Accepted Manuscript

Complexes of *cis*-dioxomolybdenum(VI) with unsymmetrical tripodal NO₃-donor ligands: Synthesis, characterization and catalytic applications

Sathish Kumar Kurapati, Swamy Maloth, Samudranil Pal

PII:	S0020-1693(15)00115-2
DOI:	http://dx.doi.org/10.1016/j.ica.2015.02.022
Reference:	ICA 16440
To appear in:	Inorganica Chimica Acta
Received Date:	9 January 2015
Revised Date:	20 February 2015
Accepted Date:	21 February 2015



Please cite this article as: S.K. Kurapati, S. Maloth, S. Pal, Complexes of *cis*-dioxomolybdenum(VI) with unsymmetrical tripodal NO₃-donor ligands: Synthesis, characterization and catalytic applications, *Inorganica Chimica Acta* (2015), doi: http://dx.doi.org/10.1016/j.ica.2015.02.022

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Complexes of *cis*-dioxomolybdenum(VI) with unsymmetrical tripodal NO₃-donor ligands: Synthesis, characterization and catalytic applications

Sathish Kumar Kurapati, Swamy Maloth, Samudranil Pal*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

ABSTRACT

A series of *cis*-dioxomolybdenum(VI) complexes of general formula cis-[MoO₂(HLⁿ)] (1-4) have been synthesized in 80–85% yields by reacting equimolar amounts of [MoO₂(acac)₂] (acac⁻ = acetylacetonate) with 2,2'-(2-hydroxy-3,5- R_1 , R_2 -benzylazanediyl)diethanols (H₃Lⁿ, n = 1-4) in Characterization of the complexes has been performed by elemental analysis, methanol. spectroscopic (IR, UV-Vis, ¹H- and ¹³C-NMR) and electrochemical measurements. The molecular structures of all four complexes have been determined by single-crystal X-ray diffraction studies. In each of these analogous complexes, the metal centre is in a distorted octahedral NO₅ coordination sphere assembled by the single edge shared 5,5,6-membered chelate rings forming NO₃-donor $(HL^{n})^{2-}$ and two *cis* oriented oxo groups. Crystal structures of the complexes reveal formation of discrete centrosymmetric dimeric species via a pair of reciprocal intermolecular O-H···O hydrogen bonding interactions. Spectroscopic data of all the complexes are consistent with their molecular structures. In the cyclic voltammograms, the redox-active complexes display a quasi-reversible to irreversible metal centred reduction with the cathodic peak potential in the range -0.92 to -1.12 V (vs. Ag/AgCl). All the complexes have been evaluated for their catalytic activities in oxidative bromination reactions of styrene and salicylaldehyde and in benzoin oxidation reaction.

Keywords: cis-dioxomolybdenum(VI) complexes, Tetradentate tripodal ligands; Crystal structures; Physicochemical properties; Catalytic activities

1. Introduction

Complexes of *cis*-dioxomolybdenum(VI) are of considerable contemporary interest due to their potential applications as catalysts in a variety of organic oxidation reactions [1–7] and as models for mimicking the function of several molybdenum containing oxotransferase enzymes [8–10]. As a result, a vast literature on the complexes containing the *cis*- $\{MoO_2\}^{2+}$ unit with a variety of ligands is now available [5–7,11,12]. Majority of these complexes are with bi- and tridentate ligands, while reports on its complexes with tetradentate tripodal ligands are rather

* Corresponding author.

E-mail address: spal@uohyd.ac.in (S. Pal)

limited [13–23]. Tripodal ligands are structurally and electronically easily tunable and they create a pocket to hold the metal ion leaving one side open for ancillary ligands. Compared to bi- or tridentate ligands tripodal ligands are expected to bind metal ions more strongly and provide more stable complexes due to their increased denticity and hence greater chelate effect. The structural uniqueness and stability of the complexes with such ligands have led to their utilization in a wide variety of research areas such as activation of small molecules [24,25], stabilization and scrutiny of reactive intermediates [26,27], biomodeling and biomimicking [24, 25,28–30], catalysis in organic synthesis [30–32] and sensors [33,34].

In the present work, we have explored the coordination chemistry of unsymmetrical tripodal tetradentate NO₃-donor 2,2'-(2-hydroxy-3,5- R_1 , R_2 -benzylazanediyl)diethanols (H₃Lⁿ, n = 1-4) with $\{cis-MoO_2\}^{2+}$ and synthesized a series of complexes having the formula cis- $[MoO_2(HL^n)]$ (1-4) (Chart 1). The catalytic abilities of the isolated complexes in oxidative bromination reactions of styrene and salicylaldehyde and benzoin oxidation reaction have been also assessed. The reasons to study these particular reactions using 1-4 as catalysts are as follows. The bromination of organic compounds via haloperoxidase reactions is an environmentally benign approach compared to the traditional bromination reactions with Br₂. Oxovanadium(V) complexes have been extensively studied as haloperoxidase mimics [35-37], whereas very few oxomolybdenum(VI) complexes have been employed for this purpose [38-40]. α -Dicarbonyls belong to an important class of organic compounds in the context of their applications in synthetic organic chemistry. Hence, selective catalytic oxidation of benzoin to benzil is an important key reaction [41-43]. However, not many reports on benzoin oxidation reaction catalyzed by oxomolybdenum(VI) species are available in literature [38,40,44,45]. Herein, we describe the details of synthesis, X-ray structures, physicochemical properties and catalytic behaviours of cis-[MoO₂(HLⁿ)] (1–4).

2. Experimental

2.1. Materials

Bis(acetylacetonato)dioxomolybdenum(VI), [MoO₂(acac)₂], was prepared according to a literature procedure [46]. 2,2'-(2-hydroxy-3,5- R_1 , R_2 -benzylazanediyl)diethanols (H₃Lⁿ) were synthesized using a procedure very similar to that reported earlier [47,48]. A general synthetic

procedure and some characterization (LC-MS and NMR) data for H_3L^n have been provided in the supplementary material. All other chemicals were of analytical grade available commercially and used as received. Solvents were purified by standard procedures [49].

2.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used to obtain the elemental (C, H, N) analysis data. A Shimadzu LCMS 2010 liquid chromatograph mass spectrometer was used for the purity verification of H_3L^n . Room temperature magnetic susceptibility measurements were performed with a Sherwood Scientific balance. Solution electrical conductivities were measured using a Digisun DI-909 conductivity meter. The infrared spectra were obtained with the help of a Thermo Scientific Nicolet 380 FT-IR spectrophotometer. The electronic spectra were collected with the help of a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. The ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded using tetramethylsilane as internal standard on a Bruker NMR spectrometer. The cyclic voltammetric measurements were performed on a CH Instruments model 620A electrochemical analyzer. Gas chromatographic measurements were performed with the help of Shimadzu GC-2010 Plus equipped with FID and Shimadzu GCMS-QP2010 instruments.

2.3. Synthesis of complexes $cis-[MoO_2(HL^{1-4})](1-4)$

All the complexes were synthesized by using the following general procedure: 65 mg (0.2 mmol) of solid $[MoO_2(acac)_2]$ was added to a hot methanol solution (30 ml) of 0.2 mmol of the corresponding H_3L^n (n = 1–4) The resulting mixture was boiled at reflux for 1 h. Then the reaction mixture was cooled to room temperature, filtered to remove suspended particles and allowed to evaporate slowly in air. After about a day the yellow microcrystalline material separated was collected by filtration, washed first with cold methanol and then with dichloromethane and hexane (1:1) mixture and finally dried in air.

