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Complexes of *cis*-dioxomolybdenum(VI) and oxovanadium(IV) with a tridentate ONS donor ligand: Synthesis, spectroscopic properties, X-ray crystal structure and catalytic activity

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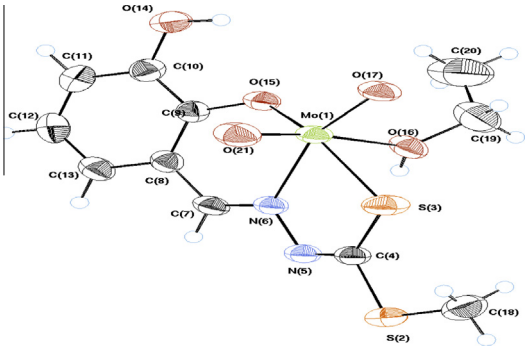
HIGHLIGHTS

- Synthesis of new *cis*-dioxomolybdenum(VI) and oxovanadium(IV) complexes with a tridentate ONS-donor ligand.
- Spectral and electrochemical characterization of the synthesized compounds.
- X-ray crystal structure for one of the complexes as a typical example.
- Reactivity of some complexes as catalytic oxidants for alcohols.

GRAPHICAL ABSTRACT

Cis-dioxomolybdenum(VI) and oxovanadium(VI) complexes with the Schiff base ligand, H_2dhsm have been prepared and characterized by spectroscopic and electrochemical studies. The X-ray structure of *cis*-[MoO_2(dhsm)(EtOH)] (shown below) indicates that the $(dhsm)^{2-}$ behaves as a dianionic ONS tridentate ligand. Some of the complexes act as catalysts toward alcohol oxidations in the presence of H_2O_2 or t-BuOOH.



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ABSTRACT

New *cis*-dioxomolybdenum(VI) and oxovanadium(IV) complexes of the Schiff base, derived from S-methyl dithiocarbazate and 2,3-dihydroxybenzaldehyde (H_2dhsm), have been synthesized. The complexes of the type *cis*-[MoO_2(dhsm)] (**1a**), *cis*-[MoO_2(dhsm)(D)] (**1b–1d**) [D = neutral monodentate ligand; EtOH, pyridine (py) or imidazole (imz)], [VO(dhsm)(N—N)] (**2a, 2b**) [N—N = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)] and [VO(dhsm)] (**2c**) have been isolated, characterized by ^{1}H NMR, IR, UV–Vis and EPR spectral studies and investigated by cyclic voltammetry. The X-ray crystal structure of *cis*-[MoO_2(dhsm)(EtOH)] (**1b**) has been determined and shows that the complex has a distorted octahedral geometry in which the H_2dhsm behaves as a dianionic ONS tridentate ligand coordinating *via* phenoxide oxygen, hydrazinic nitrogen and thiolate sulfur. The oxomolybdenum(IV) complex [MoO(dhsm)] (**1e**) has obtained from dioxomolybdenum(VI) complex (**1b**) by oxo abstraction with PPh_3. The reactivity of the complexes toward catalytic oxidation of alcohols in the presence of H_2O_2 and t-BuOOH as co-oxidants under solvent free conditions is reported.

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Introduction

The transition metal complexes of S-methyl- and S-benzyl dithiocarbazate Schiff bases derived from *o*-hydroxy aldehydes and ketones have been widely studied [1–5]. Interest in metal complexes of these ligands is simulated by their interesting physico-chemical properties and significant biological activities [6,7]. EXAFS spectroscopic studies have implicated the presence of a sulfur atom, besides oxygen and nitrogen, at the active sites of oxo transfer molybdoenzymes whose catalytic reactions are known to involve oxidation states Mo(VI) and Mo(IV) [8,9]. Thus, mixed hard-soft donor sets in ONS tridentate ligands and their related complexes of high valent oxo moieties is of current interest as model systems for the active sites of molybdoenzymes such as xanthine oxidase and sulfite oxidase [3,10,11]. Vanadium complexes having sulfur functionality have been found to be orally active insulin-mimetic agent in the treatment of diabetic model animals [12,13]. Dioxo- and oxovanadium(V) complexes of ONS donor ligands derived from S-benzyl/S-methyl dithiocarbazate with pyridoxal have been found more effective than metronidazole, a commonly used drug against amoebiasis [2].

