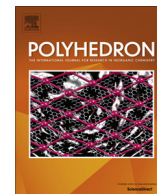




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Complexes of *cis*-dioxomolybdenum(VI) with a chiral tetradentate tripodal-like ligand system: Syntheses, structures and catalytic activities

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ABSTRACT

Racemic complexes with the general formula *cis*-[MoO₂(bzacLⁿ)] (**1–4**) (H₂bzacLⁿ = 2-((4/5-R-2-hydroxyphenylamino)(pyridin-2-yl)methyl)-1-phenylbutane-1,3-dione, where *n* = 1–4 for R = H, 5-Me, 5-Cl and 4-Me, respectively and 2Hs represent the dissociable phenolic proton and the active tertiary CH proton) have been synthesized in 75–82% yields by reacting [MoO₂(bzac)₂] (Hbzac = benzoylacetone) with the potentially N₂O-donor 5,5-membered fused chelate rings forming Schiff bases 4/5-R-2-(2-pyridylaldimine)phenols (HLⁿ; *n* = 1–4 for R = H, 4-Me, 4-Cl and 5-Me, respectively) in hot methanol. The chiral ligand system (bzacLⁿ)^{2–} in **1–4** is formed via metal assisted Mannich-type addition of benzoylacetone methine to the azomethine fragment of HLⁿ. All four complexes have been characterized by elemental (CHN) analysis, solution conductivity, magnetic susceptibility, spectroscopic (IR, UV–Vis and NMR) and electrochemical measurements. The molecular structures of **1–3** have been established by single crystal X-ray crystallography. In each complex, the chiral (bzacLⁿ)^{2–} acts as a tetradentate, N₂O₂-donor, tripodal-like ligand system and along with the two mutually *cis* oxo groups forms a distorted octahedral N₂O₄ coordination environment around the molybdenum(VI) center. All four complexes are diamagnetic and non-electrolytic. The infrared spectra are generally consistent with the structural formulas of **1–4**. The electronic spectra of **1–4** in dimethylformamide display two strong absorption bands in the range 245–300 nm. The cyclic voltammograms of **1–4** in dimethylformamide exhibit a metal centered one-electron reduction response within –0.64 to –0.74 V. All these complexes (**1–4**) and the analogous *cis*-[MoO₂(acacL^{1–4})] (**5–8**) synthesized from [MoO₂(acac)₂] (Hacac = acetylacetone) and HL^{1–4} have been evaluated for their bromoperoxidase activities.

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1. Introduction

The growing interest in the coordination complexes of *cis*-dioxomolybdenum(VI) is primarily due to their potential abilities to act as catalysts in various organic oxidation reactions [1–7] and as structural and functional models of a number of molybdenum containing enzymes [8–12]. Consequently, there are continuous efforts in synthesizing new *cis*-dioxomolybdenum(VI) complexes which will perform as better catalysts or will serve as better enzyme models. The general approach for realizing such complexes is to modify the denticity as well as the electronic and the steric characteristics of the ligands being used. Tridentate meridionally spanning Schiff bases are very attractive due to the following reasons: they are easy to prepare, their electronic and steric characteristics can be readily tuned by varying the substituents on the amine or on the carbonyl or on both and the availability of the sixth coordi-

nation site *trans* to one of the two strong *trans*-labilizing oxo groups for a monodentate ligand in their complexes. During the past few years, we have been working on *cis*-dioxomolybdenum(VI) complexes with some tri- and tetradentate ligands and their applications as catalysts in oxidative bromination and benzoin and sulfide oxidation reactions [13–16]. Recently in our attempts to prepare complexes of *cis*-dioxomolybdenum(VI) with a potentially meridional N₂O-donor 5,5-membered fused chelate rings forming Schiff base system (HLⁿ) derived by condensing 2-pyridylaldehyde with 2-aminoethanol and/or 2-amino-4/5-R-phenol using [MoO₂(acac)₂] (acac[–] = acetylacetonate) as the starting material, we have encountered a metal assisted ligand transformation reaction and isolated a series of racemic complexes of formula *cis*-[MoO₂(acacLⁿ)], where (acacLⁿ)^{2–} represents the transformed ligand system [15]. The N₂O₂-donor chiral tripodal-like (acacLⁿ)^{2–} is the product of the Mannich-type addition of the methine group (=CH–) of acac[–] to the azomethine group (–CH=N–) of HLⁿ. Very recently the same ligand transformation reaction assisted by *cis*-dioxomolybdenum(VI) and the racemic complexes with the

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transformed ligands which are analogous to $(\text{acacl}^n)^{2-}$ have been reported by another research group [17]. In the present work, we have examined the generality of this ligand transformation reaction using $[\text{MoO}_2(\text{bzac})_2]$ ($\text{bzac}^- = \text{benzoylacetate}$) and 4/5-R-2-(2-pyridylaldimine)phenols (HL^n ; $n = 1-4$ for R = H, 4-Me, 4-Cl and 5-Me, respectively). Here also the Mannich-type reaction involving bzac^- and HL^n occurs and a series of analogous racemic complexes with the formula $\text{cis}-[\text{MoO}_2(\text{bzacL}^n)]$ (**1-4**) is formed (Scheme 1). The identities of these complexes have been established by various physical measurements and X-ray crystallography. In addition, the catalytic abilities of **1-4** as well as those of our previously reported $\text{cis}-[\text{MoO}_2(\text{acacl}^n)]$ (**5-8**) [15] in oxidative bromination of various organic substrates have been also investigated. In the following account, we have described the syntheses, structures and physical properties of **1-4** and the bromoperoxidase activities of **1-8**.