2.3.1. $cis-[MoO_2(HL^1)]$ (1)

Yield 81%. Anal. calcd for $C_{12}H_{17}MoNO_5$: C, 41.04; H, 4.88; N, 3.99. Found C, 41.28; H, 4.56; N, 4.12 %. Selected IR data (cm⁻¹): 2947 (v_{C-H} of CH₃), 2837–2668 (v_{C-H} of -CH₂-), 908 and 881 (*cis*-{MoO₂}²⁺). UV-Vis data (λ_{max} (nm) (10⁻³ x ε (M⁻¹ cm⁻¹)): 320sh (4.0), 285sh

(6.7). ¹H NMR (δ (ppm) (*J* (Hz))): 9.03 (s, 1H, Mo-OH), 6.92 (8) (d, 1H, H³), 6.89 (s, 1H, H⁵), 6.56 (8) (d, 1H, H²), 4.77 (15) (d, 1H, H^{7a}), 4.56 (m, 1H, H^{10a}), 4.40 (m, 1H, H^{10b}), 4.00 (15) (d, 1H, H^{7b}), 3.66 (m, 1H, H^{8a}), 3.58 (m, 1H, H^{8b}), 3.26 (m, 1H, H^{11a}), 3.19 (m, 1H, H^{11b}), 2.76 (m, 1H, H^{9a}), 2.55 (m, 1H, H^{9b}), 2.20 (s, 3H, CH₃ of 4-Me). ¹³C NMR (δ (ppm)): 160.50 (1C, C¹), 132.18 (1C, C⁴), 131.30 (1C, C⁶), 131.03 (1C, C²), 124.66 (1C, C⁵), 120.62 (1C, C³), 74.52 (1C, C⁷), 64.16 (1C, C¹⁰), 62.32 (1C, C⁸), 59.47 (1C, C¹¹), 57.83 (1C, C⁹) and 22.75 (1C, 4-Me). $E_{1/2}$ (V) (Δ E_p (mV)): -0.74 (360).

2.3.2. $cis-[MoO_2(HL^2)]$ (2)

Yield 80%. Anal. calcd for C₁₃H₁₉MoNO₅: C, 42.75; H, 5.24; N, 3.83. Found C, 42.68; H, 4.91; N, 3.95 %. Selected IR data (cm⁻¹): 2964 (v_{C-H} of CH₃), 2854–2662 (v_{C-H} of -CH₂-), 914 and 892 (*cis*-{MoO₂}²⁺. UV-Vis data (λ_{max} (nm) (10⁻³ x ε (M⁻¹ cm⁻¹)): 321sh (2.6), 282sh (4.5). ¹H NMR (δ (ppm) (*J* (Hz))): 9.03 (s, 1H, Mo-OH), 6.95 (8) (d, 1H, H³), 6.91 (s, 1H, H⁵), 6.59 (8) (d, 1H, H²), 4.82 (15) (d, 1H, H^{7a}), 4.57 (m, 1H, H^{10a}), 4.40 (m, 1H, H^{10b}), 4.03 (15) (d, 1H, H^{7b}), 3.67 (m, 1H, H^{8a}), 3.58 (m, 1H, H^{8b}), 3.26 (m, 1H, H^{11a}), 3.19 (m, 1H, H^{11b}), 2.77 (m, 1H, H^{9a}), 2.56 (m, 1H, H^{9b}), 2.49 (2H, CH₂ of 4-Et), 1.13 (8) (t, 3H, CH₃ of 4-ethyl). ¹³C NMR (δ (ppm)): 158.47 (1C, C¹), 135.38 (1C, C⁴), 128.73 (1C, C⁶), 127.85 (1C, C²), 122.44 (1C, C⁵), 118.43 (1C, C³), 72.34 (1C, C⁷), 62.04 (1C, C¹⁰), 60.10 (1C, C⁸), 57.22 (1C, C¹¹), 57.65 (1C, C⁹), 27.74 (1C, CH₂ of 4-Et) and 16.28 (1C, CH₃ of 4-Et). *E*_{1/2} (V) (ΔE_p (mV)): -0.77 (440).

2.3.3. $cis-[MoO_2(HL^3)]$ (3)

Yield 83%. Anal. calcd for $C_{15}H_{23}MoNO_5$: C, 45.81; H, 5.89; N, 3.56. Found C, 45.86; H, 5.68; N, 3.51 %. Selected IR data (cm⁻¹): 2958 (v_{C-H} of CH₃), 2859–2670 (v_{C-H} of $-CH_{2}-$), 925 and 886 (*cis*-{MoO₂}²⁺). UV-Vis data (λ_{max} (nm) (10⁻³ x ε (M⁻¹ cm⁻¹)): 320sh (2.7), 275sh (5.0). ¹H NMR (δ (ppm) (*J* (Hz))): 9.05 (s, 1H, Mo-OH), 7.14 (8) (d, 1H, H³), 7.08 (s, 1H, H⁵), 6.60 (8) (d, 1H, H²), 4.80 (15) (d, 1H, H^{7a}), 4.59 (m, 1H, H^{10a}), 4.40 (m, 1H, H^{10b}), 4.07 (15) (d, 1H, H^{7b}), 3.68 (m, 1H, H^{8a}), 3.60 (m, 1H, H^{8b}), 3.27 (m, 1H, H^{11a}), 3.20 (m, 1H, H^{11b}), 2.77 (m, 1H, H^{9a}), 2.55 (m, 1H, H^{9b}), 1.23 (s, 9H, CH₃ of 4-*t*-Bu). ¹³C NMR (δ (ppm)): 158.19 (1C, C¹), 142.37 (1C, C⁴), 126.01 (1C, C⁶), 125.38 (1C, C²), 121.93 (1C, C⁵), 118.11 (1C, C³), 72.40 (1C, C⁷), 62.24 (1C, C¹⁰), 60.01 (1C, C⁸), 57.17 (1C, C¹¹), 55.70 (1C, C⁹), 34.19 (1C, 4-*t*-Bu) and 31.82 (3C, 4-*t*-Bu). E_{pc} (V): -0.96.

