# **Inorganic Chemistry**

# Triazolyl, Imidazolyl, and Carboxylic Acid Moieties in the Design of Molybdenum Trioxide Hybrids: Photophysical and Catalytic Behavior

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# **S** Supporting Information

ABSTRACT: Three organic ligands bearing 1,2,4-triazolyl donor moieties, (S)-4-(1-phenylpropyl)-1,2,4-triazole (trethbz), 4-(1,2,4-triazol-4-yl)benzoic acid (trPhCO<sub>2</sub>H), and 3-(1H-imidazol-4-yl)-2-(1,2,4-triazol-4-yl)propionic acid (trhis), were prepared to evaluate their coordination behavior in the development of molybdenum(VI) oxide organic hybrids. Four compounds,  $[Mo_2O_6(trethbz)_2] \cdot H_2O$  (1),  $[Mo_4O_{12}(trPhCO_2H)_2] \cdot 0.5H_2O$  (2a),  $[Mo_4O_{12}(trPhCO_2H)_2] \cdot$  $H_2O$  (2b), and  $[Mo_8O_{25}(trhis)_2(trhisH)_2] \cdot 2H_2O$  (3), were synthesized and characterized. The monofunctional tr-ligand resulted in the formation of a zigzag chain  $[Mo_2O_6(trethbz)_2]$ built up from cis-{MoO<sub>4</sub>N<sub>2</sub>} octahedra united through common  $\mu_2$ -O vertices. Employing the heterodonor ligand



with  $tr/-CO_3H$  functions afforded either layer or ribbon structures of corner- or edge-sharing {MoO\_sN} polyhedra (2a or 2b) stapled by tr-links in axial positions, whereas  $-CO_2H$  groups remained uncoordinated. The presence of the *im*-heterocycle as an extra function in trhis facilitated formation of zwitterionic molecules with a protonated imidazolium group  $(imH^+)$  and a negatively charged  $-CO_2^-$  group, whereas the tr-fragment was left neutral. Under the acidic hydrothermal conditions used, the organic ligand binds to molybdenum atoms either through [N-N]-tr or through both [N-N]-tr and  $\mu_2$ -CO<sub>2</sub><sup>-</sup> units, which occur in protonated bidentate or zwitterionic tetradentate forms (trhisH<sup>+</sup> and trhis, respectively). This leads to a new zigzag subtopological motif (3) of negatively charged polyoxomolybdate  $\{Mo_8O_{25}\}_n^{2n-}$  consisting of corner- and edge-sharing cis- $\{MoO_4N_2\}$  and  $\{MoO_6\}$  octahedra, while the tetradentate zwitterrionic *trhis* species connect these chains into a 2D net. Electronic spectra of the compounds showed optical gaps consistent with semiconducting behavior. The compounds were investigated as epoxidation catalysts via the model reactions of achiral and prochiral olefins (*cis*-cyclooctene and *trans-\beta*methylstyrene) with tert-butylhydroperoxide. The best-performing catalyst (1) was explored for the epoxidation of other olefins, including biomass-derived methyl oleate, methyl linoleate, and prochiral DL-limonene.

# INTRODUCTION

The chemistry of polyoxomolybdate organic solids rightfully occupies one of the most striking and intriguing domains of materials science that, because of multiple potential applications, is of extremely high impact and has received intense interest.<sup>1</sup> In this regard, the employment of organic ligands with different donor functions offers abundant opportunities for generating new organically modified molybdenum(VI) oxide hybrids which have unusual structures and possess desirable properties. Among a wide choice of accessible organic donors, N-heterocyclic derivatives such as pyridine, 1,2,4-triazole, imidazole, and carboxylic acids provide sufficiently stiff and strong interactions with the molybdenum trioxide matrix,

leading to thermally stable materials with potential to operate in the high-temperature range of up to ~400 °C. These solids were found to demonstrate remarkable catalytic efficiency in epoxidation of olefins,<sup>2-4</sup> oxidation of alcohols,<sup>5</sup> etc. Another interesting application arises from their promising semiconducting behavior that unites multiple attributes such as tunable band gaps, reduced thermal conductivity, enhanced dielectric constant, and negative thermal expansion.<sup>6</sup>

Interaction of layered  $\beta$ -MoO<sub>3</sub>·H<sub>2</sub>O with nonchelating 1,2,4triazolyl ligands can be rationalized as follows (Scheme 1).

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Scheme 1. Representation of Known Structure Types of Molybdenum Trioxide Modified by 1,2,4-Triazolyl-Based Linkers: Layered Perovskite and One-Dimensional Motifs (Ribbon, Chain, Hydrated Chain, and Helix)<sup>a</sup>



"The coordination of organic [N-N]-tr and inorganic  $\mu_2/\mu_3$ -O-bridges displays a complementary role (for simplicity, molybdenyl bonds are not shown).

Scheme 2. Under Typical Synthetic Conditions Used Either Pyridinecarboxylic Acids or Alpha-Amino Acids Serve as Neutral Zwitterionic Anchors Supporting the Inorganic Oxide Matrix through Negatively Charged  $-CO_2^-$  Donor Groups



Similar to pyridine, pyrazine, and 4,4'-*bipy* building blocks,<sup>7–10</sup> the employment of 1H-1,2,3-triazole and 1H-1,2,4-triazole molecules affords rare organic—inorganic perovskite-like  $MoO_3(1H$ -1,2,3- $tr)_{0.5}$  and  $MoO_3(1H$ -1,2,4- $tr)_{0.5}$ .<sup>8b,10</sup> However, various nonchelating 4-substituted 1,2,4-tr derivatives clearly tend to support one-dimensional molybdenum(VI) oxide topological motifs (e.g., chains, hydrated chains, ribbons, and helixes). Recently, we showed a rational strategy for preparing the preprogrammed 2D and 3D metal oxide organic frameworks (MOOFs) by the linkage of 1D Mo(VI) oxide motifs through suitable bistriazolyl ligand modules.<sup>11</sup> On the other hand, the presence of an extra donor group such as amine, pyrazole, or 1H-tetrazole in the structure of *tr*-based ligands did not lead to high-dimensional coordination networks, because

the secondary function typically behaves as a noncoordinating H-donor/H-acceptor unit.  $^{11\mathrm{b}}$ 

Unlike this case, the coordination of some heteroarylcarboxylic acids (nicotinic, isonicotinic acids)<sup>12a,b</sup> and even tripeptide glycyl–glycyl–glycine<sup>12c</sup> revealed interesting differences. Under typical reaction conditions the molecules behave in neutral zwitterionic forms as short  $syn,syn-\mu_2-\eta^1:\eta^1 - COO^$ links toward oxomolybdates, whereas pyridyl and amino groups act as proton-acceptor sites (Scheme 2). The resultant polymeric array [Mo<sub>2</sub>O<sub>6</sub>(RCO<sub>2</sub>)]<sub>n</sub> reminds one of molybdenum(VI) oxide 1,2,4-triazolyl-based organic solids having a ribbon-like scaffold [Mo<sub>2</sub>O<sub>6</sub>(tr)], shown in Scheme 1. Both bridges,  $syn,syn-\mu_2-\eta^1:\eta^1$  carboxylate and  $\mu_2-[N-N]-tr$ , can be regarded as competing and complementary donor units, and thus, heterofunctional  $tr/CO_2H$  ligands are of extraordinary interest. In order to comprehend how the ligand choice can further modify the structure and properties of molybdenum trioxide, we have launched the current project starting from the single-*tr* molecule through heterobifunctional  $tr/-CO_2H$  and then to heterotrifunctional  $tr/-CO_2H$ /plus extra heteryl units.

In this paper we report on 1,2,4-triazolyl derivatives (enantiopure (S)-4-(1-phenylpropyl)-1,2,4-triazole, *trethbz*; 4-(1,2,4-triazol-4-yl)benzoic acid, *trPhCO*<sub>2</sub>H; and racemic 3-(1H-imidazol-4-yl)-2-(1,2,4-triazol-4-yl)propionic acid, *trhis*) containing different kinds and numbers of donor substituents for fabricating extended Mo(VI) oxide organic solids (Scheme 3).

Scheme 3. 1,2,4-Triazolyl-Based Ligands Containing Different Numbers of Functional Groups (Enantiopure (S)trethbz with a Single tr-Group,  $trPhCO_2H$  with a  $tr/-CO_2H$ Couple, and Racemic trhis with Three Different Donors,  $tr/im/-CO_2H$ ) Utilized in This Work



The ligands have been investigated in the hydrothermal reaction with an oxomolybdate matrix, although 4-(1,2,4-triazol-4-yl)benzonitrile was preferably used as a precursor to  $trPhCO_2H$ . These afforded diverse 1D and 2D assemblies, including homo- and heterochiral types. The photophysical properties of the resultant solids have been investigated in detail. Subsequently, the molybdenum(VI) oxide complexes have been examined as epoxidation catalysts via the model reactions of achiral and prochiral olefins (*cis*-cyclooctene (Cy) and *trans-* $\beta$ -methylstyrene (TBMS)) with *tert*-butylhydroper-oxide (TBHP), at 55–70 °C. The best-performing catalyst (1) was further explored for the epoxidation of several olefins with TBHP, including biomass-derived methyl oleate, methyl linoleate, and prochiral DL-limonene. The influence of the type of oxidant (TBHP or H<sub>2</sub>O<sub>2</sub>) was studied.