As a continuation of our research on tridentate ligands containing sulfur atom with different transition metals [14–16], we describe herein the preparation, spectroscopic characterization and redox properties of Mo(VI), Mo(IV) and V(IV) complexes of 2,3-dihydroxybenzaldhyde Schiff base of S-methyldithiocarbazate (H_2dhsm). We also report the X-ray crystal structure of the complex [MoO_2(dhsm)(EtOH)] which exhibits oxo transfer to PPh_3 in acetonitrile medium leading to the formation of [$Mo^{IV}O$(dhsm)]. The catalytic activity of these complexes toward oxidation of alcohols in the presence of t-BuOOH and H_2O_2 as co-oxidants in comparison with the previous work on catalytic oxidants by dioxomolybdenum(VI) [17] and oxovanadium(IV) complexes [14,18] has been studied.

Experimental

Analytical and physical measurements

IR spectra were measured on a JASCO 4100 FTIR spectrometer (4000–400 cm^{-1}) as KBr disks. ^{1}H NMR spectra were measured on a Varian Gemini WM-200 spectrometer (Laser Centre, Cairo University). Electronic spectra in CH_2Cl_2 were recorded using a Perkin–Elmer Lambda 2S spectrophotometer. ESR spectra were recorded with a Bruker EMX spectrometer (Radiation Technology Centre, Cairo). Cyclic voltammetric studies were carried out on an electroanalyzer CHI 610A, the three electrode cell comprised a reference Ag wire, Pt auxiliary, and working electrodes, solutions of the complexes (10^{-3} M) in 0.1 M (n-Bu_4N)PF_6 as supporting electrolyte were used. Magnetic measurements were taken on a Johnson Matthey magnetic susceptibility balance.

X-ray crystallography

Orange triclinic crystals of [MoO_2(dhsm)(EtOH)] **(1b)** having appropriate dimensions were measured on Bruker Kappa CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), the unit cell dimensions and intensity data were measured at 298 K. The structure was solved by least square fit of the angular setting of strong reflection based on F^2. Program used to solve structure was SIR92 [19], while the program used to refine structure was maXus [20]. Integration and scaling of the reflections were performed with the HKL Denzo-scale pack system of programs [21]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data for the complex **(1b)** are summarized in Table 1.

Synthesis of the ligand (H_2dhsm)

A solution of S-methyldithiocarbazate [22] (1.22 g, 10 mmol) in ethanol (10 mL) was added to an ethanolic solution (10 mL) of 2,3-dihydroxybenzaldehyde (1.38 g, 10 mmol). The reaction mixture was heated under reflux for 30 min, during which a yellow precipitate was formed after cooling to room temperature. The crystalline solid product was isolated by filtration and recrystallized from ethanol, then dried in *vacuo*. Yield, 2.1 g (~88%); m.p. 225 °C. Anal. Calcd. for $C_9H_{10}N_2O_2S_2$: C, 44.6; H, 4.1; N, 11.6. Found: C, 44.5; H, 4.0; N, 11.5. IR, cm^{-1}: ν(O—H) 3350(s,b), 3220(b), ν(N—H) 3109(s), ν(C=N) 1620(m), 1600(s), δ(OH) 1365(s), ν(C—O) 1280(s), 1260(s), ν(C=S) 1323(vs). ^{1}H NMR (d_6-Me_2SO, δ/ppm): 2.47 (s, 3H, SCH_3); aromatic protons: 6.68 (t, 1H), 6.84(d, 1H), 7.08 (d, 1H); 8.48 (s, 1H, —CH=N); 9.51 (S, 1H, NH); 9.57 (S, 1H, 3-OH); 13.33 (S, 1H, 2-OH).

*Synthesis of [MoO_2 (dhsm)] (**1a**)*

To dry acetonitrile solution (20 mL) of [MoO_2 (acac)$_2$] [23] (0.16 g, 0.5 mmol), the ligand, H_2dhsm (0.12 g, 0.5 mmol) was added. The mixture was refluxed for 1 h, during which a brown precipitate was formed. This was filtered off, washed with acetonitrile and then dried in *vacuo*. Yield, 0.12 g (~75%); diamagnetic. Anal. Calcd. for $C_9H_8N_2O_4S_2Mo$: C, 29.4; H, 2.2; N, 7.6. Found: C, 29.3; H, 2.1; N, 7.5. IR, cm^{-1}: ν(O—H) 3359(vs), ν(C=N) 1593(vs), 1563(vs), δ(OH) 1363(s), ν(C—O) 1271(s), 1232(s), $\nu^s(MoO_2)$ 931(s), $\nu^{as}(MoO_2)$ 891(s) ν(Mo=O···Mo) 793(vs), ν(Mo—N) 499(m). ^{1}H NMR (d_6-Me_2SO, δ/ppm): 2.49 (s, 3H, SCH3); aromatic protons: 6.88 (t, 1H), 7.08 (d, 1H), 7.21 (d, 1H); 8.85 (s, 1H, —CH=N); 9.41 (S, 1H, 3-OH).