2.3.4. $cis-[MoO_2(HL^4)]$ (4)

Yield 85%. Anal. calcd for $C_{19}H_{31}MoNO_5$: C, 50.78; H, 6.95; N, 3.12. Found C, 50.72; H, 6.71; N, 3.32 %. Selected IR data (cm⁻¹): 2953 (v_{C-H} of CH₃), 2848–2660 (v_{C-H} of $-CH_{2}-$), 903 and 881 (*cis*-{MoO₂}²⁺). UV-Vis data (λ_{max} (nm) (10⁻³ x ε (M⁻¹ cm⁻¹)): 332 (3.6), 278sh (5.7). ¹H NMR δ ((ppm) (*J* (Hz))): 8.81 (s, 1H, Mo-OH), 7.12 (s, 1H, H⁵), 6.95 (s, 1H, H³), 4.75 (14) (d, 1H, H^{7a}), 4.54 (m, 1H, H^{10a}), 4.40 (m, 1H, H^{10b}), 4.04 (14) (d, 1H, H^{7b}), 3.65 (m, 1H, H^{8a}), 3.47 (m, 1H, H^{8b}), 3.31 (m, 1H, H^{11a}), 3.17 (m, 1H, H^{11b}), 2.81 (m, 1H, H^{9a}), 2.58 (m, 1H, H^{9b}), 1.31 (s, 9H, CH₃ of 2-*t*-Bu) 1.23 (s, 9H, CH₃ of 4-*t*-Bu). ¹³C NMR (δ (ppm)): 159.42 (1C, C¹), 143.51 (1C, C⁴), 139.34 (1C, C²), 126.34 (1C, C⁶), 124.56 (1C, C⁵), 124.28 (1C, C³), 73.77 (1C, C⁷), 64.91 (1C, C¹⁰), 62.62 (1C, C⁸), 59.59 (1C, C¹¹), 57.62 (1C, C⁹), 36.55 (1C, 2-*t*-Bu), 32.32 (3C, 2-*t*-Bu), 37.42 (1C, 4-*t*-Bu) and 34.12 (3C, 4-*t*-Bu). $E_{1/2}$ (V) (ΔE_p (mV)): -0.71 (830).

2.4. Procedure for oxidative bromination of styrene

A 10 ml round bottom flask containing 4 ml of 1:1 acetonitrile and water mixture was charged with 0.01 mmol of *cis*-[MoO₂(HLⁿ)], 520 μ l (5 mmol) of styrene, 1.2 ml of 30% w/w aqueous solution (10 mmol) of H₂O₂, 1.2 g (10 mmol) of KBr and 1.2 ml of 60% aqueous (10 mmol) HClO₄. The mixture was stirred at 60° C for 4 h and then cooled to room temperature. After cooling it was diluted with 15 ml of water and extracted with dichloromethane (2 x 4 ml). The combined dichloromethane extracts were dried over anhydrous sodium sulphate and then subjected to GC analysis for calculation of yields from the areas under the peaks. The products were identified by GC-MS.

2.5. Procedure for oxidative bromination of salicylaldehyde:

0.01 mmol of the *cis*-[MoO₂(HLⁿ)], 530 μ l (5 mmol) of salicylaldehyde, 1.2 ml of 30% w/w aqueous solution (10 mmol) of H₂O₂, 1.2 g (10 mmol) of KBr and 1.2 ml of 60% aqueous (10 mmol) HClO₄ were added to 4 ml of 1:1 acetonitrile and water mixture in a 10 ml round bottom flask. The mixture was stirred at 60°C for 1 h. After cooling to room temperature the mixture was diluted with 15 ml of water and then extracted with dichloromethane (2 x 4 ml). The dichloromethane extracts were combined, dried over anhydrous sodium sulphate and then subjected to GC-MS analysis for identification of the products and calculation of yields from the areas under the peaks.

2.6. Procedure for benzoin oxidation:

0.01 mmol of the *cis*-[MoO₂(HLⁿ)] and 1.2 ml of 30% w/w aqueous solution (10 mmol) of H_2O_2 were added to 1.07 g (5 mmol) of benzoin taken in 3 ml of methanol. The resulting mixture was stirred at 60° C for 4 h. The reaction progress was monitored with TLC. After completion of the reaction the mixture was diluted with 15 ml of water and then extracted with dichloromethane (2 x 4 ml). After drying over anhydrous sodium sulphate the combined dichloromethane extracts were analyzed by GC-MS to identify the products and calculate the yields from the areas under the peaks.

2.7. X-ray crystallography

Single crystals of 1 and 3 were obtained by recrystallization of the corresponding complexes from hot acetonitrile and that of 2 and 4 were collected from the crystalline materials obtained during their synthesis. The unit cell parameters and the intensity data at 298 K for 1, 3 and 4 were obtained with the help of an Oxford Diffraction Xcalibur Gemini single crystal X-ray diffractometer equipped with a graphite monochromator and a Mo K α fine-focus sealed tube (λ = 0.71073 Å). The CrysAlisPro software [50] was used for data collection, reduction and absorption correction. Some residual absorption effects in the dataset of 4 were treated with XABS2 program [51]. Determination of the unit cell parameters and the collection of the intensity data at 298 K for 2 were performed on a Bruker-Nonius SMART APEX CCD single crystal diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The SMART and the SAINT-Plus [52] programs were used for data acquisition and data extraction, respectively. An empirical absorption correction was applied using the SADABS program [53]. The structure of each of 1-4 was solved by direct method and refined on F^2 by full-matrix leastsquares procedures. All non-hydrogen atoms were refined using anisotropic thermal parameters. All hydrogen atoms were included in the structure factor calculations at idealized positions by using a riding model. The SHELX-97 programs [54] provided in the WinGX package [55] were used for structure solution and refinement. The Platon [56] and the Mercury [57] packages were used for molecular graphics. Selected crystallographic data for 1–4 are listed in Table 1.

3. Results and discussion

3.1. Synthesis and some properties

The tripodal 2,2'-(2-hydroxy-3,5- R_1 , R_2 -benzylazanediyl)diethanols (H₃Lⁿ) (Chart 1) were synthesized in 75–85% yields by Mannich condensation reactions of equimolar amounts of bis(2-hydroxyethyl)amine, corresponding substituted phenols and formaldehyde in methanol under reflux condition. The complexes *cis*-[MoO₂(HLⁿ)] (1–4) were synthesized by reacting the appropriate H₃Lⁿ and [MoO₂(acac)₂] in hot refluxing methanol. All four complexes were isolated as yellow microcrystalline materials in very good yields (80–85%). The elemental analysis data are in good agreement with those calculated for 1–4. Magnetic susceptibility measurements indicate the diamagnetic character of all the complexes. The diamagnetic behaviour is consistent with the +6 oxidation state of the metal centre in each of the four complexes. All the complexes are highly soluble in dimethylformamide and dimethylsulfoxide, moderately soluble in methanol, ethanol, acetonitrile, chloroform and dichloromethane and insoluble in diethylether, hexane and toluene. In solution, each of the four complexes is electrically non-conducting.