# EXPERIMENTAL SECTION

**Measurements.** Elemental analysis (C, H, and N) was carried out with a Vario EL-Heraeus microanalyzer. IR spectra (400–4000 cm<sup>-1</sup>) were measured with a PerkinElmer FTIR spectrometer (KBr pellets) and with a Mattson 7000 spectrometer, using a globar source, a DTGS detector, and KBr cells, with 2 cm<sup>-1</sup> resolution and triangular apodization. <sup>1</sup>H NMR spectra recorded on a Bruker 400 MHz spectrometer are illustrated in Figures S10 and S11. The room temperature (rt) powder X-ray diffraction (PXRD) patterns were measured using a Stoe STADIP (Cu K<sub>a1</sub>, using a Mythen detector). The temperature-dependent X-ray measurements were recorded on a Stoe STADIP with a high-temperature attachment and an image plate detector system. Simultaneous thermogravimetric/differential thermal analysis/mass spectrometry (TG/DTA-MS) studies were carried out on a Netzsch F1 Jupiter device connected to an Aeolos mass spectrometer. Samples were heated at a rate of 10 K min<sup>-1</sup>.

The absorption spectra of polycrystalline samples of compounds 1, 2a, and 3 were recorded in the 800-200 nm range at 298 K on a Cary-5000 UV-vis-NIR spectrophotometer. In order to obtain the spectrum, a well-ground mixture of the sample with some paraffin oil was placed between two quartz plates, approximately 1 cm in diameter, and pressed to get a transparent layer.

The theoretical calculations were carried out using the CASTEP module<sup>13</sup> of a commercial software package (Materials Studio 8.0). Generalized gradient approximations (GGA) with the Perdew–

Burke–Ernzerhof (PBE) exchange–correlation functional (xc) were used in calculations.

Crystal Structure Determination. The diffraction data were collected with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å) using a Stoe image plate diffraction system (face-indexed numerical absorption correction using X-RED and X-SHAPE<sup>14</sup>). The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELX-97 package.<sup>15</sup> In the structure of 2a, very high thermal motion parameters for the solvate water molecules suggested 0.5 partial occupancies of their positions. These partial contributions are further equally disordered over closely situated positions across a 2-fold axis, and, therefore, no hydrogen atoms were added to these molecules. In all other cases, CH-hydrogen atoms were constrained, while NH and OH hydrogen atoms were located and then included with fixed bond distances (0.87 and 0.85 Å, respectively) and  $U_{iso}$  values at the level of  $1.5U_{eq}$  of the carrier N (O) atoms. In the structure of 2b, a set of similarity restraints was applied to the thermal motion of the noncoordinated carboxylic group in order to improve the refinement stability. Graphical visualization of the structures was made using the program Diamond 2.1e.<sup>10</sup>

Crystallographic data and experimental details for structural analyses are summarized in Table S1. The crystallographic material can also be obtained from the CCDC, through deposition numbers CCDC 1519096–1519099 for 1, 2a, 2b, and 3, respectively.

Catalytic Performance Tests. Catalytic experiments were carried out under autogenous pressure in borosilicate reactors (5 mL) equipped with a magnetic stirring bar and a Teflon valve for sampling. cis-Cyclooctene (Cy, 95%, Alfa Aesar), methyl oleate (Ole, 99%, Aldrich), methyl linoleate (LinOle, 95%, Alfa Aesar), 1-octene (1C8, 98%, Aldrich), trans-2-octene (2C8, 97%, Aldrich), cyclododecene (Cy12; mixture of cis and trans isomers, 96%, Aldrich), DL-limonene (DL-Lim,  $\geq$  95%, Merck), and *trans-\beta*-methylstyrene (99%, Aldrich) were the substrates tested, and tert-butylhydroperoxide (5.0-6.0 M in decane, Aldrich) and  $H_2O_2$  (30% aqueous, Aldrich) were chosen as oxidants. The reactors were charged with the molybdenum catalyst (using an amount equivalent to 18  $\mu$ mol of molybdenum), 1.8 mmol of substrate, and 2 mL of cosolvent ( $\alpha_1\alpha_1\alpha_2$ -trifluorotoluene (TFT,  $\geq$ 99%, Aldrich) or acetonitrile (CH<sub>3</sub>CN,  $\geq$ 99%, Aldrich)). Subsequently, the reactors were immersed in an oil bath thermostated at the desired reaction temperature (55 or 70 °C), under stirring for 10 min, followed by the addition of 2.75 mmol of oxidant. The initial instant of the catalytic reaction was taken to be the moment that the oxidant solution was added to the reactor. The reactions were carried out under air; molecular oxygen did not influence the catalytic reaction, ascertained by the fact that no reaction of Cy occurred in the presence of the molybdenum catalysts without TBHP. The evolutions of the catalytic reactions were monitored via sampling throughout 24 h. The samples were analyzed using a Varian 3900 GC equipped with an FID detector and a capillary column (J&W Scientific DB-5, 30 m  $\times$ 0.25 mm  $\times$  0.25  $\mu$ m), and undecane (>99%) or methyl decanoate (99%) was used as internal standard for the reactions of Cy/1C8/ 2C8/Cy12/DL-Lim and Ole/LinOle, respectively. The reaction products were identified by GC-MS (Trace GC 2000 Series Thermo Quest CE Instruments GC; Thermo Scientific DSQ II), using He as the carrier gas.

**Catalyst Stability Studies.** The reaction mixtures using TBHP as oxidant were biphasic solid–liquid after 24 h. After a 24 h batch run, the reaction mixture was cooled to ambient temperature. The solid phase was separated from the liquid phase by centrifugation (3500 rpm); the solid was washed with diethyl ether and pentane and vacuum-dried (ca. 0.1 bar) at 55 °C for 1 h, giving the solid denoted as i-TBHP-*T* (i corresponds to compound **1**, **2a**, or **3**\*, and *T* = 55 or 70 (°C)). In a similar fashion, solids (*trPhCO*<sub>2</sub>*H*-TBHP-55 and *trhis*-TBHP-55) were isolated from a 24 h batch run using the free ligands *trPhCO*<sub>2</sub>*H* and *trhis* of compounds **2a** and **3**\*, respectively, for Cy/TBHP reaction, at 55 °C.

For the catalytic reaction system  $1/Cy/H_2O_2/CH_3CN/55$  °C, a yellow-colored solution was obtained after a 24 h batch run. The solution was filtered through a 0.2  $\mu$ m PTFE membrane, and after addition of pentane and diethyl ether it was stored at 4 °C overnight.

The precipitate obtained was separated by centrifugation (3500 rpm), washed with acetone, and vacuum-dried (ca. 0.1 bar) at 55 °C for 1 h, giving the solid 1-H<sub>2</sub>O<sub>2</sub>-55.

The catalytic contribution of the dissolved metal species of the system 1/TBHP (which led to the best catalytic results) was investigated by carrying out a contact test (CT). Hence, a mixture of 1, oxidant, and cosolvent (without substrate) was stirred at 55 °C for 24 h. Afterward, the mixture was cooled to ambient temperature and centrifuged (3500 rpm) to separate the solid and liquid phases. The liquid phase was passed through a filter equipped with a 0.2  $\mu$ m PTFE membrane, giving the solution 1-CT-L. This solution was transferred to a 5 mL reactor, preheated for 10 min under stirring, and then used for the homogeneous catalytic reaction of Cy/TBHP. Specifically, Cy (which was separately preheated at 55 °C) was added to 1-CT-L in an amount corresponding to an initial substrate concentration of 0.7 M, and this solution was stirred for 24 h at 55 °C. On the other hand, the undissolved metal species of the CT (1-CT-S) were isolated as described above for the normal catalytic runs and subsequently tested for Cy epoxidation using the same initial mass of solid as that used for the original compound 1 under typical conditions (the initial molar ratio olefin:oxidant was the same for all catalytic tests). After a 24 h batch run using 1-CT-S, the solid was recovered ((1-CT-S)-run 1) and characterized.

The isolated metal species were characterized by attenuated total reflectance (ATR) FT-IR spectroscopy and PXRD. The PXRD data were collected at ambient temperature on a Philips Analytical Empyrean ( $\theta/2\theta$ ) diffractometer equipped with a PIXcel1D detector, with automatic data acquisition (X'Pert Data Collector software v4.2) using monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). Intensity data were collected by the step-counting method (step 0.02°), in continuous mode, in the ca.  $5^{\circ} \leq 2\theta \leq 70^{\circ}$  range. Attenuated total reflectance FT-IR spectra were measured on a Mattson 7000 FT-IR spectrometer, equipped with a Specac Golden Gate Mk II ATR accessory having a diamond top-plate and KRS-5 focusing lenses.