Table 1
Crystal data and structure refinement parameters for *cis*-[MoO_2(dhsm)$_2$(EtOH)] **(1b).**

Empirical formula	$C_{11}H_{14}$ Mo N_2 O_5S_2
Formula weight	414.31
Temperature	298 K
Wavelength	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a	8.4588(2) Å
b	9.7139(2) Å
c	11.3107(4) Å
α	110.6334(12)°
β	100.6194(14)°
γ	109.6044(14)°
Volume	769.59(4) Å^3
Z	2
Density	1.788 Mg m^{-3}
Absorption coefficient	1.14 mm^{-1}
Theta range for data collection	2.91–28.70°
Index ranges	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 15$
Independent reflections	4053
Observed reflections	2833
Absorption correction	None
Reflections collected [$I > 3\sigma(I)$]	2833
Refinement method	Full-matrix least squares on F^2
Reflections/restraints/ parameters	4053/0/190
$\Delta\rho$max, $\Delta\rho$min (e Å^{-3})	0.55, −0.69
Goodness of fit	0.943
Final *R* indices	R_1 = 0.033, wR_2 = 0.064
R indices (all data)	R_1 = 0.052, wR_2 = 0.069

*Synthesis of [MoO_2(dhsm)(EtOH)] (**1b**)*

To a solution of [MoO_2 (acac)$_2$] (0.16 g, 0.5 mmol) in ethanol (10 mL), H_2dhsm (0.12 g, 0.5 mmol) was added. The mixture was stirred at room temperature for 1 h, during which an orange solution was obtained. This was then left for slow evaporation at room temperature. The orange crystals so formed were suitable for X-ray diffraction; they were filtered off, washed carefully with little ethanol, followed by ether, and dried in *vacuo*. Yield, 0.15 g (~80%); diamagnetic. Anal. Calcd. for $C_{11}H_{14}N_2O_5S_2Mo$: C, 31.9; H, 3.4; N, 6.8. Found: C, 31.7; H, 3.3; N, 6.7. IR, cm^{-1}: ν(O—H) 3382(s,b), ν(C=N) 1590(s), 1556(s), δ(OH) 1365(m), ν(C—O) 1277(s), 1224(s), $\nu^{s}(MoO_2)$ 939(s), $\nu^{as}(MoO_2)$ 904(vs), ν(C—S) 783(m), ν(Mo—N) 507(m). ^{1}H NMR (d_6-Me_2SO, δ/ppm): 1.03 (t, 3H, CH_3); 2.47 (s, 3H, SCH_3); 3.41 (q, 2H, CH_2); 4.35 (b, 1H, OH); aromatic protons: 6.85 (t, 1H), 7.05 (d, 1H), 7.18 (d, 1H); 8.85 (s, 1H, —CH=N); 9.41 (S, 1H, 3-OH).

*Synthesis of [MoO_2(dhsm)(py)] (**1c**)*

To a solution of [MoO_2 (acac)$_2$] (0.16 g, 0.5 mmol) in ethanol (10 mL), H_2dhsm (0.12 g, 0.5 mmol) was added. The mixture was stirred at room temperature for 30 min, during which an orange solution was obtained, and then pyridine (0.04 g, 0.5 mmol) was added. This mixture was refluxed for 1 h and the resulting solution was concentrated to one-third volume and cooled to room temperature. A brown precipitate was formed, filtered off, washed with little ethanol, and then ether, and dried in *vacuo*. Yield, 0.11 g (~70%); diamagnetic. Anal. Calcd. for $C_{14}H_{13}N_3O_4S_2Mo$: C, 37.6; H, 2.9; N, 9.4. Found: C, 37.4; H, 2.7; N, 9.2. IR, cm^{-1}: ν(O—H) 3420(s,b), ν(C=N) 1630(m), 1593(vs), δ(OH) 1363(m), ν(C—O) 1261(vs), 1210(m), $\nu^{s}(MoO_2)$ 930(s), $\nu^{as}(MoO_2)$ 887(vs), ν(C—S) 781(m), ν(Mo—N) 499(m). ^{1}H NMR (d_6-Me_2SO, δ/ppm): 2.50 (s, 3H, SCH_3); aromatic protons: 6.90 (t, 1H), 7.06 (d, 1H), 7.20 (m, 1H); pyridine protons: 7.50 (t, 2H), 7.90 (t, 1H), 8.60 (d, 2H); 8.87 (s, 1H, —CH=N); 9.37 (S, 1H, 3-OH).