3.2. X-ray structural studies

Complexes 1, 2 and 4 crystallize in the monoclinic P_{2_1}/c space group without any lattice solvent molecule, while 3 crystallizes in the triclinic P_1^- space group with acetonitrile molecules (Table 1). Asymmetric unit of each of 1, 2 and 4 contains one complex molecule and that of 3 contains one complex and two acetonitrile molecules. The molecular structures of 1 and 2 are illustrated in Fig. 1 and those for 3 and 4 are provided in Fig. S1 (Supplementary material). The bond lengths and angles related to the metal centres are listed in Table 2. Overall molecular structures of all the complexes are very similar. In each complex, the dianionic tripodal ligand $(HL^n)^{2-}$ coordinates the metal centre through the amine-N, the ethanol-O, the ethanolate-O and the phenolate-O atoms. The intraligand bond parameters are unexceptional. The phenolate-O, the amine-N and the ethanolate-O atoms span meridionally, while the ethanol-O and the two mutually *cis* oxo groups occupy the other meridian and complete a distorted octahedral NO₅ coordination sphere around the metal centre. The Mo(1)–O(3) (2.287(6)–2.292(4) Å) and the Mo(1)–N(1) (2.320(8)–2.364(4) Å) bonds, which are *trans* to the two oxo groups (O(4) and

O(5)), are significantly longer compared to the Mo(1)–O(1) (1.922(6)-1.941(4) Å) and Mo(1)–O(2) (1.958(6)-1.967(3) Å). It is very likely that the *trans* lengthening of the Mo(1)–O(3) facilitates the proton to be on O(3) rather than on the more strongly metal bound O(1) or O(2), where it will be more acidic and hence easily dissociable. There is no effect of the single substituent at *para* to the phenolate-O (O(1)) on the Mo–O(1) bond lengths in 1–3. However, the Mo–O(1) bond length is shorter by ~0.02 Å in 4 compared to the corresponding bond lengths in 1–3 (Table 2). This shortening indicates that the Mo–O(1) bond is relatively stronger in 4 than in 1–3. This is very likely due to the combined positive inductive effect of the two *t*-butyl groups at both *ortho* and *para* positions with respect to the phenolate-O (O(1)) in 4. Overall, the bond lengths and the bond angles associated with the metal centres in all four complexes are within the ranges reported for *cis*-dioxomolybdenum(VI) complexes with ligands bearing similar coordinating atoms [13–23,40,58–66].

Considering the presence of one protonated ethanol arm of $(HL^n)^{2-}$ and several hydrogen bond acceptors in *cis*-[MoO₂(HLⁿ)] (1–4), we have searched for the conventional intermolecular hydrogen bonding interaction and the subsequent self-assembled supramolecular structure for all four complexes. Indeed the metal coordinated ethanol-OH (O(3)–H) participates in a strong O–H···O interaction involving the metal coordinated ethanolate-O (O(2)) of another molecule. The O(3)···O(2) distances vary within the range 2.586(4)–2.606(2) Å, while the O(3)–H···O(2) angles are ~175° for this interaction in 1–4 (Table 3). In the crystal lattice, the molecules of each of the four complexes dimerise via two such reciprocal O(3)–H···O(2) interactions [66]. The dimers of 1 and 2 are represented in Fig. 2 and those of 3 and 4 are shown in Fig. S2 (Supplementary material).

We have also collected the powder X-ray diffraction patterns using the crystalline samples of all the complexes and compared them with the corresponding simulated diffraction patterns generated from the single crystal X-ray diffraction data (Fig. S3, Supplementary material). The satisfactory agreement between the simulated and the experimental diffraction patterns indicates the bulk purity of sample and phase for each of 1, 2 and 4. However, the experimental curve is somewhat different than the simulated curve for $3.2CH_3CN$ (Fig. S3). In

all probability, this difference is due to the loss of some of the lattice acetonitrile molecules during grinding of the sample.

3.3. Spectroscopic properties

Infrared spectra of H_3L^n and the corresponding complexes (1–4) were recorded in KBr pellets. The spectra show a large number of bands of various intensities in the range 4000–400 cm⁻¹. However, except for the following selected few we have not attempted to assign the remaining bands. The spectra of H_3L^n show a strong and broad band around 3350 cm⁻¹ corresponding to its three hydroxyl functionalities. In contrast, the complexes display a very weak broad band centred at ~3420 cm⁻¹. The disappearance of the strong broad band is consistent with deprotonation of two out of three hydroxyl groups of the ligand due to complexation. The weak band at ~3420 cm⁻¹ is perhaps due to the lone hydrogen bonded metal coordinated OH group in the complexes. The bands corresponding to the symmetric and asymmetric stretches of the *cis*-{MoO₂}²⁺ core in 1–4, are observed in the ranges 925–903 and 892–881 cm⁻¹, respectively [13–15,18,21,23,59–66].

The electronic spectra of **1**–**4** were recorded in dimethylsulfoxide solutions. The spectral profiles are very similar. The spectrum of **2** is shown in Fig. 3, while the spectra of the remaining complexes are depicted in Fig. S4. All the complexes display two strong absorptions in the ranges 332-317 and 285-280 nm. Comparable absorptions observed for complexes of *cis*-dioxomolybdenum(VI) with ligands having similar coordinating atoms have been assigned to ligand-to-metal charge transfer and ligand centred transitions, respectively [40,59–66].

¹H-, ¹³C- and ¹³C-DEPT NMR spectroscopic measurements with DMSO-d₆ solutions of **1–4** have been performed. All the spectra are illustrated in Figs. S5–S7 (Supplementary material). The spectral data of all four complexes are consistent with the corresponding molecular structures as established by X-ray crystallography. The ¹H-NMR spectra (Fig. S5) of **1–3** show two doublets in the ranges δ 6.56–6.60 and 6.92–7.14 ppm for the protons at C² and C³, respectively (Chart 1). The singlet observed at δ 7.12 ppm in the spectrum of **4** is assigned to the proton at C³. The C⁵ proton of **1–4** resonates as a singlet within δ 6.89–7.08 ppm. Each signal corresponding to the protons at C³ and C⁵ show a small splitting due to the spatial interaction with protons of the alkyl substituent. The methyl group (at C⁴) protons of **1** are

observed as a singlet at δ 2.19 ppm, while the *t*-butyl group (at C⁴) protons of each of **3** and **4** appear as singlet at δ 1.23 ppm. In the case of **2**, the methyl protons of the ethyl group (at C⁴) resonate as a triplet at δ 1.13 ppm, while the signal corresponding to the methylene protons of the same ethyl substituent coincides with the residual DMSO signal at 2.49 ppm. The tertiary butyl group (at C²) protons of **4** resonate as a singlet at δ 1.31 ppm. A relatively broad signal observed within δ 8.81–9.05 ppm for **1–4** is attributed to the metal coordinated hydroxyl group proton. Because of diastereotopicity, the five methylene group protons of each complex show ten signals in the range δ 2.5–5.0 ppm. The methylene group (*ortho* to the phenolate) protons (at C⁷) show two clear doublets at δ ~4.79 and ~4.04 ppm. The protons at C¹⁰, the methylene group (bonded to N) of the protonated arm of (HLⁿ)^{2–} appear as two multiplets at δ ~4.57 and ~4.40 ppm. On the other hand, the corresponding methylene group (bonded to N) protons at C⁸ of the methylene group (bonded to coordinated OH) protons at C¹¹ show two multiplets at δ ~3.29 and 3.19 ppm. In contrast, the multiplets corresponding to the methylene group (bonded to the ethanolate-O) protons at C⁹ are observed at δ ~2.79 and ~2.57 ppm.