**Caution!** Hydrofluoric acid (HF) is toxic and corrosive, even if a diluted aqueous solution is used, and must be handled in a well-ventilated fume hood with extreme caution using appropriate protective gear.

**Synthesis.** All chemicals were of reagent grade and used as received without further purification. 4-(1,2,4-Triazol-4-yl)benzonitrile  $(trPhCN)^{17}$  and 4-(1,2,4-triazol-4-yl)-benzoic acid  $(trPhCO_2H)^{18}$  were synthesized according to the procedure described by Bartlett and Humphrey.<sup>19</sup>

**(S)**-4-(1-Phenylpropyl)-1,2,4-triazole, *trethbz*. A solution of (S)-(-)- $\alpha$ -ethylbenzylamine (or (S)-(-)-1-phenylpropylamine) (2.70 g, 20.0 mmol), *N*,*N*-dimethylformamide azine (3.36 g, 23.6 mmol), and TsOH (0.38 g, 2.21 mmol) in toluene (5 mL) was heated at reflux for 38 h. Afterward, toluene was removed in vacuo to give a brownish oil, which solidified on cooling. The solid was washed with CH<sub>3</sub>CN/Et<sub>2</sub>NH (5 mL:0.5 mL) and diethyl ether and dried yielding white crystals (1.12 g, 30%). Anal. Calcd for C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>: C, 70.56; H, 7.00; N, 22.44. Found: C, 70.50; H, 7.10; N, 22.40. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.19 (2H, *tr*), 7.14–7.40 (5H, m, *C*<sub>6</sub>H<sub>5</sub>), 5.08 (dd, 1H, *J* = 8.0 and 7.6 Hz, *CH*), 2.17–2.35 (2H, m, *CH*<sub>2</sub>), 0.94 (dd, 3H, *J* = 7.3 and 7.0 Hz, *CH*<sub>3</sub>).

**3-(1***H***-Imidazol-4-yl)-2-(1,2,4-triazol-4-yl)propionic acid,** *trhis***. A mixture of racemic histidine monohydrochloride monohydrate ((l,d)-His·HCl·H<sub>2</sub>O) (3.14 g, 15.0 mmol),** *N***,***N***-dimethylformamide azine (4.26 g, 30.0 mmol), and TsOH (0.28 g, 1.47 mmol) in toluene (15 mL) was heated at reflux. Water, HCl, and toluene were removed from the mixture as an azeotrope using a Dean–Stark trap, and the refluxing was continued for 50 h.The reaction mixture was cooled to rt. The precipitate formed was isolated by decanting the solution, washed with toluene, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN, and CH<sub>3</sub>CN, and dried, yielding a white solid (2.16 g, 69%). Anal. Calcd for C<sub>8</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>: C, 46.38; H, 4.38; N, 33.80. Found: C, 46.22; H, 4.50; N, 33.67. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): 8.46 (s, 1H,** *im***), 8.38 (s, 2H,** *tr***), 7.00 (s, 1H,** *im***), 5.06–5.18 (dd, 1H,** *J* **= 9.2 and 4.9 Hz, CH), 3.32–3.56 (m, 2H, CH<sub>2</sub>).** 

 $[Mo_2O_6(trethbz)_2] \cdot H_2O$  (1). trethbz (18.7 mg, 0.100 mmol), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (35.3 mg, 28.6 µmol), and 2.5 mL of water were sealed in a 20 mL Teflon-lined autoclave. The autoclave was heated to 140 °C, held for 24 h, and cooled to rt for 48 h. The resultant colorless crystals of the desired product were filtered off, washed with water and CH<sub>3</sub>OH, and air-dried (yield: 26.4 mg, 78%). Anal. Calcd for  $C_{22}H_{28}Mo_2N_6O_7$ : C, 38.84; H, 4.15; N, 12.35. Found: C, 38.80; H, 4.16; N, 12.33.

 $[Mo_4O_{12}(trPhCO_2H)_2] \cdot 0.5H_2O$  (2a)/ $[Mo_4O_{12}(trPhCO_2H)_2] \cdot H_2O$  (2b). A mixture of MoO<sub>3</sub> (30.0 mg, 0.208 mmol), trPhCN (17.0 mg, 0.100 mmol), water (5 mL), and a 7% aqueous solution of HF (100  $\mu$ L) was sealed in a 20 mL Teflon-lined autoclave. The presence of diluted HF was aimed at enhancing the hydrolysis of the nitrile precursor as well as at mineralizing molybdenum trioxide. The autoclave was then heated to 140 °C, held for 48 h, and cooled to rt for 24 h. The resultant mixture consisted of two crystalline phases: the prevalent green prisms of complex 2a and traces of colorless needles of compound 2b in ca. 60:1 weight ratio. The mixture was filtered off, washed with water, and air-dried. Samples 2a/2b were mechanically separated from one another under a microscope that yielded compound 2a in 58% yield (28.0 mg) and compound 2b in 1% yield (0.5 mg).

For complex 2a: Anal. Calcd for  $C_{18}H_{15}Mo_4N_6O_{16.5}$ : C, 22.45; H, 1.57; N, 8.73. Found: C, 22.40; H, 1.62; N, 8.68.

For complex **2b**: Anal. Calcd for  $C_{18}H_{16}Mo_4N_6O_{17}$ : C, 22.24; H, 1.66; N, 8.65. Found: C, 22.19; H, 1.70; N, 8.64.

Several dozen identical experiments reproducibly afforded **2a** and **2b** in varying yields of 55–65% and 0.5–2.5%, respectively. The dominant complex **2a** was selected to evaluate the catalytic potential in olefin epoxidation reaction. Replacing *trPhCN* with poorly soluble  $trPhCO_2H$  noticeably shifts the hydrothermal reaction toward formation of a mixture of white solids containing preferably initial  $trPhCO_2H$  itself, compound **2b**, and traces of complex **2a**. This emphasizes that the employment of triazolylnitriles can be an essential synthetic approach in preparing not only triazolylcarboxylic acids but also their molybdenum(VI) oxide hybrids.

 $[Mo_8O_{25}(trhis)_2(trhisH)_2]\cdot 2H_2O$  (3). Trhis (21.0 mg, 0.101 mmol), MoO<sub>3</sub> (28.8 mg, 0.200 mol), and 3 mL of water were sealed in a 20 mL Teflon-lined autoclave. The autoclave was heated to 140 °C, held for 24 h, and gradually cooled to rt for 48 h. The resultant white solid contained colorless crystals of the desired complex, though as a minor component, which were mechanically collected under a microscope, washed with water, and dried at rt (yield: ~1 mg, ~2%). Anal. Calcd for C<sub>32</sub>H<sub>42</sub>Mo<sub>8</sub>N<sub>20</sub>O<sub>35</sub>: C, 18.89; H, 2.08; N, 13.77. Found: C, 18.74; H, 2.15; N, 13.60. A major phase of the reaction mixture was identified by elemental analysis and PXRD as complex **3**\* assuming the composition MoO<sub>3</sub>:trhis:H<sub>2</sub>O = 2:1:1 (or  $[Mo_2O_6(trhis)]\cdotH_2O$ ). Anal. Calcd for C<sub>8</sub>H<sub>11</sub>Mo<sub>2</sub>N<sub>5</sub>O<sub>9</sub>: C, 18.73; H, 2.16; N, 13.65. Found: C, 18.65; H, 2.22; N, 13.50. The major sample **3**\* was further used to investigate the catalytic activity.

#### RESULTS AND DISCUSSION

Synthesis and Crystal Structures. We recently developed a series of molybdenum(VI) oxide solids decorated with various triazolyl-based ligands. Under slightly acidic hydrothermal conditions (pH  $\sim$ 4-6) usually applied for the synthesis, the 1,2,4-triazolyl functional group exists in an uncharged neutral form since the  $pK_B$  of 1*H*-1,2,4-triazole is around 2.39.<sup>20</sup> The simultaneous presence of basic and acidic functions in 4-(1,2,4triazol-4-yl)benzoic acid  $(trPhCO_2H)$  requires two pK values. Taking into account the corresponding values of  $\sim$ 2.39 for the  $pK_B(HtrH^+/trH)$  of 1*H*-1,2,4-triazole and ~4.19 for the  $pK_A(C_6H_5CO_2H/C_6H_5CO_2^-)$  of benzoic acid, it can be readily concluded that under the experimental conditions employed both ionizable groups should be in their neutral forms; that is, protonation of the *tr*-ring is only possible at low pH, less than 2. This explains why the 1,2,4-triazolyl unit typically participates in the coordination to Mo(VI) centers utilizing a [N-N] coordination mode (complexes 1-3), while the extra donor groups, for instance, -COOH or 1H-tetrazole, remain