*Synthesis of [MoO_2(dhsm)(imz)] (**1d**)*

This reddish brown complex was prepared by a similar procedure to that for complex **1c**, using imidazole (0.04 g, 0.5 mmol) instead of pyridine. Yield, 0.15 g (~74%); diamagnetic. Anal. Calcd. for $C_{12}H_{12}N_4O_4S_2Mo$: C, 33.0; H, 2.8; N, 12.8. Found: C, 32.8; H, 2.6; N, 12.6. IR, cm^{-1}: ν(O—H) 3430(s,b), ν(N—H) 3143(vs), ν(C=N) 1620(m), 1587(s), δ(OH) 1365(w), ν(C—O) 1260(vs), 1219(m), $\nu^{s}(MoO_2)$ 930(s), $\nu^{as}(MoO_2)$ 899(vs), ν(C—S) 780(m), ν(Mo—N) 499(m), other imidazole bands: 3143(vs), 2974(s), 2895(s). ^{1}H NMR (d_6-Me_2SO, δ/ppm): 2.48 (s, 3H, SCH3); aromatic protons: 6.90 (t, 1H), 7.06 (d, 1H), 7.20 (m, 1H); imidazole protons: 6.10 (b, 1H, NH), 7.20 (m, 2H, CH), 7.95 (s, 1H, —CH=N); 8.85 (s, 1H, —CH=N); 9.46 (b, 1H, 3-OH).

*Synthesis of [MoO(dhsm)] (**1e**)*

To an acetonitrile solution (20 mL) of [MoO_2 (dhsm)(EtOH)] (0.21 g, 0.5 mmol), PPh_3 (0.2 g, 0.75 mmol) was added. The orange solution mixture was refluxed for 2 h, where a reddish brown precipitate was obtained, filtered off washed with MeCN, followed by ether and then dried in *vacuo*. Yield, 0.15 g (~80%); diamagnetic. Anal. Calcd. for $C_9H_8N_2O_3S_2Mo$: C, 30.7; H, 2.3; N, 8.0. Found: C, 30.6; H, 2.2; N, 7.9. IR, cm^{-1}: ν(O—H) 3464(m), ν(C=N) 1608(m), 1577(s), δ(OH) 1358(m), ν(C—O) 1274(s), 1218(s), ν(Mo=O) 962(vs), 868(m), ν(C—S) 773(m), ν(Mo—N) 503(m).

*Reaction of [$Mo^{IV}O$(dhsm)] (**1e**) and Me_2SO*

To a solution of the complex [$Mo^{IV}O$(dhsm)] (0.1 g, 0.28 mmol) in deoxygenated Me_2SO (2 mL) and DMF (0.5 mL), pyridine (0.1 mL, 1.2 mmol) was added. The reaction mixture was stirred and heated at 70 °C for 7 h, then the solvents were evaporated at *ca.* 90 °C with passing vigorous N_2 gas. Addition of excess Et_2O afforded a reddish brown precipitate which was thoroughly washed with solvent, filtered off and dried in *vacuo*. IR and UV–Vis spectra identified the product and found typically as [$Mo^{VI}O_2$(dhsm)(py)] (**1c**) above. Yield: 0.09 g (~71%).