The ¹³C-NMR spectra (Fig. S6) of **1–4** display the resonances corresponding to the aromatic carbons C¹–C⁶ in the ranges δ 158.2–160.5, 125.4–139.3, 118.1–124.4, 132.2–143.5, 121.9–124.7 and 126.0–131.3 ppm, respectively. The methylene carbon (C⁷) attached to the phenolate ring resonates within δ 72.3–74.5 ppm. Two signals observed in the ranges δ 60.0–62.6 and 55.7–57.8 ppm are attributed to the methylene carbon atoms C⁸ and C⁹, respectively of the ethanolate arm of (HLⁿ)^{2–}. Two more signals appeared within δ 62.0–64.9 and 55.7–59.6 ppm are assigned to the methylene carbon atoms C¹⁰ and C¹¹ of the ethanol arm of (HLⁿ)^{2–}. The carbon atom of the methyl substituent in **1** resonates at δ 22.75 ppm, while the primary and the secondary carbon atoms of the ethyl substituent in **2** are observed at δ 16.28 and 27.74 ppm, respectively. The quaternary carbon atom of the *t*-butyl group at *para* position of the phenolate ring appears at δ 34.19 and 37.42 ppm for **3** and **4**, respectively. The primary carbon atoms of the *t*-butyl group at *ortho* position

of the pehenolate ring in 4 are observed at δ 36.55 and 32.32 ppm, respectively. The ¹³C-DEPT NMR spectra (Fig. S7) of 1–4 also substantiates the spectral assignments described above.

3.4. Electron-transfer properties

Electron-transfer properties of 1-4 have been investigated by cyclic voltammetry using their $\sim 10^{-3}$ M solutions in acetonitrile-dimethylformamide (9:1) containing tetrabutylammonium perchlorate as the supporting electrolyte. The measurements were carried out under nitrogen atmosphere at 298 K with the three electrode setup comprised of a Pt-disk working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode. The ferrocenium/ferrocene (Fc⁺/Fc) couple appeared at $E_{1/2} = 0.63$ V under identical condition. The cyclic voltammogram of 2 is illustrated in Fig. 4 and the cyclic voltammograms of 1, 3 and 4 are provided in Fig. S8 (Supplementary material). All the complexes display a quasi-reversible to irreversible reduction response on the cathodic side of the Ag/AgCl reference electrode. The E_{pc} values of this reduction span the range -0.92 to -1.12 V. The reduction is irreversible for 3 while the E_{pa} values for the remaining three complexes (1, 2 and 4) are within -0.29 to -0.56 V. The ratio of peak currents (i_{pc}/i_{pa}) for the quasi-reversible responses varies from 2 to 4. The cathodic peak currents are comparable with that of Fc⁺/Fc couple and other known one electron-transfer processes [63,67]. Similar electron-transfer responses observed for *cis*-dioxomolybdenum(VI) complexes with ligands containing comparable donor atoms have been assigned to $Mo(VI) \rightarrow$ Mo(V) process [14,15,40,63-65].

3.5. Catalytic studies

The catalytic behaviours of **1–4** in oxidative bromination reactions of styrene and salicylaldehyde and in benzoin oxidation reaction have been investigated. Various solvents, different temperatures and catalyst loadings have been screened using **1** as the catalyst for optimization of all the three reaction conditions. In each reaction, irrespective of the types of the products and their selectivities, only complete or nearly complete conversion of the substrate has been considered during the optimization. These optimized reaction conditions have been used for scrutiny of the remaining three complexes (**2–4**) as catalysts (Scheme 1). The details of the yields, selectivity and TOF values are summarized in Table 4. Generally in the present catalytic

studies less number of significant products has been detected when compared with earlier studies on the same reactions in presence of *cis*-dioxomolybdenum(VI) complexes with various tridentate ligands as catalysts [38–40]. However, for all the three reactions the TOF values obtained with 1–4 as catalysts are lower than the corresponding values reported earlier.

3.5.1. Oxidative bromination of styrene

The catalyst *cis*-[MoO₂(HLⁿ)], styrene, H₂O₂, KBr and HClO₄ in the mole ratio of 0.01:5:10:10:10 in acetonitrile-water (1:1) mixture at 60 °C have been found as the best condition for maximum conversion of the substrate in about 4 h. Under this condition, three products 2-bromo-1-phenylethane-1-ol (**a**), 2-bromo-1-phenylethane-1-one (**b**) and styrene oxide (**c**) have been identified (Scheme 1) for each of the four catalysts (**1–4**). The yield of **b** is significantly higher than that of the other two products (**a** and **c**). It is important to note that the formation of **b** has occurred most likely through the oxidation of **a**. The change of the catalyst from **1** to **4** does not affect too significantly the percentage substrate conversion and product salectivity. Under specified condition as mentioned above the control experiment without catalyst has been carried out. The control experiment shows only 10% conversion of the substrate to 2-bromo-1-phenylethane-1-ol (**a**) as the major product. The product selectivities observed here are slightly different than that reported for the bromination reaction of the same substrate catalyzed by *cis*-dioxomolybdenum(VI) complexes [38–40]. In the previous studies, with **a** and **c** formation of 1,2-diol and 1,2-dibromo derivatives instead of **b** have been observed. We could detect a trace amount (< 1%) of the dibromo product but no diol.

3.5.2. Oxidative bromination of salicylaldehyde

The optimized reaction condition for oxidative bromination of salicylaldehyde using *cis*- $[MoO_2(HL^n)]$ as catalyst is same as described above for oxidative bromination of styrene. But here the maximum conversion of the substrate has been realized within 1 h. The catalytic behaviours of **1**–**4** in this reaction are comparable (Table 4). In all the cases, 5-bromosalicylaldehyde (**d**), 3,5-dibromosalicylaldehyde (**e**) and 3-bromosalicylaldehyde (**f**) have been identified as the products (Scheme 1). The 5-bromosalicylaldehyde (**d**) has been produced more selectively than the other two products with essentially complete conversion of the

substrate. In the control experiment without any catalyst, only 30% of substrate conversion with 100% selectivity for 5-bromosalicylaldehyde (\mathbf{d}) has been observed in 4 h of reaction time. In earlier studies on bromination of salicylaldehyde using *cis*-dioxomolybdenum(VI) complexes as catalysts [38,40], \mathbf{d} was the major product as observed here. However, unlike the present observation 2,4,6-tribromo phenol was also reported with \mathbf{e} and \mathbf{f} as a minor product.

3.5.3. Benzoin oxidation

The *cis*-[MoO₂(HLⁿ)] catalyzed benzoin oxidation reactions have been carried out in methanol employing H₂O₂ as the oxidant. The mole ratio of catalyst, substrate and oxidant used for the reaction is 0.01:5:10. It may be noted that comparable results were obtained when acetonitrile or ethanol was used instead of methanol as the reaction solvent. In all the cases, benzoic acid (**g**), benzil (**h**) and α, α -dimethoxytoluene (**i**) have been detected as the products with complete conversion of benzoin (Scheme 1, Table 4). Benzoic acid (**g**) is preferentially formed as the major product followed by benzil (**h**) and then α, α -dimethoxytoluene (**i**). A trace amount (< 1%) of methylbenzoate was also detected. As observed in the preceding two catalytic reactions, here also the catalytic efficiencies of **1**–**4** do not vary in a significant way. Previous studies on benzoin oxidation reactions employing cis-dioxomolybdenum(VI) complexes as catalysts have demonstrated benzoic acid (**g**) to be the major product as found here, but along with (**h**) and (**i**) a comparable amount of methylbenzoate has been also reported as an additional minor product [38,40].