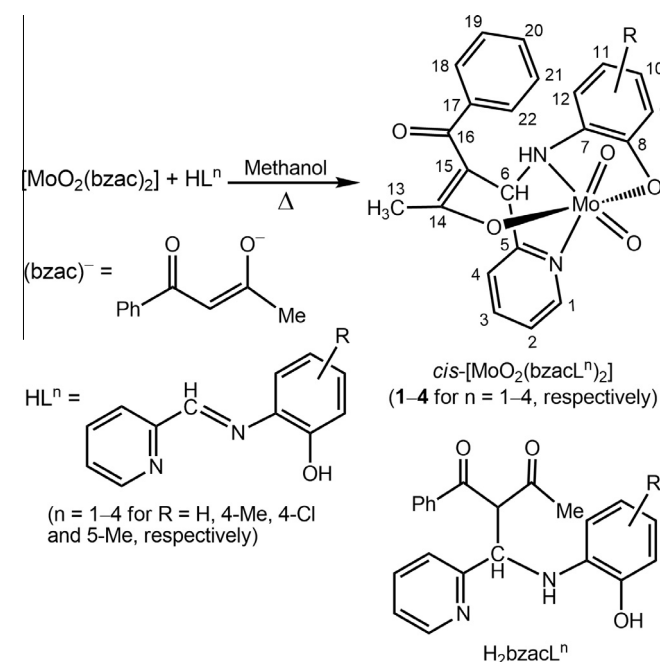
2. Experimental

2.1. Materials

Bis(benzoylacetato)dioxomolybdenum(VI), $[\text{MoO}_2(\text{bzac})_2]$, was prepared using a literature method [18]. The Schiff bases (HL^n) were prepared from equimolar amounts of 2-pyridylaldehyde and the corresponding amino phenols according to literature procedures [19,20]. All other chemicals and solvents used in this work were of analytical grade and were used as supplied without further purification.

2.2. Physical measurements

Elemental (CHN) analysis data were obtained with the help of a Thermo Finnigan Flash EA1112 series elemental analyzer. A Shimadzu LCMS 2010 liquid chromatograph mass spectrometer was used for the purity verification of the Schiff bases. Solid state magnetic susceptibility measurements were performed with a Sherwood Scientific balance. A Digisun DI-909 conductivity meter



Scheme 1. Synthesis of $\text{cis}-[\text{MoO}_2(\text{bzacL}^n)]$ and molecular diagrams of 4/5-R-2-(2-pyridylaldimine)phenol (HL^n), benzoylacetate (bzac^-), 2-((4/5-R-2-hydroxyphenylamino)-(pyridin-2-yl)methyl)-1-phenylbutane-1,3-dione (H_2bzacL^n) and $\text{cis}-[\text{MoO}_2(\text{bzacL}^n)]$.

was used to measure the solution electrical conductivities. The infrared spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrophotometer. A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used to collect the electronic spectra. The ^1H (400 MHz) and the ^{13}C (100 MHz) NMR spectra were recorded with the help of a Bruker NMR spectrometer. Cyclic voltammograms were collected on a CH Instruments model 620A electrochemical analyzer.

2.3. Syntheses of $[\text{MoO}_2(\text{bzacL}^n)]$ (**1-4**)

A general procedure was used for the syntheses of all four complexes. The details are as follows: solid $[\text{MoO}_2(\text{bzac})_2]$ (0.2 mmol) was added to a solution of the corresponding Schiff base HL^n (0.2 mmol) in 30 ml of methanol and the resulting mixture was heated on a steam bath for 45 min. After cooling to room temperature the reaction mixture was filtered to remove any solid present. The filtrate was allowed to evaporate slowly at room temperature till the volume reduces to about 2–3 ml. The complex separated as a yellow to light brown crystalline material was collected by filtration, washed with ice-cold methanol and dichloromethane and finally dried in air. The yield was in the range of 75–82%.

