



Scheme 2. Studied oxidation reactions.

reactions were run at 25, 40, and 50 °C in $CDCl_3$ solutions while the reaction course was monitored by ^{1}H NMR (results are seen in table 1). The control experiments were carried out without any catalyst where no reactions occurred. Conversely, the catalytic reactions started immediately and no induction time was observed in these experiments. At room temperature, *trans*-**1** shows low activity for the epoxidation reaction, but it performs better in higher temperatures whereas *cis*-**1** has a good activity in all experiments. The conversions of alkene were practically quantitative in all experiments, although the selectivity for epoxide was only *ca.* 75–85% while *cis*-cyclooctene oxide was the only detectable product. At 50 °C, epoxidation activities of *cis*-**1** (TOF = 154 h^{-1}) and *trans*-**1** (TOF = 125 h^{-1}) are comparable with that of several dioxomolybdenum(VI) complexes under related conditions, *e.g.* $[MoO_2(OSiPh_3)(2,2'\text{-bipyridine})]$ [32], $[MoO_2Cl(HC(bim)_3)]Cl$ ($HC(bim)_3$ = tris(benzimidazolyl)methan) [34], and $[MoO_2(acac)(^RN,O)]$ ($^RN,OH$ = imino-alcohol derivative of α-pinene) [30]. However, activities were clearly lower than those reported for structurally closely similar amine trisphenolate complex $[MoOCl((tBuPhO)_3N)]$ (TOF = 7500 h^{-1}) [3], possibly due to the lower stability of the studied carboxylate complexes. Especially, *cis*-**1** seems not to survive applied turn-over conditions, so the actual reacting species may be some decomposition product instead of the distinct complex.

Oxidation of organic sulfides to sulfoxides with *tert*-butyl hydroperoxide as oxidant can be catalyzed by various molybdenum complexes, *e.g.* $[MoOCl((tBuPhO)_3N)]$ [3] or $MoO_2Cl_2(MeTolSO)_2$ (MeTolSO = (R)-(+)-methyl-*p*-tolylsulfoxide) [35], whereas the second oxidation step may yield corresponding sulfones as by-products. In our experiments, the sulfoxidation of methyl-*p*-tolylsulfide was run readily with catalysts *cis*-**1** and *trans*-**1** without any formation of sulfone. Again, *cis*-**1** shows higher activity at 25 °C although the reaction rates are practically equal at higher temperatures. On the other hand, sulfoxidation reactions are known to be self-catalytic, especially in high temperatures, which may affect the reaction rates [36]. In general, these carboxylate complexes show higher activities for oxidation reactions than corresponding alkoxide complexes.

4. Conclusion

$[MoO_2Cl_2(DMSO)_2]$ reacts with a tetradentate O_3 N-type ligand precursor N,N-bis(3,5-di-tert-butyl-2-hydroxybenzyl)aminoacetic acid (H_3L) to form the oxomolybdenum(VI) complex [MoOCl(L)] as two separable isomers (*cis* and *trans*) along with minor quantities of a dioxo product $[MoO_2(HL)]$. Isomers of [MoOCl(L)] form monomeric molecules in which the ligand coordinates as a tetradentate trianionic ligand through two phenolate oxygen donors, one carboxylate and one nitrogen donor. In the *cis* isomer, the phenolato moieties are at *cis* positions, while the chloride is *cis* to the carboxylate oxygen. In the *trans* isomer, the phenolato moieties are at *trans* positions. The overall structure of these isomers is very similar to active oxidation catalyst $[MoOCl((tBuPhO)_3N)]$, although the catalytic activities are lower. Both isomers of [MoOCl(L)] catalyze selectively the epoxidation of *cis*-cyclooctene and sulfoxidation of methyl-*p*-tolylsulfide with *tert*-butyl hydroperoxide. The *cis* isomer is more active of the two and compares with a number of dioxomolybdenum(VI) complexes used as catalysts for the epoxidation of cyclooctene.

Supplementary material

These 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 E-mail: deposit@ccdc.cam.ac.uk.

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