*Synthesis of [VO (dhsm)(bipy)] (**2a**)*

To a solution of [VO (acac)$_2$] [24] (0.13 g, 0.5 mmol) in ethanol (10 mL), H_2dhsm (0.12 g, 0.5 mmol) was added. The mixture was stirred at room temperature for 30 min, then 2,2′-bipyridyl (0.078 g, 0.5 mmol) was added. This mixture was then refluxed for 1 h and the resulting brown solution was concentrated to one-third volume and cooled to room temperature. A brown precipitate was formed, filtered off, washed carefully with little ethanol, followed by ether, and dried in *vacuo*. Yield: 0.17 g (75%); μ_{eff} = 1.72 BM. Anal. Calcd. for $C_{19}H_{16}N_4O_3S_2V$: C, 49.3; H, 3.5; N, 12.1. Found: C, 49.1; H, 3.4; N, 12.0. IR, cm^{-1}: ν(O—H) 3420(b), ν(C=N) 1610(s), 1585(s), δ(OH) 1362(m), ν(C—O) 1309(m), 1223(s), ν(V=O) 957(s), ν(C—S) 765(s), ν(V—N) 499(w), bipy vibrations: 1485(s), 868(m). EPR (CH_2Cl_2, 298 K): Experimental g_{av} 1.976, A_{av} 82.6 × 10^{-4} cm^{-1}; Calcd. $g \perp$ 1.983, $g_{//}$ 1.935, g_{av} 1.967.

*Synthesis of [VO (dhsm)(phen)] (**2b**)*

This complex was prepared by a similar procedure to that for complex **2a**, using 1,10-phenanthroline (0.1 g, 0.5 mmol) instead of 2,2′-bipyridyl. Yield: 0.194 g (80%); μ_{eff} = 1.75 BM. Anal. Calc. for $C_{21}H_{16}N_4O_3S_2V$: C, 51.8; H, 3.3; N, 11.5. Found: C, 51.7; H, 3.2; N, 11.4. IR, cm^{-1}: ν(O—H) 3420(b), ν(C=N) 1610(m), 1581(m), δ(OH) 1365(m), ν(C—O) 1304(m), 1226(vs), ν(V=O) 957(vs), ν(C—S) 779(s), ν(V—N) 497(m), phen vibrations: 1480(s), 839(s). EPR (CH_2Cl_2, 298 K): Experimental g_{av} 1.973, A_{av} 82.4 × 10^{-4} cm^{-1}; Calcd. $g \perp$ 1.982, $g_{//}$ 1.936, g_{av} 1.967.

*Synthesis of [VO (dhsm)] (**2c**)*

To a solution of [VO(acac)$_2$] (0.13 g, 0.5 mmol) in ethanol (10 mL), H_2dhsm (0.12 g, 0.5 mmol) was added. The mixture was reflux and stirred at 70 °C for 2 h, during which a violet precipitate was obtained. This precipitate was filtered off, washed with little ethanol, followed by ether, and dried in *vacuo*. Yield, 0.2 g (72%); μ_{eff} = 1.10 BM. Anal. Calcd. for $C_9H_8N_2O_3S_2V$: C, 35.2; H, 2.6; N, 9.1. Found: C, 35.3; H, 2.4; N, 9.0. IR, cm^{-1}: ν(O—H) 3442(b), ν(C=N) 1585(vs), 1530(vs), δ(OH) 1360(w), ν(C—O) 1290(s), ν(V=O) 995(vs), ν(V—O···V) 823(m), ν(C—S) 780(m), ν(V—N) 500(m).

Catalytic oxidations with t-BuOOH or H_2O_2

The oxidation of benzyl alcohol by [MoO_2 (dhsm)(EtOH)] (**1b**) is typical. To the alcohol (2.5 mmol), complex (**1b**) (0.01 mmol) and 70% in water t-BuOOH (5 mmol) were added. The reaction mixture was stirred at 70 °C for 3 h, extracted with CH_2Cl_2 (3 × 10 mL). The extracts were combined, dried over anhydrous Na_2SO_4, evaporated to dryness and aldehyde product was quantified as its 2,4-dinitrophenylhydrazone derivative [8,9] (equivalent to 1 mmol of benzaldehyde product was obtained). The absence of benzoic product was detected by TLC techniques. The same experiment

were carried out using 30% H_2O_2 (5 mmol) instead of 70% t-BuOOH where 0.25 mmol benzaldehyde was produced.

Results and discussion

The free ligand, H_2dhsm (Scheme 1) was prepared by condensation of equimolecular amounts of 2,3-dihydroxybenzaldehyde and S-methyldithiocarbazate in ethanol. The ^{1}HNMR spectrum of H_2dhsm in $(CD_3)_2SO$ shows singlet at δ 9.51, 9.57 and 13.33 ppm which are absent when using $(CD_3)_2SO/D_2O$ as solvent, these attributed to protons of NH, free and hydrogen-bond hydroxyl groups (3-OH, 2-OH), respectively. The azomethine hydrogen appears at δ 8.48 ppm, aromatic protons shifts are found within the range δ 6.68–7.08 ppm (3 protons), while methyl protons of SCH_3 resonate as singlet at 2.47 ppm. Similar ^{1}H NMR spectra have been reported for related Schiff base ligands [3,25] and these data indicate that the free ligand is in the thione form **(a)**.