2.3.1. $\text{cis}-[\text{MoO}_2(\text{bzacL}^1)]$ (**1**)

Yield 78%. Anal. Calc. for $\text{C}_{22}\text{H}_{18}\text{MoN}_2\text{O}_5$ (486.32): C, 54.33; H, 3.73; N, 5.76. Found C, 54.23; H, 3.79; N, 5.68. Selected IR bands (cm^{-1}): 3129 (N–H), 1616 (C=O), 926 and 882 ($\text{cis}-\text{MoO}_2$). UV-Vis data (λ_{max} (nm) (ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$))): 246 (12.6) and 289 (8.9). ^1H NMR data (δ (ppm) (J (Hz))): 8.90 (4) (d, 1H, H^1), 8.89 (s, 1H, NH), 7.98 (8, 8) (dd, 1H, H^3), 7.82 (8) (d, 1H, H^4), 7.62–7.54 (m, 3H, H^2 , H^{18} , H^{22}), 7.47–7.39 (m, 3H, H^{19-21}), 7.23 (8) (d, 1H, H^{12}), 7.09 (8, 8) (dd, 1H, H^{10}), 6.87 (8, 8) (dd, 1H, H^{11}), 6.66 (8) (d, 1H, H^9), 5.55 (s, 1H, H^6), 2.09 (s, 3H, Hs on C^{13}). ^{13}C NMR data (δ (ppm)): 207.0 (C^{16}), 195.9 (C^{14}), 172.0 (C^8), 161.9 (C^5), 157.3 (C^3), 148.7 (C^1), 141.6 (C^{17}), 141.2 (C^{20}), 133.2 (C^{10}), 132.4 (C^7), 129.7 (C^4), 129.1 (C^{19}), 128.9 (C^{21}), 126.3 (C^{18}), 125.6 (C^{22}), 122.6 (C^2), 121.2 (C^{11}), 117.4 (C^{12}), 114.4 (C^9), 65.1 (C^{15}), 31.2 (C^6), 24.0 (C^{13}). $E_{1/2}$ (V) (ΔE_p (mV)): -0.69 (320).

2.3.2. $\text{cis}-[\text{MoO}_2(\text{bzacL}^2)]$ (**2**)

Yield 80%. Anal. Calc. for $\text{C}_{23}\text{H}_{20}\text{MoN}_2\text{O}_5$ (500.35): C, 55.21; H, 4.03; N, 5.60. Found C, 55.17; H, 4.12; N, 5.56. Selected IR bands (cm^{-1}): 3114 (N–H), 1622 (C=O), 931 and 896 ($\text{cis}-\text{MoO}_2$). UV-Vis data (λ_{max} (nm) (ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$))): 251 (15.1) and 289 (11.1). ^1H NMR data (δ (ppm) (J (Hz))): 8.88 (4) (d, 1H, H^1), 8.77 (s, 1H, NH), 7.96 (6, 6) (dd, 1H, H^3), 7.80 (6) (d, 1H, H^4), 7.60 (6, 6) (dd, 1H, H^2), 7.58–7.39 (m, 5H, H^{18-22}), 7.20 (s, 1H, H^{12}), 6.88 (4) (d, 1H, H^{10}), 6.53 (8) (d, 1H, H^9), 5.54 (s, 1H, H^6), 3.15 (s, 3H, 5-Me), 2.17 (s, 3H, Hs on C^{13}). ^{13}C NMR data (δ (ppm)): 207.0 (C^{16}), 196.0 (C^{14}), 172.0 (C^8), 159.7 (C^5), 157.4 (C^3), 148.6 (C^1), 141.6 (C^{17}), 141.3 (C^{20}), 132.9 (C^{11}), 132.4 (C^{12}), 130.4 (C^{10}), 130.2 (C^7), 129.1 (C^{19}), 128.9 (C^{21}), 126.3 (C^{18}), 125.5 (C^{22}), 122.7 (C^4), 116.9 (C^2), 114.5 (C^9), 65.0 (C^{15}), 31.2 (C^6), 24.0 (5-Me), 20.5 (C^{13}). $E_{1/2}$ (V) (ΔE_p (mV)): -0.68 (350).

2.3.3. $\text{cis}-[\text{MoO}_2(\text{bzacL}^3)]$ (**3**)

Yield 75%. Anal. Calc. for $\text{C}_{22}\text{H}_{17}\text{ClMoN}_2\text{O}_5$ (520.77): C, 50.74; H, 3.29; N, 5.38. Found C, 50.65; H, 3.24; N, 5.31. Selected IR bands (cm^{-1}): 3100 (N–H), 1625 (C=O), 935 and 890 ($\text{cis}-\text{MoO}_2$). UV-Vis data (λ_{max} (nm) (ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$))): 245 (21.5) and 295 (15.4). ^1H NMR data (δ (ppm) (J (Hz))): 8.95 (s, 1H, NH), 8.89 (4) (d, 1H, H^1), 8.01 (8, 8) (dd, 1H, H^3), 7.83 (8) (d, 1H, H^4), 7.63–7.43 (m, 6H, H^2 , H^{18-22}), 7.24 (s, H^{12}), 7.14 (8) (d, 1H, H^{10}), 6.69 (8) (d, 1H, H^9), 5.61 (s, 1H, H^6), 2.08 (s, 3H, Hs on C^{13}). ^{13}C NMR data (δ (ppm)): 207.0 (C^{16}), 196.0 (C^{14}), 171.0 (C^8), 161.0 (C^5), 157.1 (C^3), 148.7

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