uncoordinated (see compounds 2a and 2b).<sup>11,21</sup> Another situation was observed for some heteroaryl carboxylic acids (e.g., for 4-pyridinecarboxylic acid:  $pK_A(pyCO_2H/pyCO_2^{-})$ ~1.77 and  $pK_B(HpyCO_2H^+/pyCO_2H)$  ~4.84) and amino acids (e.g., for glycine with  $pK_A \sim 2.34$  and  $pK_B \sim 9.60$ ), in which the  $pK_{\rm B}$  is significantly higher than the  $pK_{\rm A}$ . This allows formation of zwitterionic molecules with coordinating carboxylate  $(-CO_2^{-})$  and noncoordinating heteroaryl or amino functions  $(pyH^+ or -NH_3^+)$ , as depicted in Scheme 2). Following this line of thought, the trhis molecule might be of special interest. A combination of three different functional groups, as two basic heterocycles (1,2,4-triazole&imidazole) and one acidic function  $(-CO_2H)$ , would result in at least three dissociation constants. First, a simple histidine molecule (His), a starting precursor for the synthesis of *trhis*, could be a representative example for this consideration. This molecule possesses three pK values:  $pK_1(CO_2H/CO_2^{-}) \sim 1.82$ ,  $pK_2(HimH^+/Him) \sim 6.04$ , and  $pK_3(\alpha - NH_3^+/-NH_2) \sim 9.17$ . The transamination of *His* by introduction of an electron-withdrawing tr – instead of a strong electron-donating group  $(-NH_2)$  should lead to a decrease of the corresponding pK and appearance of a low  $pK(HtrH^+/trH)$ of 2.39 versus a  $pK_3(\alpha$ -NH<sub>3</sub><sup>+</sup>/-NH<sub>2</sub>) of ~9.17. Apparently, at low pH of the reaction medium (pH ~4) the carboxylic fragment of trhis should be deprotonated, having a negative charge (-1), the imidazole ring should appear as a positively charged (+1) imidazolium cation, whereas the triazolyl termini would rather prefer to be neutral. So, formation of the zwitterionic species is highly expected. This interesting case is achieved in compound  $[Mo_8O_{25}(trhis)_2(trhisH)_2] \cdot 2H_2O$  (3).

The crystal structure of  $[Mo_2O_6(trethbz)_2]$ ·H<sub>2</sub>O (1) is based on the distorted octahedra of molybdenum atoms in a typical *cis*-{N<sub>2</sub>O<sub>4</sub>} arrangement. The polyhedra are joined via common vertexes of  $\mu_2$ -O atoms forming parallel zigzag chains (Figure 1). Each two Mo atoms are alternatively bridged by either a double [N-N]-tr and  $\mu_2$ -O links or exceptionally through  $\mu_2$ -O atoms, thus separating Mo atom pairs within the chain at distances of 3.628 and 3.812 Å, respectively. The crystallizating water molecules display a key role in the formation of the 2D hydrogen-bonded network, as shown in Figure 1. Since



**Figure 1.** Formation of zigzag chains in  $[Mo_2O_6(trethbz)_2]$ ·H<sub>2</sub>O (1) running along the *c*-axis. The uncoordinated water molecules crosslink the neighboring chains through H-bonding interactions forming a H-bonding layer (symmetry codes: (i) x, -y, -z; (ii) -x, y, -z+1/2. (iii) -x+1, y, -z+1/2) (some Mo atoms shown as green polyhedra).

enantiopure (S)-trethbz was employed, the self-assembly process led to a homochiral coordination polymer as confirmed by the Flack parameter, which refined to the value of 0.00(7).

Interactions between *tr*-ligands and the oxomolybdate matrix might generally result in multiple products of five different structural types (Scheme 1).<sup>8b,11</sup> They, however, have the dominant composition ratio of *tr*-ligands:Mo<sup>VI</sup> as 1:2, for instance  $[Mo_2O_6(tr_2ad)]\cdot 6H_2O$  and  $[Mo_2O_6(tr_2ad)]\cdot H_2O^{11a,b}$  or  $[Mo_2O_6(Hpz-tr)(H_2O)_2]$  and  $[Mo_2O_6(Hpz-tr)]\cdot H_2O,^{11b,22}$  where  $tr_2ad = 1,3$ -bis(1,2,4-triazol-4-yl)adamantane and Hpz-tr = 4-(3,5-dimethylpyrazol-4-yl)-1,2,4-triazole. Under hydrothermal conditions  $trPhCO_2H$  or its nitrile precursor (trPhCN) reacts with MoO<sub>3</sub>, affording a mixture of the two complexes,  $[Mo_4O_{12}(trPhCO_2H)_2]\cdot 0.5H_2O$  (2a)/ $[Mo_4O_{12}(trPhCO_2H)_2]\cdot H_2O$  (2b), which exhibit a very similar composition but totally different structures.

The crystal structure of **2a** belongs to the perovskite type, a rare example for triazolyl-based molybdenum(VI) oxide solids, which was reported just for the simplest 1*H*-1,2,3-*tr* and 1*H*-1,2,4-*tr* ligands.<sup>8b,10</sup> The 2D sheets are built up from distorted MoO<sub>3</sub>N octahedra, each of which is interconnected by four common vertices of  $\mu_2$ -O atoms (Figures 2 and 3 and Table 1).



**Figure 2.** Perovskite-type solid  $[Mo_4O_{12}(trC_6H_4CO_2H)_2]\cdot 0.5H_2O$ (2a) was formed as a major product of the hydrothermal reaction between MoO<sub>3</sub> and 4-(1,2,4-triazol-4-yl)benzonitrile in dilute aqueous HF.

In axial positions the octahedra are clamped by [N-N]-tr links with a strict alternation above and below the layer, whereas the carboxylic acid fragments are left uncoordinated. The ligand length and anchoring binding mode predetermine the molybdenum trioxide interlayer spacing of b = 13.6620(6) Å. Each two ligand molecules bound on one side of the layer are tightly stacked in a pair via  $\pi - \pi$  interactions, as suggested by centroid-centroid distances of 3.622 and 3.686 Å between closely disposed tr-rings. A closer inspection of the packing reveals that eight molybdenyl oxygen atoms within the MoO<sub>3</sub> layer form a cyclic and shape-complementary cavity around the tr-pair (Figure 4), leaving the  $-C_6H_4CO_2H$  fragments to be located outside the host cavity. This perfect fit of triazoles and oxide matrix is achieved through four unprecedented noncovalent contacts between C atoms of tr and O atoms of molybdenyl groups (~2.83-2.88 Å). Likely, these interactions can be responsible for the deep green color of the complex. The small interlayer voids are filled by uncoordinated water



**Figure 3.** (a) Space filling model of the 2D perovskite-like layer of compound **2a** consisting of distorted MoO<sub>5</sub>N octahedra joined by vertices of  $\mu_2$ -O and stapled axially through [N–N]-*tr* fragments; (b) set of intralayer  $\pi - \pi$  interactions and C(*tr*)---O contacts; (c) the  $-CO_2H$  groups are involved in H-bonding interactions between the adjacent layers (water molecules are not shown).

Table 1. Principal Structural Features of  $[Mo_2O_6(trethbz)_2]$ ·H<sub>2</sub>O (1),  $[Mo_4O_{12}(trPhCO_2H)_2]$ ·0.5H<sub>2</sub>O (2a),  $[Mo_4O_{12}(trPhCO_2H)_2]$ ·H<sub>2</sub>O (2b), and  $[Mo_8O_{25}(trhis)_2(trhisH)_2]$ ·2H<sub>2</sub>O (3)

compound	coord. polyhedra	ligand binding mode	oxygen atom bridges	polyhedral connectivity	Mo(VI) oxide-subtopology and overall topology
$[Mo_2O_6(trethbz)_2] \cdot H_2O(1)$	cis- $\{N_2O_4\}$	$\mu_{2}$ -(N,N) <sup>tr</sup>	μ <sub>2</sub> -Ο	vertex shared	1D, ribbon
$\begin{bmatrix} Mo_4O_{12}(trPhCO_2H)_2 \end{bmatrix} \cdot \\ 0.5H_2O(2a) \end{bmatrix}$	${NO_5}$	$\mu_2$ -(N,N) <sup>tr</sup>	μ <sub>2</sub> -Ο	vertex shared	2D, perovskite-like layer
$\begin{bmatrix} Mo_4O_{12}(trPhCO_2H)_2 \end{bmatrix} \cdot H_2O$ (2b)	${NO_5}$	$\mu_2$ -(N,N) <sup>tr</sup>	μ <sub>3</sub> -Ο	vertex shared	1D
$ \begin{array}{l} [Mo_8O_{25}(trhis)_2(trhisH)_2] \\ 2H_2O~(3) \end{array} $	$\begin{array}{c} \textit{cis-} \{N_2O_4\} \\ \{O_6\} \end{array}$	$\mu_{2}$ -(N,N) <sup>tr</sup> & $\mu_{4}$ -(N,N) <sup>tr</sup> , (O,O)	μ <sub>2</sub> -Ο, μ <sub>3</sub> -Ο	vertex and edge shared	$1D \rightarrow 2D$

molecules which engage in H-bonding interactions with molybdenyl oxygen atoms.