4. Conclusions

The N-capped unsymmetrical tripodal tetradentate 2,2'-(2-hydroxy-3,5- R_1 , R_2 benzylazanediyl)diethanols (H₃Lⁿ) afford complexes of general molecular formula *cis*-[MoO₂(HLⁿ)] (1–4) in very good yields. X-ray crystallographic studies reveal the same gross molecular structure for all the complexes. In each complex, the ligand (HLⁿ)^{2–} acts as 5,5,6membered chelate rings forming NO₃-donor towards the *cis*-{MoO₂}²⁺ unit. In the crystal lattice, the molecules of each complex form discrete dimers via two reciprocal intermolecular O–H···O interactions involving the ethanol-OH and the ethanolate-O both being metal coordinated. The spectroscopic (IR, UV-Vis and NMR) features of 1–4 complement their

molecular structures very well. The redox-active complexes are also catalytically active in oxidative bromination reactions of styrene and salicylaldehyde and in benzoin oxidation reaction. The overall catalytic performances of 1-4 in these reactions are generally invariant to the type and number of substituents on the phenolate moiety of the ligands.

Appendix A. Supplementary material

CCDC 1042110–1042113 contain the supplementary crystallographic data for 1–4, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary materials (synthetic procedure and the characterization data for H_3L^n and Figs. S1–S8) associated with this article can be found in the online version.

Acknowledgements

S. K. Kurapati S. Maloth thank the Council of Scientific and Industrial Research (CSIR), New Delhi for research fellowships. We are grateful to the Department of Science and Technology (DST), New Delhi and the University Grants Commission (UGC), New Delhi for the facilities provided under the FIST and the CAS programs, respectively.

References

- [1] T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329–2363.
- [2] F.E. Kühn, A.M. Santos, M. Abrantes, Chem. Rev. 106 (2006) 2455–2475.
- [3] R. Sanz, M.R. Pedrosa, Curr. Org. Synth. 6 (2009) 239–263.
- [4] M.R. Maddani, K.R. Prabhu, J. Indian Inst. Sci. 90 (2010) 287–297.
- [5] J.A. Brito, B. Royo, M. Gómez, Catal. Sci. Technol. 1 (2011) 1109–1118.
- [6] R.G. de Noronha, A.C. Fernandes, Curr. Org. Chem. 16 (2012) 33–64.
- [7] A. Syamal, M.R. Maurya, Coord. Chem. Rev. 95 (1989) 183–238.
- [8] R. Hille, Chem. Rev. 96 (1996) 2757–2816.
- [9] J.H. Enemark, J.J.A. Cooney, Chem. Rev. 104 (2004) 1175–1200.
- [10] A. Majumdar, S. Sarkar, Coord. Chem. Rev. 255 (2011) 1039–1054.
- [11] M.J. Morris, Coord. Chem. Rev. 172 (1998) 181–245.
- [12] R.D. Chakravarthy, D.K. Chand, J. Chem. Sci. 123 (2011) 187–199.

- [13] C.J. Hinshaw, G. Peng, R. Singh, J.T. Spence, J.H. Enemark, M. Bruck, J. Kristofzski, S.L. Merbs, R.B. Ortega, P.A. Wexler, Inorg. Chem. 28 (1989) 4483–4491.
- [14] Y.-L. Wong, Y. Yan, E.S.H. Chan, Q. Yang, T.C.W. Mak, D.K.P. Ng, J. Chem. Soc., Dalton Trans. (1998) 3057–3064.
- [15] A. Lehtonen, M. Wasberg, R. Sillanpää, Polyhedron 25 (2006) 767–775
- [16] S. Khatua, H. Stoeckli• Evans, T. Harada, R. Kuroda, M. Bhattacharjee, Inorg. Chem. 45 (2006) 9619–9621.
- [17] S. Khatua, T. Harada, R. Kuroda, M. Bhattacharjee, Chem. Commun. (2007) 3927–3929.
- [18] Y.L. Wong, L.H. Tong, J.R. Dilworth, D.K.P. Ng, H. K. Lee, Dalton Trans. 39 (2010) 4602–4611.
- [19] L. H. Tong, Y. L. Wong, H. K. Lee, J. R. Dilworth, Inorg. Chim. Acta. 383 (2012) 91–97.
- [20] F. Madeira, S. Barroso, S. Namorado, P.M. Reis, B. Royo, A.M. Martins, Inorg. Chim. Acta. 383 (2012) 152–156.
- [21] X. Lei, N. Chelamalla, Polyhedron 49 (2013) 244–251.
- [22] A. Riisioe, A. Lehtonen, M.M. Hanninen, R. Sillanpää, Eur. J. Inorg. Chem. (2013) 1499–1508.
- [23] T. Heikkila, R. Sillanpää, A. Lehtonen, J. Coord. Chem. 67 (2014)1863–1872.
- [24] X. Hu, K. Meyer, J. Organomet. Chem. 690 (2005) 5474–5484.
- [25] L.M. Berreau, Eur. J. Inorg. Chem. (2006) 273–283.
- [26] J.G. Verkade, Acc. Chem. Res. 26 (1993) 483-489.
- [27] R.A. Schrock, Acc. Chem. Res. 30 (1997) 9–16.
- [28] A.S. Borovik, Acc. Chem. Res. 38 (2005) 54–61.
- [29] A.G. Blackman, Polyhedron 24 (2005) 1–39.
- [30] M. Palaniandavar, M. Velusamy, R. Mayilmurugan, J. Chem. Sci. 118 (2006) 601–610.
- [31] Yamaguchi, H. Masuda, Sci. Technol. Adv. Mater. 6 (2005) 34–47.
- [32] A.G. Blackman, Eur. J. Inorg. Chem. (2008) 2633–2647.

- [33] B. Kuswandi, Nuriman, W. Verboom, D.N. Reinhoudt, Sensors 6 (2006) 978–1017.
- [34] Z. Dai, J.W. Canary, New J. Chem. 31 (2007) 1708–1718.
- [35] V. Contea, A. Coletti, B. Floris, G. Licini, C. Zonta, Coord. Chem. Rev. 255 (2011) 2165–2177.
- [36] M.R. Maurya, J. Chem. Sci. 123 (2011) 215–228.
- [37] R. Wever, M.A.V. Horst, Dalton Trans. 42 (2013) 11778–11786.
- [38] M.R. Maurya, S. Dhaka, F. Avecilla, Polyhedron 67 (2014) 145–159.
- [39] M.R. Maurya, N. Kumar, F. Avecilla, J. Mol. Catal. A. Chem. 392 (2014) 50-60.
- [40] S. Pasayat, S.P. Dash, S. Roy, R. Dinda, S. Dhaka, M.R. Maurya, W. Kaminsky, Y.P. Patil, M. Nethaji, Polyhedron 67 (2014) 1–10.
- [41] M. Kirihara, Y. Ochiai, S. Takizawa, H. Takahata, H. Nemoto, Chem. Commun. (1999) 1387–1388.
- [42] K.A. Al-Sou'od, B.F. Ali, R. Abu-El-Halawa, A.-A.-H.H. Abu-Nawas, Int. J. Chem. Kinet. 37 (2005) 444–449.
- [43] C. Joo, S. Kang, S.M. Kim, H.Han, J.W. Yang, Tetrahedron Lett. 51 (2010) 6006– 6007.
- [44] N. Ueyama, N. Yoshinaga, A. Nakamura, J. Chem. Soc. Dalton. Trans. (1990) 387– 394.
- [45] R.K. Bhatia, G.N. Rao, J. Mol. Catal. A. Chem. 121 (1997) 171–178.
- [46] G.J.J. Chen, J.W. McDonald, W.E. Newton, Inorg. Chem. 15 (1976) 2612–2615.
- [47] P.-P. Yang, H.-B. Song, X.-F. Gao, L.-C. Li, D.-Z. Liao, Cryst. Grow. Des. 9 (2009) 4064–4069.
- [48] A. Joohuan, M. Yanyan, R. Chris, C. Rodolphe, B. Colette, Aust. J. Chem. 62 (2009) 1124–1129.
- [49] D.D. Perrin, W.L.F. Armarego, D.P. Perrin, Purification of Laboratory Chemicals, 2nd ed., Pergamon, Oxford, 1983.
- [50] CrysAlisPro version 1.171.36, Agilent Technologies, Yarnton, Oxfordshire, UK, 2013.
- [51] S. Parkin, B. Moezzi, H. Hope, J. Appl. Cryst. 28 (1995) 53-56.