Dioxomolybdenum(VI) complex (**1a**) of the formula [MoO_2(dhsm)] was prepared by refluxing [MoO_2(acac)] with the ligand (H_2dhsm) in 1:1 M proportion using CH_3CN as a solvent, while the complex [MoO_2(dhsm)(EtOH)] (**1b**) was isolated as orange crystals when EtOH used. The complexes [MoO_2(dhsm)D] [D = pyridine (**1c**), imidazole (**1d**)] were similarly prepared as the complex (**1b**), but in the presence of added equivalent amounts from pyridine or imidazole. The reddish brown oxomolybdenum(IV) complex [MoO(dhsm)] (**1e**) was prepared by oxo-abstraction reaction of (**1b**) with PPh_3 in MeCN medium, as similarly obtained for related molybdenum(IV) complexes of ONS-donor ligands [26,27]. The complex [MoO_2(dhsm)(py)] (**1c**) has been also obtained from reaction of [$Mo^{IV}O$(dhsm)] (**1e**) and Me_2SO in the presence of pyridine indicating oxo-accepting behavior of $Mo^{IV}O_2^{2+}$ core with a consequent oxidation to $Mo^{VI}O_2^{2+}$ complex. This is similarly related to other molybdenum(IV) complexes and to the behavior of oxido-reductase enzymes, through two electron reduction of the substrate by removing an oxo ligand [26]. Vanadium complexes of the formula [VO(dhsm)bipy/phen] (**2a**, **2b**) were isolated by reflux of equimolar quantities of [$VO(acac)_2$], H_2dhsm and bipy/phen in MeOH, while the complex [VO(dhsm)] (**2c**) was obtained simply by a similar way in absence of bipy/phen. All the compounds are readily soluble in CH_2Cl_2, MeCN and DMF and their molar conductivities in CH_2Cl_2 are very low. They are also soluble in diluted aqueous NaOH.

Crystal Structure of cis-[MoO_2(dhsm)(EtOH)] ***(1b)***

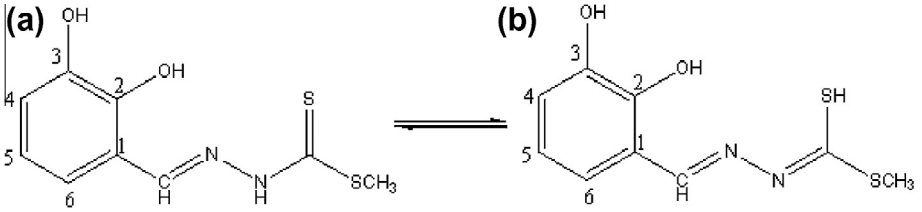
The perspective view of the complex **1b** is shown in Fig. 1. As indicated by the bond angles in Table 2, this six coordinate complex is appreciably distorted from ideal octahedral geometry. In particular, the angles, O16—Mo1—O21 [169.65(9)°], O17—Mo1—N6 [157.93(9)°] and S3—Mo1—O15 [153.96(7)°], are less than the ideal value of 180°, similarly typical to that found for the related bond angles in the complex *cis*-[MoO_2(ONS)(H_2O)] (ONS = dianione of the tridentate Schiff base ligand of salicylaldehyde with S-methyl dithiocarbazate) [3,27]. The donor atoms O15, N6, S3 from the tridentate ligand (H_2dhsm), and the terminal oxo atom O17, occupy the meridional plane. Both the other oxo terminal atom O21 and O16 from the coordinated ethanol molecule, define the axial positions. The O17=Mo=O21 bond angle is 105.90(11)° and the bond lengths; Mo1=O17=1.707(2) Å and Mo1=O21=1.691(2) Å are usual for *cis*-dioxomolybdenum(VI) complexes [27,28].

The Mo—O16 bond *trans* to the terminal oxygen atom O21 has been significantly lengthened [2.331(2) Å], compared to the Mo1—O15 distance [1.936(2) Å] occupying *cis*-position indicating that EtOH molecule is weakly coordinated to the metal center. Also, the imine nitrogen N6 is *trans* to the oxo terminal atom O17 and the Mo—N6 bond length of 2.283(2) Å is rather long due to *trans* effect. The C4—N5 length [1.293(4) Å] is close to usual C=N bond length [3,29]. This thiol form is also identified by the fact that the hydrazinic nitrogen N5 is not covalently bonded to any hydrogen atom.