The crystal structure of the related complex  $[Mo_4O_{12}(trPhCO_2H)_2]\cdot H_2O$  (2b) forming under identical conditions belongs to the more common ribbon type (Figure 5, Scheme 1). The linear sequences of distorted  $MoO_5N$  octahedra are linked by two O–O edges and supported alternatively by bindings of *tr*-fragments above and below. The ribbons and water molecules are further self-assembled via hydrogen bonds that lead to 2D layers. A similar structural motif was recently described for related Mo(VI) oxide solids decorated with heterofunctional triazolyl derivatives.<sup>11b</sup> At first glance, the carboxylic acid group seems to be inert toward the Mo(VI) oxide matrix.<sup>21</sup> However, the crystal structure of  $[Mo_8O_{25}(trhis)_2(trhisH)_2]\cdot 2H_2O$  (3) disproves this trend.

The asymmetric unit of compound 3 consists of four independent molybdenum atoms, 12 and a half oxygen atoms of the oxide matrix, two organic ligands, and a water molecule as shown in Figures 6 and S7. Except for atom O4, which occupies a crystallographic inversion center with the site occupancy factor of 0.5, all other atoms occupy general positions. The molybdenum atoms having distorted octahedral  $\{O_6\}$  and *cis*- $\{N_2O_4\}$  environments are linked in a wavelike chain combining common vertices and edges from oxygen atoms (Figure 7a). The motif contains a unique sequence of alternating fragments  $[MoO_2-(\mu_2-O)(tr)_2-MoO_2-(\mu_2-O)]_2$  and  $[MoO_2-(\mu_3-O)(\mu_2-O)(\mu_2-CO_2)-MoO_2]_2$ , in which the coordinating groups [N-N]-tr and *syn,syn*- $\mu_2$ - $\eta^{1:}\eta^{1-}$ -CO<sub>2</sub><sup>-</sup> appear simultaneously and synergistically with small inorganic bridges. Taking into account the fact that carboxylate coordination to



**Figure 4.** (a) Eight MoO<sub>3</sub> fragments are arranged in a cyclic bowlshaped cavity that incorporates two  $\pi$ -stacked triazolyl groups from two organic ligands. (b) Phenylene spacers and terminal carboxylic acid groups stay away from the cavity, while the accommodation of two *tr*-rings is supported through direct coordination to Mo and four unprecedentedly short noncovalent C(*tr*)···O=Mo contacts (~2.83– 2.88 Å).

Mo oxide typically affords linear ribbons (Scheme 2), whereas triazolyl coordination preferably leads to chainlike coordination polymers (Scheme 1), the obtained { $[MoO_2-(\mu_2-O)(tr)_2 MoO_2-(\mu_2-O)]_2-[MoO_2-(\mu_2-O)(\mu_2-O)(\mu_2-CO_2)-MoO_2]_2]_{\mu_2}$ subtopology can be rationally explained as follows. Under the above-mentioned reaction conditions the organic ligand trhis behaves in two forms: neutral zwitterionic tr-CH(CH<sub>2</sub>-Him<sup>+</sup>H)-CO<sub>2</sub><sup>-</sup> (or *trhis*), and positively charged protonated species  $tr-CH(CH_2-im2H^+)-CO_2H$  (or  $trhisH^+$ ). In 3, the composition ratio between them is the same, thus compensating the negatively charged polyoxomolybdate matrix  ${Mo_8O_{25}}_n^{2n-}$ . Since a racemic mixture of *trhis* was employed, crystals of 3 contain both enantiomers, resulting in the centrosymmetric space group  $P2_1/c$ . The neutral zwitterion trhis acts as a tetracoordinating unit exploiting both triazolyl and carboxylate bridging functions. This leads to tight interconnections between nearby chains forming a 2D coordination network (Figure 7). For the protonated  $trhisH^+$ species, only a triazolyl group serves as a [N-N]-bidentate bridge, whereas the carboxylic acid functional group remains uncoordinated. Thus, compound 3 can be considered as the first example of a zwitterionic complex of Mo(VI) oxide with a three-functional zwitterionic ligand. The polyoxomolybdate matrix bears the negative charge, whereas the positive charge is concentrated at the imidazolium ring of the ligand.



**Figure 6.** In the crystal structure  $[Mo_8O_{25}(trhis)_2(trhisH)_2]\cdot 2H_2O$  (3) the coordination environments of the Mo atoms are completed by bridging tr-,  $-CO_2^-$ , and  $\mu_2$ -O/ $\mu_3$ -O (symmetry code: (i) *x*, *y*+1, *z*; (iii) -x, -y, -z+1; (v) *x*, *y*-1, *z*).

**Thermal Stability.** We recently demonstrated that molybdenum oxide solids decorated by triazolyl-based ligands exhibit appreciably high thermal stability, usually reaching 300–350 °C and sometimes even more. The results correlate well with the nature of extra functional moieties introduced at the ligand platform, in addition to the 1,2,4-*tr* heterocycle, as well as the resultant network topology of the coordination polymer; that is, the low dimension of nets dictates the relatively low thermal stability often occurring with temperature-induced crystal structure transformation.<sup>11</sup> To the best of our knowledge, the highest thermal stability was documented for the related tungsten(VI) oxide complex with 4,4'-*bipy* (530 °C).<sup>9b</sup>

The thermal stability of the compounds was examined by measurements of temperature-dependent PXRD. For the 1D coordination polymer  $[Mo_2O_6(trethbz)_2]\cdot H_2O$  (1), the initial diffraction pattern shows significant changes in positions of peaks in the temperature ranges of 120-130 °C and 250-260 °C (Figure S12b). The first thermal transition can be attributed to dehydration, while the second one clearly indicates complete decomposition of the coordination polymer. As evidenced by thermogravimetry/mass spectrometry (TG-MS) studies (Figure S13), the dehydration process proceeds gradually in a wide



Figure 5. (a) Ribbon-type motif in complex  $[Mo_4O_{12}(trPhCO_2H)_2]\cdot H_2O$  (2b) supported by [N-N]-triazole coordination. 2b was isolated as a minor phase in the hydrothermal process. (b) The carboxylic acid functions  $(-CO_2H)$  are left uncoordinated and are involved in a wide set of H-bonding interactions between adjacent ribbons as well as water molecules.



Figure 7. Crystal structure of  $[Mo_8O_{25}(trhis)_2(trhisH)_2]\cdot 2H_2O$  (3): (a) the wavelike chain consists of a sequence of two alternating domains,  $[MoO_2-(\mu_2-O)(tr)_2-MoO_2-(\mu_2-O)]_2$  and  $[MoO_2-(\mu_3-O)(\mu_2-O)(\mu_2-O_2)-MoO_2]_2$ , which are supported by different bridging types either through  $\mu_2$ -O/[N-N]-tr or  $\mu_2$ -O/ $\mu_3$ -O/ $\mu_2$ -[O=C-O]; (b) the domains from neighboring chains are interlinked by a tetradentate zwitterionic *trhis* unit forming the layered structure; (c) the adjacent layers are involved in hydrogen bonding.



Figure 8. UV-vis absorbance spectra (a) and Tauc plots (b) for thin films of samples 1, 2a, and 3.

temperature range of 60–130 °C with a weight loss of 2.71% corresponding to one water molecule (m/z = 18, 2.64% calcd). The TGA curve above 250–260 °C shows high weight loss (over 40 wt %) accompanied by intense evolution of H<sub>2</sub>O and CO<sub>2</sub> (m/z = 18 and 44), suggesting ligand decomposition. Unlike this case, the thermal stability of the 1D coordination polymer [Mo<sub>4</sub>O<sub>12</sub>(*trPhCO*<sub>2</sub>H)<sub>2</sub>]·0.5H<sub>2</sub>O (**2b**) is somewhat higher, which can be explained by the existence of a highly effective H-bonding network cross-linking through the polymeric structure. The complex begins to lose its crystallinity beyond 320 °C. On the basis of its 2D perovskite-type structure, the thermal stability of the related complex

 $[Mo_4O_{12}(\textit{trPhCO}_2H)_2]{\cdot}0.5H_2O$  (2a) is even higher, reaching up to 350 °C.

**Absorption Spectra.** Absorption spectra recorded for thin films of samples 1-3 are shown in Figure 8a. For 2a a strong absorption band starts at about 526 nm (19 000 cm<sup>-1</sup>) and extends toward the UV region with two maxima, at ca. 25 800 cm<sup>-1</sup> (388 nm) and 35 300 cm<sup>-1</sup> (283 nm). Due to the absorption in the visible region, the complex exhibits a deep green color. The spectra of the colorless compounds 1 and 3 are dominated by strong absorption in the UV region. For complex 3 the maximum of the absorption band is observed at ca. 32 800 cm<sup>-1</sup> (305 nm), whereas for 1 it is shifted toward the

UV region, with the maximum at ca.  $35\,000 \text{ cm}^{-1}$  (286 nm) and a shoulder at ca.  $39\,900 \text{ cm}^{-1}$  (250 nm). Unlike the related oxomolybdate with 3,5-di(4*H*-1,2,4-triazol-4-yl)benzoic acid recently reported,<sup>21</sup> none of the three samples investigated here exhibit any luminescence when excited at absorption bands using a Xe lamp.