- [52] SMART version 5.630 and SAINT• plus version 6.45, Bruker• Nonius Analytical X• ray Systems Inc., Madison, WI, USA, 2003.
- [53] G.M. Sheldrick, SADABS, Program for Area Detector Absorption Correction, University of Göttingen, Göttingen, Germany, 1997.
- [54] G.M. Sheldrick, Acta Crystallogr., Sect. A, 64 (2008) 112–122.
- [55] L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849• 854.
- [56] A.L. Spek, Platon, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2002.
- [57] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, J. Appl. Cryst. 41 (2008) 466• 470.
- [58] S.K. Kurapati, Acta Crystallogr. Sect. E 69 (2013) m460–m461.
- [59] A. Lymberopoulou-Karaliota, D. Hatzipanayioti, M. Kamariotaki, M. Potamianou,
 C. Litos, V. Aletras, Inorg. Chim. Acta 358 (2005) 2975–2995.
- [60] Y. Zhu, W. Yan, Y. Zhang, J. Coord. Chem. 64 (2011) 1104–1112.
- [61] S.K. Kurapati, U. Ugandhar, S. Maloth, S. Pal, Polyhedron 42 (2012) 161–167.
- [62] X. Lei, N. Chelamalla, Polyhedron 49 (2013) 244-251.
- [63] S.K. Kurapati, S. Pal, Dalton Trans. 44 (2015) 2401–2408.
- [64] S. Gupta, S. Pal, A.K. Barik, S. Roy, A. Hazra, T.N. Mandal, R.J. Butcher, S.K. Kar, Polyhedron 28 (2009) 711–720.
- [65] N.K. Ngan, K.M. Lo, C.S.R. Wong, Polyhedron 30 (2011) 2922–2932.
- [66] M. Bagherzadeh, M.M. Haghdoost, A. Ghanbarpour, M. Amini, H.R. Khavasi, E. Payab,A. Ellern, L.K. Woo, Inorg. Chim. Acta 411 (2014) 61–66.
- [67] S. Pal, R.N. Mukherjee, M. Tomas, L.R. Falvello, A. Chakravorty, Inorg. Chem. 25 (1986) 200–207.

Table 1

Selected crystal data and structure refinement summary

Complex	1	2	3·2CH ₃ CN	4
Chemical formula	C ₁₂ H ₁₇ MoNO ₅	C13H19MoNO5	$C_{19}H_{29}MoN_3O_5$	C ₁₉ H ₃₁ MoNO ₅
Formula weight	351.21	365.23	475.39	449.39
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c	Pī	<i>P</i> 2 ₁ /c
<i>a</i> (Å)	6.582(4)	13.9819(9)	7.0365(5)	22.232(3)
<i>b</i> (Å)	32.2225(12)	6.9127(4)	11.8658(8)	7.3594(14)
<i>c</i> (Å)	7.0812(9)	15.0916(10)	14.0224(10)	12.894(2)
α(°)	90	90	70.158(6)	90
β(°)	119.653(6)	94.6510(10)	77.337(6)	90.071(17)
γ(°)	90	90	86.791(5)	90
$V(\text{\AA}^3)$	1340.09(19)	1453.84(16)	1074.27(13)	2109.6(6)
Ζ	4	4	2	4
ho (g cm ⁻³)	1.741	1.669	1.47	1.415
$\mu (\mathrm{mm}^{-1})$	0.994	0.920	0.644	0.648
Reflections collected	4886	13382	6862	5203
Reflections unique	2349	2567	3780	3251
Reflections $[I \ge 2\sigma(I)]$	2217	2342	3134	2121
Parameters	172	182	255	241
<i>R</i> 1, <i>wR</i> 2 [$I \ge 2\sigma(I)$]	0.0613, 0.1064	0.0242, 0.0650	0.0504, 0.1171	0.0832, 0.1585
R1, $wR2$ [all data]	0.0663, 0.1081	0.0269, 0.0663	0.0640, 0.1281	0.1263, 0.1778
GOF on F^2	1.449	1.083	1.042	1.056
Largest diff. peak / hole (e $Å^{-3}$)	0.663 / -1.107	0.360 / -0.313	0.913 / -0.886	1.662 / -1.174
		18		

Complex	1	2	3.2CH ₃ CN	4
Mo-O(1)	1.941(4)	1.9406(17)	1.941(3)	1.922(6)
Мо-О(2)	1.960(4)	1.9639(16)	1.967(3)	1.958(6)
Мо-О(3)	2.292(4)	2.2932(17)	2.288(3)	2.287(6)
Mo-O(4)	1.693(4)	1.6938(18)	1.693(3)	1.686(6)
Mo-O(5)	1.704(5)	1.7009(17)	1.698(4)	1.724(6)
Mo-N(1)	2.361(5)	2.3422(18)	2.364(4)	2.320(8)
O(1)-Mo-O(2)	153.01(19)	153.26(7)	152.45(15)	152.8(3)
O(1)-Mo-O(3)	80.29(17)	80.66(7)	80.20(11)	80.6(2)
O(1)-Mo-O(4)	94.5(2)	94.05(9)	94.94(14)	96.0(3)
O(1)-Mo-O(5)	103.3(2)	104.07(9)	104.35(14)	104.1(3)
O(1)-Mo-N(1)	78.69(18)	78.73(6)	78.45(12)	78.6(3)
O(2)-Mo-O(3)	84.94(16)	85.69(7)	85.39(11)	85.1(3)
O(2)-Mo-O(4)	95.1(2)	95.03(9)	94.58(14)	93.7(3)
O(2)-Mo-O(5)	87.4(2)	96.82(8)	97.11(15)	96.9(3)
O(2)-Mo-N(1)	75.24(2)	75.17(6)	74.77(13)	75.0(3)
O(3)-Mo-O(4)	167.1(2)	168.51(8)	168.35(16)	169.1(3)
O(3)-Mo-O(5)	84.12(19)	82.89(8)	83.45(14)	83.1(3)
O(3)-Mo-N(1)	71.55(17)	71.53(6)	71.69(12)	71.4(2)
O(4)-Mo-O(5)	108.6(2)	108.36(9)	108.08(18)	107.8(3)
O(4)-Mo-N(1)	96.0(2)	97.53(8)	97.02(15)	97.8(3)
O(5)-Mo-N(1)	155.0(2)	153.57(8)	154.26(14)	153.7(3)