Our DFT calculations show that samples 2a, 3, and 1 are direct band gap semiconductors with band gaps increasing from 1.67 and 2.47 to 2.56 eV, respectively (Figures S24, S26, and S22). On the basis of the UV/vis spectra the second-power  $(ah\nu)^2$  was used for the Tauc plots (Figure 8b), yielding band gap values of 2.61, 3.44, and 3.58 eV for 2a, 3, and 1, respectively. DFT calculations usually underestimate band gap values,<sup>23,24</sup> in our case by ca. 1 eV. However, the experimentally observed trend is well reflected in the calculations. Similar energy gaps are calculated for samples 1 and 3, and they are larger by about 1 eV than that for sample 2a.

Partial densities of states calculated for molybdenum and organic ligands are shown in Figures S21, S23, and S25. In each case the bands below the Fermi level mainly consist of p-states of ligands. Although some Mo d-states are also present, they are centered at about -4 eV and do not contribute significantly to the valence band. Contribution of Mo d-states is much more pronounced in the conduction band. Moreover, these states are lying on the edge of the conduction band, leading to the assumption that the optical absorption is associated with energy transfer from organic ligands to molybdenum d-levels.

**Catalytic Performance and Stability Tests.** The epoxidation activity and stability of compounds 1, 2a, and  $3^*$  were investigated via the model reaction of *cis*-cyclooctene with *tert*-butylhydroperoxide (TBHP) as oxidant, at 55 °C (Figure 9,



Figure 9. Epoxidation of *cis*-cyclooctene with TBHP, using the systems  $1/\text{TFT}/55 \,^{\circ}\text{C}(\bigcirc)$ ,  $2a/\text{TFT}/55 \,^{\circ}\text{C}(\thickapprox)$ ,  $3^*/\text{TFT}/55 \,^{\circ}\text{C}(\blacksquare)$ ,  $1/\text{TFT}/70 \,^{\circ}\text{C}(\textcircled{\bullet})$ ,  $1-\text{CT-L}/\text{TFT}/55 \,^{\circ}\text{C}(\clubsuit)$ , and  $1-\text{CT-S}/\text{TFT}/55 \,^{\circ}\text{C}(\Box)$ . Selectivity to 1,2-epoxycclooctane (CyO) was always 100%. The dashed lines are visual guides.

Table 2). The three compounds led to 1,2-epoxycyclooctane (CyO) as the only product (100% selectivity); without catalyst, Cy conversion was negligible. The reaction rate (based on conversion at 24 h) followed the order 1 (97%) > (2a) (82%) >  $3^*$  (47%). The results for 1 and 2a are comparable or superior to those for commercially available MoO<sub>3</sub> (Scharlau, >99% purity), tested as catalyst under identical Cy reaction conditions (83% conversion at 24 h, Table 2).

Table 2. Epoxidation of *cis*-Cyclooctene in the Presence ofMo Compounds Studied in This Work

sample	T (°C); cosolvent; oxidant	CyO yield at 1 h/6 h/24 h (%) <sup>d</sup>
2a	55; TFT; TBHP <sup>a</sup>	5/44/82
3*	55; TFT; TBHP <sup>a</sup>	0/12/47
1	55; TFT; TBHP <sup>a</sup>	28/77/97
MoO <sub>3</sub>	55; TFT; TBHP	-/16/83
none	55; TFT; TBHP	-/-/<1
1-CT-L	55; TFT; TBHP <sup>b</sup>	35/61/89
1-CT-S	55; TFT; TBHPb <sup>c</sup>	36/66/92
1	70; TFT; TBHP <sup>a</sup>	68/98/100
1	55; CH <sub>3</sub> CN; H <sub>2</sub> O <sub>2</sub> <sup><i>a</i></sup>	-/-/77

<sup>*a*</sup>Initial molar ratios Mo:Cy:oxidant = 1:100:153 ( $[Cy]_0 = 0.7 \text{ M}$ ; 2 mL of cosolvent). <sup>*b*</sup>The initial concentration of Cy was equal to that used for a typical catalytic batch run (with 1). <sup>*c*</sup>Using a mass amount of recovered solid similar to that used for a typical catalytic batch run with fresh catalyst. <sup>*d*</sup>Cyclooctene oxide (CyO) yield (selectivity was 100%).

For 1, 2a, and  $3^*$ , the solids recovered from a 24 h catalytic batch run at 55 °C (i-TBHP-55, i = 1, 2a, and  $3^*$ ; details given in the Experimental Section) were characterized by ATR FT-IR spectroscopy and PXRD. For each compound, the IR spectra and PXRD patterns of the fresh and used solids were comparable (Figures 10–12), suggesting that their chemical and structural features were essentially preserved during the catalytic reaction. The main differences in characterization data were slight changes in the relative intensities of some weak peaks in the case of  $3^*$ , which may be due to partial recrystallization under the catalytic reaction conditions (which are different from the synthesis conditions).

The molybdenum centers in compounds 1, 2a, and  $3^*$  are responsible for the epoxidation activity, since under metal-free conditions, in the presence of the corresponding free organic ligands *trethbz*, *trPhCO*<sub>2</sub>*H*, or *trhis* (used in molar amounts equivalent to those added together with the corresponding molybdenum compounds), the Cy reaction at 55 °C was very sluggish; the best result was 9% conversion at 24 h, for *trethbz*. Hence, the active species contain molybdenum. Attempts to isolate the ligands after a 24 h batch run were successful in the cases of *trPhCO*<sub>2</sub>*H* and *trhis*, *trPhCO*<sub>2</sub>*H*-TBHP-55, and *trhis*-TBHP-55, respectively. The ATR FT-IR spectra and PXRD patterns of the original and used solids are similar (Figures 10 and 11). These results are consistent with the characterization studies of the hybrid polymers, which indicate fairly good stability under the catalytic conditions.

The activity trends for compounds 1, 2a, and 3\* may be due to an interplay of Lewis acidity, catalyst solubility, and/or structural dimensionality of the hybrid compounds. It is generally accepted that molybdenum-catalyzed epoxidation of olefins with alkylhydroperoxides involves the reaction between the (Lewis acid) metal centers and the (basic) oxidant molecules, giving active species that possess linear or  $\eta^2$ -peroxo ligands ({Mo-O-O} or  $\{Mo-(O)_2\}$ ) involved in the O atom transfer reaction to the olefin, finally giving the epoxide product (and an alcohol as coproduct of the consumption of the oxidant).<sup>25,26</sup> Accordingly, the Lewis acidity of the metal centers can determine the epoxidation activity and is influenced by the type of coordinated organic ligands. The three compounds possess different coordination environments, which may partly account for the difference in reaction kinetics. On the other hand, differences in catalyst solubility and initial



Figure 10. FT-IR ATR spectra (A) and PXRD patterns (B) of ligands  $trPhCO_2H$  (a) and  $trPhCO_2H$ -TBHP-55 (b) and compounds 2a (c) and 2a-TBHP-55 (d).



Figure 11. FT-IR ATR spectra (A) and PXRD patterns (B) of ligands trhis (a) and trhis-TBHP-55 (b) and compounds 3\* (c) and 3\*-TBHP-55 (d).

dissolution rates may affect the overall reaction rate. Consistently, the kinetic profiles showed an initial induction period (10–60 min) that decreased in the order  $1 > 2a > 3^*$ ; longer initial induction periods may be partly due to slower initial dissolution of the catalyst. The structure of the three compounds is very different, and steric hindrance effects may be less important for (most active catalyst) 1, in comparison to 2a and 3<sup>\*</sup>. The monofunctional *tr* ligand in 1 led to a 1D zigzag chain (ribbon) structure. On the other hand, 2a, bearing the heterodonor ligand *tr*/CO<sub>2</sub>H, possesses a 2D structure, and 3<sup>\*</sup>, bearing the heterodonor ligand im/*tr*/CO<sub>2</sub>H are coordinated to Mo centers; these structural features may lead to the lower accessibility/inaccessibility of some metal centers for coordination.

Compound 1 is a homogeneous catalyst, which was confirmed by a contact test approach (details in the Experimental Section). Specifically, the liquid and solid phases (1-CT-L and 1-CT-S, respectively) obtained from contacting 1 with TBHP/TFT/55 °C for 24 h (without substrate) were tested separately for Cy reaction and led to relatively high conversions (89% and 92% conversion at 24 h, respectively), which reasonably parallels that for 1 used in a typical batch run (97% conversion) (Figure 9); some differences in reaction rates are likely due to differences in the amount of catalyst. The PXRD patterns and ATR FT-IR spectra of the solids 1-CT-L and 1-CT-S and of the solid (1-CT-S run 1) recovered from the catalytic test using 1-CT-S were similar to the corresponding data for 1 (Figure 12). These results suggest that the epoxidation reaction is essentially promoted by the solubilized metal species, and the active metal species are stable when dissolved or not in the oxidizing medium.