Table 2

Selected bond lengths (Å) and angles (°) for 1, 2, 3.2CH₃CN and 4

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Complex	D–H···A	H···A (Å)	$D \cdots A$ (Å)	$D-H\cdots A$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	$O(3)-H(3A)\cdots O(2)^{i}$	1.77	2.586(6)	175
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3 $O(3)$ -H(3A)···O(2) ⁱⁱⁱ 1.77 2.586(4) 174 4 $O(3)$ -H(3A)···O(2) ^{iv} 1.78 2.594(9) 176 Symmetry transformations used: (i) -x + 2, -y, -z + 2; (ii) -x, -y + 2, -z + 2; (iii) -x, -y + 2, -z + 1; (iv) -x + 1, -y, -z + 1.	3 $O(3)$ -H(3A)···O(2) ⁱⁱ 1.77 2.586(4) 174 4 $O(3)$ -H(3A)···O(2) ^{iv} 1.78 2.594(9) 176 Symmetry transformations used: (i) -x + 2, -y, -z + 2; (ii) -x, -y + 2, -z + 1; (iv) -x + 1, -y, -z + 1.	2	$O(3)-H(3A)\cdots O(2)^{ii}$	1.79	2.606(2)	174
$\frac{4}{(i) - H(3A) \cdots O(2)^{iv}} 1.78 2.594(9) 176}$ Symmetry transformations used: (i) - x + 2, -y, -z + 2; (ii) - x, -y + 2, -z + 2; (iii) - x, -y + 2, -z + 1; (iv) - x + 1, -y, -z + 1.	4 $O(3)-H(3A)\cdots O(2)^{iv}$ 1.78 2.594(9) 176 Symmetry transformations used: (i) $-x + 2, -y, -z + 2$; (ii) $-x, -y + 2, -z + 2$; (iii) $-x, -y + 2, -z + 1$; (iv) $-x + 1, -y, -z + 1$.	$\frac{4}{(i) - x + 2, -y, -z + 2; (ii) - x, -y + 2, -z + 2; (iii) - x, -y + 2, -z + 1; (iv) - x + 1, -y, -z + 1.}$	3	$O(3)-H(3A)\cdots O(2)^{iii}$	1.77	2.586(4)	174
Symmetry transformations used: (i) -x + 2, -y, -z + 2; (ii) -x, -y + 2, -z + 2; (iii) -x, -y + 2, -z + 1; (iv) -x + 1, -y, -z + 1.	Symmetry transformations used: (i) -x + 2, -y, -z + 2; (ii) -x, -y + 2, -z + 2; (iii) -x, -y + 2, -z + 1; (iv) -x + 1, -y, -z + 1.	Symmetry transformations used: (i) -x + 2, -y, -z + 2; (ii) -x, -y + 2, -z + 2; (iii) -x, -y + 2, -z + 1; (iv) -x + 1, -y, -z + 1.	4	$O(3)-H(3A)\cdots O(2)^{iv}$	1.78	2.594(9)	176
(i) -x + 2, -y, -z + 2; (ii) -x, -y + 2, -z + 2; (iii) -x, -y + 2, -z + 1; (iv) -x + 1, -y, -z + 1.	(i) -x + 2, -y, -z + 2; (ii) -x, -y + 2, -z + 2; (iii) -x, -y + 2, -z + 1; (iv) -x + 1, -y, -z + 1.	(i) -x + 2, -y, -z + 2; (ii) -x, -y + 2, -z + 2; (iii) -x, -y + 2, -z + 1; (iv) -x + 1, -y, -z + 1.	Symmetry tra	nsformations used:			
					NA		

Tabel 3

Hydrogen bonding parameters

Table 4

Catalysis data

Reaction and catalyst	Conversion	TOF	Produ	ict select	ivity
	(%)	(h^{-1})		(%)	
Bromination of styrene			(a)	(b)	(c)
1	99	124	15	73	11
2	98	123	23	68	7
3	96	120	10	73	11
4	95	119	15	68	10
Bromination of salicyladehyd	le		(d)	(e)	(f)
1	99.5	497	74	19	7
2	99.8	499	70	26	4
3	99.6	498	67	28	5
4	99.7	499	62	34	4
Benzoin oxidation			(g)	(h)	(i)
1	99.9	125	59	29	12
2	99.9	125	57	28	15
3	99.9	125	53	30	17
4	99.9	125	60	33	7

Figure Captions

Chart 1. Tripodal 2,2'-(2-hydroxy-3,5- R_1 , R_2 -benzylazanediyl)diethanols (H₃Lⁿ) and the corresponding complexes *cis*-[MoO₂(HLⁿ)].

Fig. 1. X-ray molecular structures of cis-[MoO₂(HL¹)] (1) (top) and cis-[MoO₂(HL²)] (2) (bottom). For both structures all non-hydrogen atoms are shown in their 30% probability thermal ellipsoids.

Fig. 2. Hydrogen-bonded dimers of cis-[MoO₂(HL¹)] (1) (top) and cis-[MoO₂(HL²)] (2) (bottom).

Fig. 3. Electronic spectrum of cis-[MoO₂(HL²)] (2) in (CH₃)₂SO.

Fig. 4. Cyclic voltammogram (scan rate of 100 mVs⁻¹) of *cis*-[MoO₂(HL²)] (**2**) in CH₃CN-(CH₃)₂NC(O)H (9:1) employing the experimental condition described in the text.

Scheme 1. Substrates and the products obtained using cis-[MoO₂(HL¹⁻⁴)] (1–4) as catalysts.



 $H_{3}L^{n}$ (n = 1–4) n = 1 for R_{1} = H and R_{2} = Me n = 2 for R_{1} = H, R_{2} = Et n = 3 for R_{1} = H and R_{2} = ^tBu n = 4 for R_{1} = ^tBu and R_{2} = ^tBu



cis-[MoO₂(HLⁿ)] **1** (n = 1), **2** (n = 2), **3** (n = 3) and **4** (n = 4)

Chart 1











Graphical Abstract: Pictogram



Graphical Abstract: Synopsis

Four new complexes of cis-{MoO₂}²⁺ with tripodal NO₃-donor 2,2'-(2-hydroxy-3,5- R_1 , R_2 -benzylazanediyl)diethanols (H₃Lⁿ) are reported. Molecular structures of the diamagnetic and redox active complexes of general formula cis-[MoO₂(HLⁿ)] are established by spectroscopic and X-ray crystallographic measurements. The catalytic activities of all the complexes in some organic oxidation reactions are described.

Highlights

• Complexes of cis-{MoO₂}²⁺ complexes with unsymmetrical tripodal NO₃-donor ligands were synthesized.

- The solid state structures of all the complexes were determined by X-ray crystallography.
- Spectroscopic and electron transfer characteristics of the complexes were scrutinized.
- The catalytic activities of the complexes in some organic oxidation reactions were assessed.