The catalytic conversion could be improved by increasing the reaction temperature from 55 to 70  $^{\circ}$ C, without affecting selectivity and catalyst stability; CyO yield at 6 h increased from 77% at 55  $^{\circ}$ C to 98% at 70  $^{\circ}$ C (Figure 9, Table 2). The FT-IR ATR spectra and PXRD patterns of the recovered solid 1-TBHP-70 were similar to the corresponding data for the original compound 1, suggesting fairly good stability (Figure 12).

The catalytic performance of **1** was superior to that reported for other molybdenum oxide-based hybrid polymers tested as



Figure 12. FT-IR ATR spectra (A) and PXRD patterns (B) of ligand *trethbz* (a) and compounds 1 (b), 1-TBHP-55 (c), 1-CT-S-run 1 (d), 1-CT-S (e), 1-TBHP-70 (f), and  $1/H_2O_2$  (g).

olefin	T (°C)	conv. (%) <sup>a</sup>	product	select. (%) <sup>b</sup>	ee (%) <sup>c</sup>	de (%) <sup>d</sup>
Су	70	98/100	1,2-epoxycyclooctane	100/100		
Cy12	70	97/100	1,2-epoxycyclododecane	100/100		
1C8	70	41/63	1,2-epoxyoctane	100/100		
2C8	70	88/99	2,3-epoxyoctane	100/100		
Ole	70	92/100	methyl 9,10-epoxyoctadecanoate	95/92		
			methyl 9,10-dihydroxyoctadecanoate	3/6		
LinOle	70	63/78	9,10-epoxy-12Z-octadecenoate + methyl 12,13-epoxy-9Z- octadecenoate	88/81		
			methyl 9,10;12,13-diepoxyocta-decanoate	12/19		
Prochiral	olefins					
TBMS	55	43/66	(1R,2R)-(+)-phenylpropylene oxide	100/100	0/0	
			(1S,2S)-(-)-phenylpropylene oxide			
DL-Lim	55	78/90	1,2-epoxy- <i>p</i> -menth-8-ene	85/82	13/12 ((+)-cis); 8/8 ((+)-trans)	2/3 ((-)-cis); 8/8 ((+)-cis)
			1,2;8,9-diepoxy- <i>p</i> -menthane	9/13		

Table 3. Epoxidation of Different Olefins with TBHP, in the Presence of 1, Using TFT as Co-solvent

<sup>*a*</sup>Initial molar ratios Mo:Cy:oxidant = 1:100:153, 2 mL of TFT. <sup>*b*</sup>Conversion at 6/24 h. Selectivity at 6 h/24 h. <sup>*c*</sup>Enantiomeric excess at 6 h/24 h. <sup>*d*</sup>Diastereomeric excess at 6 h/24 h.

catalysts in the same model reaction, under somewhat comparable conditions (Table S10); namely,  $[Mo_2O_6(trpzH)-(H_2O)_2]_n$  (trpzH = 4-(3,5-dimethyl-1H-pyrazol-4-yl)-1,2,4-triazole),<sup>11b</sup>  $[MoO_3(bipy)][MoO_3(H_2O)]\}_n$  (bipy = 2,2'-bipyridine),<sup>3b</sup>  $[Mo_2O_6(HpypzA)]_n$  (HpypzA = [3-(pyridinum-2-yl)-1H-pyrazol-1-yl]acetate),<sup>3t</sup>  $[MoO_3(1H-1,2,4-tr)_{0.5}]$ ,<sup>3g</sup> and  $[Mo_3O_9(pypz)]_n$  (pypz = 2-[3(5)-pyrazolyl]-pyridine).<sup>3c</sup> Compounds  $[MoO_3(bipy)]_n^{27}$  and  $[Mo_2O_6(pent-pp)]_n$  (pent-pp =  $(2-(1-pentyl-3-pyrazolyl)pyridine)^{28}$  led to higher Cy conversions than 1. Differences in catalytic activity may be associated with different structural and chemical properties of the hybrid materials, which may lead to differences in catalyst solubility and electronic (Lewis acidity)

and steric (ligand lability, accessibility of reactant molecules to the metal centers) effects. Compounds  $[{\rm MoO}_3({\rm bipy})]_n^{27}$  and  $[{\rm Mo}_2{\rm O}_6({\rm pent-pp})]_n^{28}$  both consist of 1D chains of cornersharing distorted  $\{{\rm MoO}_4{\rm N}_2\}$  octahedra (relatively "flexible") and led to higher Cy conversions than 1. Clear comparisons with other molybdenum-based polymers (e.g., possessing salycilidene- or pyridoxal-based ligands) are not straightforward due to considerably different reaction conditions used between different works.

The versatility of 1 as a catalyst was further explored for the epoxidation of various substrates using TBHP as oxidant at 70  $^{\circ}$ C (Table 3). The reaction of the linear olefins *trans*-2-octene (2C8) and 1-octene (1C8) gave the corresponding epoxide

products with 100% selectivity. The reaction of 2C8 (88%/99% conversion at 6 h/24 h) was faster than that of 1C8 (41%/63% conversion at 6 h/24 h). This may be explained in light of the mechanistic considerations discussed above. The internal double bond of 2C8 is electron richer than the terminal double bond of 1C8, and thus the nucleophilic attack of the olefin on the active oxidizing species and the O atom transfer to the olefin is more favorable for 2C8. Somewhat consistent with this hypothesis, the cyclic substrate Cy is more reactive than the linear octenes.<sup>29</sup>

The epoxidation cyclododecene (Cy12) in the presence of 1 led to 97% conversion at 6 h, which is comparable to that for the less bulky cyclic olefin Cy. It seems that electronic effects are more considerable than steric ones for these epoxidation systems. Compound 1 was further explored for the epoxidation of the biomass-derived olefins methyl oleate and methyl linoleate, which are fatty acid methyl esters (FAMEs) produced from vegetable oils by transesterification.<sup>30</sup> Epoxidized FAMEs have widespread use as, for example, PVC stabilizers and plasticizers and as intermediates in the production of polyurethane polyols.<sup>31</sup>

The epoxidation of Ole gave methyl 9,10-epoxyoctadecanoate in 87%/92% yield at 92%/100% conversion (6 h/24 h); methyl 9,10-dihydroxyoctadecanoate was formed in 6% yield at 24 h. The reaction of LinOle gave epoxides in a total selectivity of 100%: specifically, at 63%/78% conversion and 6 h/24 h reaction, the monoepoxy isomers methyl 9,10-epoxy-12*Z*-octadecenoate and methyl 12,13-epoxy-9*Z*-octadecenoate were formed in equimolar amounts and 56%/63% total yield, and methyl 9,10;12,13-diepoxyoctadecanoate was formed in 8%/15% yield. LinOle was less reactive than Ole, which may be partly associated with the fact that the former possesses two double bonds.

Only a few other hybrid organic/inorganic molybdenum compounds have been studied as catalysts for Ole epoxidation with TBHP. On the basis of the OleOx yields at 6 h/24 h, the performance of 1 is comparable or slightly superior to that reported for the molybdenum oxide/bipyridine dicarboxylate hybrid material (DMA)[MoO<sub>3</sub>(Hbpdc)]·*n*H<sub>2</sub>O (DMA = dimethylammonium; Hbpdc = deprotonated 2,2'-bipyridine-5,5'-dicarboxylic acid),<sup>3d</sup> which led to 91%/98% OleOx yield (93%/100% conversion) at 75 °C (molar ratio Mo:Ole:TBHP = 1:103:160, TFT as cosolvent). At the lower reaction temperature of 55 °C, the hybrid material [Mo<sub>2</sub>O<sub>6</sub>(2-(1-pentyl-3-pyrazolyl)pyridine)] led to 78% OleOx yield (82% conversion) at 6 h (molar ratio Mo:Ole:TBHP = 1:113:172).<sup>28</sup>

The use of  $H_2O_2$  instead of TBHP gave CyO as the only product, and the kinetics was slower: 77% and 97% conversion at 24 h, for  $H_2O_2$  and TBHP, respectively, at 55 °C (Table 2). The catalytic results for the system  $1/H_2O_2$  are similar to those reported in the literature for the polymer { $[MoO_3(bipy)]$ - $[MoO_3(H_2O)]$ }<sup>32</sup> and inferior to  $[MoO_3(tr)_{0.5}]_n$ <sup>3g</sup> and  $[Mo_2O_6(trpzH)(H_2O)_2]_n$ ,<sup>11b</sup> tested as catalysts under similar Cy reaction conditions (Table S11). Additional comparisons were difficult due to the different reaction conditions used for other systems presented in Table S11.

The slower kinetics when using  $H_2O_2$  as oxidant instead of TBHP may be partly due to differences in catalyst stability. On the other hand, water (which is added together with  $H_2O_2$ ) is a coordinating solvent that may compete with the oxidant molecules in the coordination to the metal center (based on the above mechanistic considerations).

The reaction mixture consisted of a yellow solution, whereas the as-synthesized compound 1 is a white powder, suggesting that different metal species were formed from 1 during the catalytic reaction with H2O2. The FT-IR ATR spectrum of metal species  $(1-H_2O_2-55)$  isolated from a 24 h batch run at 55 °C is different from that of 1 (Figure 12). The bands at 940, 920, and 906  $\text{cm}^{-1}$  associated with the Mo=O vibrations of 1 disappeared, and instead the solid 1-H2O2-55 exhibited two bands at 931 and 892 cm<sup>-1</sup>, as well as a shoulder at 862 cm<sup>-1</sup> and a weak band at 678 cm<sup>-1</sup> assignable to  $\nu$ (O–O) stretching vibrations and symmetric  $Mo(O_2)$  vibrational modes, respectively; a broad band centered at 540 cm<sup>-1</sup> assignable to Mo-O-Mo vibrations remained present.<sup>33,34</sup> On the other hand, 1-H<sub>2</sub>O<sub>2</sub>-55 exhibited slight differences of the ligand coordination modes in the range 1220-1150 cm<sup>-1</sup>, and a shoulder at 520  $\rm cm^{-1}$  disappeared. These spectral differences indicate that considerable changes in the coordination sphere for 1 occurred, leading to species of the type 1-H<sub>2</sub>O<sub>2</sub>-55, which seem to be polymeric, bearing oxo and peroxomolybdenum groups. Accordingly, the PXRD pattern of 1-H<sub>2</sub>O<sub>2</sub>-55 is very different from that of 1 (Figure 11); the former solid is amorphous and structurally very different. The lower catalyst stability and formation of different types of metal species for  $H_2O_2$  as oxidant in comparison to TBHP may partly explain the lower catalytic activity in the former case.

Catalytic Performance of 1 in the Reaction of *trans-\beta*-Methylstyrene. The catalytic reaction of the prochiral olefin *trans-\beta*-methylstyrene (TBMS), in the presence of the homochiral coordination polymer 1, at 55 °C, gave 100% total selectivity to the corresponding epoxide isomers (1R,2R)-(+)-phenylpropylene oxide and (1S,2S)-(-)-phenylpropylene oxide and 66% conversion at 24 h. No significant enantiomeric excess was obtained. To the best of our knowledge, there are no reports on the use of molybdenum(VI) oxide hybrid polymers possessing chiral centers in the organic component, tested as catalysts for TBMS epoxidation. A mixed Mo-Sn hybrid polymer, namely,  $[((Me)_2(menthyl)Sn)_2MoO_4(H_2O)_{3,5}]_n$ , with  $[MoO_4]_2$ -tetrahedra coordinated to  $[R_3Sn]^+$  cationic spacers, gave similar results to 1: 68% TBMS conversion and negligible ee after 24 h (molar ratio catalyst:olefin:oxidant = 1:100:150), using dichloromethane as cosolvent at 55 °C.<sup>35</sup>

Compound 1 was further explored for the epoxidation of DLlimonene (DL-Lim; consisting of a racemic mixture of S-(-)-limonene and R-(+)-limonene), using TBHP as oxidant at 55 °C, under similar reaction conditions to those used for TBMS as substrate (Table 3). The reaction of DL-Lim gave mainly isomers of 1,2-epoxy-p-menth-8-ene (LimOx) in a total yield of 66%/74% at 78%/90% conversion and 6 h/24 h; 1,2;8,9-diepoxy-p-menthane (LimDiOx) was formed with 7%/ 12% yield. The molar ratio LimOx/(LimOx+LimDiOx) was 0.9 (6 and 24 h) and 8,9-epoxy-p-menth-1-ene was not formed, suggesting high regioselectivity toward the epoxidation of the endocyclic double bond in relation to the exocyclic one. The epoxide products, LimOx and LimDiOx, have commercial importance for the production of paints and resins, for example, and can be used as intermediates in the synthesis of fragrances, agrochemicals, biodegradable polymers, and pharmaceuticals, among others.<sup>36,37</sup>

For compound 1, the product LimOx consisted of four isomers, namely, the diastereoisomers (1S,4S)-(-)-cis-limonene-1,2-epoxide and (1R,4S)-(-)-trans-limonene-1,2-epoxide formed from (S)-(-)-limonene with 3% diastereomeric excess (de) of the (-)-cis-isomer at 24 h, and the diastereoisomers

(1R,4R)-(+)-cis-limonene-1,2-epoxide and (1S,4R)-(+)-translimonene-1,2-epoxide formed from (R)-(+)-limonene with 8% de of the (+)-cis- isomer at 24 h. The catalytic results for 1 compare favorably to literature data for the polymeric material  $[((Me)_2(menthyl)Sn)_2MoO_4(H_2O)_{3,5}]$  tested for the reaction of DL-Lim, which led to 67% total monoepoxide yield at 90% conversion, 24 h (Mo:substrate:TBHP = 1:100:150; 55 °C; dichloromethane); when the pure isomer (R)-(+)-limonene or (S)-(-)-limonene was used as substrate, the corresponding *cis*isomers were formed with 5-7% de, which is somewhat comparable to the de values for 1.35 For compound 1, the isomers (1R,4R)-(+)-cis-limonene-1,2-epoxide and (1S,4R)-(+)-trans-limonene-1,2-epoxide were formed in an enantiomeric excess (ee) of  $12\overline{\%}$  (relative to the (-)-cis- isomer) and 8% (relative to the (-)-trans-isomer), respectively, at 24 h. A literature survey on molybdenum(VI) complexes bearing chiral N/O-donor ligands indicates that the induction ability of these types of catalysts for the epoxidation of prochiral olefins is generally low or negligible, which has been attributed to various factors such as the lability of the chiral ligands, <sup>38,39</sup> considerable distance between the chiral center(s) of the organic ligand and the catalytic site,<sup>40,35</sup> and/or poorly selective radical reactions. 41-4

# CONCLUSION

We employed organic ligands bearing 1,2,4-triazolyl (enantiopure (S)-trethbz), tr, and carboxylic acid (trPhCO<sub>2</sub>H) and tr, - $CO_2H$ , and imidazolyl (racemic trhis) donor moieties for the development of Mo(VI) oxide hybrid solids. The [N-N]coordination behavior of the tr-group is highly predictable and can be regarded as a clear tendency of the unit to anchor to MoO<sub>3</sub> through two-donor sites. The coordination ability of  $-CO_2H$  strongly depends on the nature of extra donors, which might specifically regulate the corresponding  $pK_A$  values of the ligands. In the acidic media, the  $-CO_2H$  group preferably serves as a H-bonding unit. The presence of basic imidazolyl fragments facilitates the formation of neutral zwitterions tr- $CH(CH_2-Him^+H)-CO_2^-$  with coordinating pairs of tr- and  $-CO_2^{-}$ , while the imidazolium species is left uncoordinated. This leads to diverse structural motifs of Mo(VI) oxide solids varying from zigzag chain 1 and ribbon 2b through rare perovskite-type 2a to the new two-domain chain 3. The optical band gaps of the complexes are in good agreement with the semiconducting behavior of molybdenum(VI) oxide hybrids.

Compounds 1-3 were investigated as epoxidation catalysts via the model reaction of cis-cyclooctene with tert-butylhydroperoxide (TBHP). The compounds are stable, based on catalytic and characterization studies, and lead to 1,2epoxycyclooctane with 100% selectivity. The catalytic activity follows the order  $1 > 2a > 3^*$ . Compound 1 effectively promoted the epoxidation of other olefins, namely, 1-octene, trans-2-octene, cyclododecene, and the bioderived olefins methyl oleate and methyl linoleate. For the epoxidation of the prochiral substrate *trans-\beta*-methylstyrene with TBHP, the total selectivity to the epoxide isomers (1R,2R)-(+)-phenylpropylene oxide and (1S,2S)-(-)-phenylpropylene oxide was 100% at 66% conversion, but enantiomeric excess was negligible. For the biobased prochiral olefin DL-limonene, four monoepoxide isomers were formed; the isomers (1R,4R)-(+)-cis-limonene-1,2-epoxide and (1S,4R)-(+)-trans-limonene-1,2-epoxide were formed in an enantiomeric excess of 12% (relative to the (-)-cis-isomer) and 8% (relative to the (-)-trans-isomer), respectively. The best performing catalyst

(1) was compared to other molybdenum-organic ligand based hybrid polymer catalysts reported in the literature. Differences in catalytic activity may be associated with different structural and chemical properties of the hybrid materials, which may lead to differences in catalyst solubility and electronic (Lewis acidity) and steric (ligand lability, accessibility of reactant molecules to the metal centers) effects.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02986.

Experimental details for X-ray structural analyses, spectral characterization data, thermal PXRD patterns, and DTA/ TG-MS data (PDF) Crystallographic data (CIF)

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#### Notes

The authors declare no competing financial interest.

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