Fig. 2 shows the intermolecular hydrogen bonding for H···O and H···N interactions characterized in the lattice for the complex **1b**. Each molecule is interconnected with the other neighboring molecules *via* hydrogen bonds between dioxo atoms (O17, O21), hydrazinic nitrogen N5 and hydroxyl oxygen O14 of the aromatic ring. The H···O bonding is defined by strong interaction O14—H14···O17 [d_H (H14···O17 = 1.971(2) Å] and a weaker one C13—H13···O21 [d_H (H13···O21) = 2.596(2) Å] or C18—H18···O14 [d_H (H18···O14) = 2.393 Å]. The d_H (H···O) distances are shorter than the maximum values 2.72 Å for the Van der Waals radii of hydrogen and oxygen atoms and considered for any contacts [30]. However, such the latter C—H···O interaction is somewhat scarce in coordination compounds; it has been recognized to play an important in protein structure and stability [31]. The theoretical calculations showed that the C—H···O association energy ~2.1 kcal mol^{-1} essentially contribute to the structure stabilization [32]. It is noteworthy to find that the coordinated ethanolic molecule in the complex **1b** participates in a more strong interaction through the alcoholic hydroxyl hydrogen H16 and the hydrazinic nitrogen N5 in O16—H16···N5 [d_H (H16···N5) = 1.853(2) Å]. Table 3 lists the different hydrogen bonding in structure **1b**.

Infrared spectra

The IR spectrum of the ligand (H_2dhsm) shows two medium broad bands near 3350 and 3220 cm^{-1} due to the ν(OH) vibrations of the free and hydrogen-bonded hydroxyl groups, respectively [25]. The low wavenumber ν(OH) vibration disappears in the complexes while the other band is still present. The medium band at 1620 cm^{-1}, attributed to ν(C=N) in the free ligand is shifted in complexes to lower wavenumbers. The observed band at 1365 cm^{-1} in the ligand, which by analogy with catechol and 2,3-dihydroxynaphthalene is assigned to δ(OH), does appear [25] in our complexes, while its absence was noted in catecholato [33] and naphthalene-2,3-diolato [34] complexes. Shifted strong bands comparable to the ligand (H_2dhsm), lie in the range 1277–1210 cm^{-1} for the complexes, consistent with the phenolic



Scheme 1.

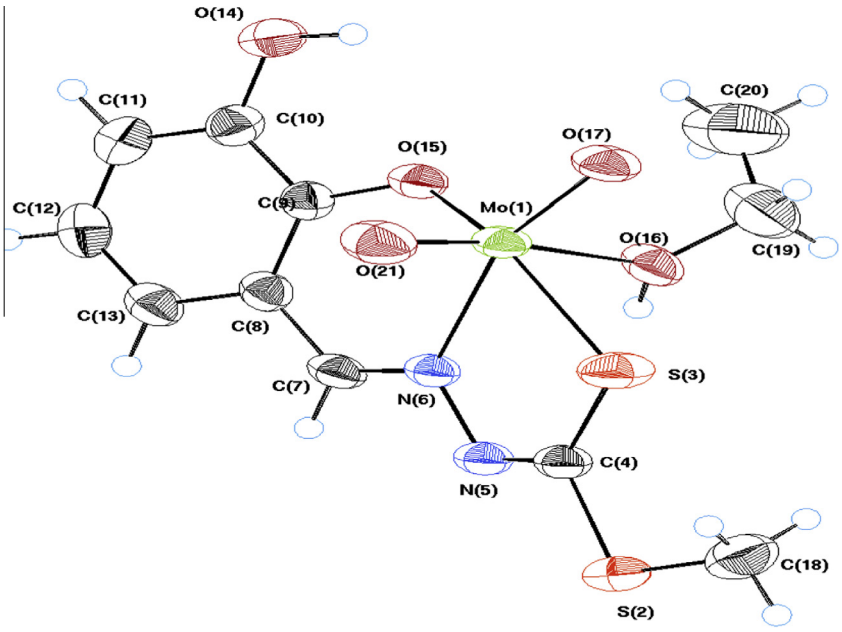


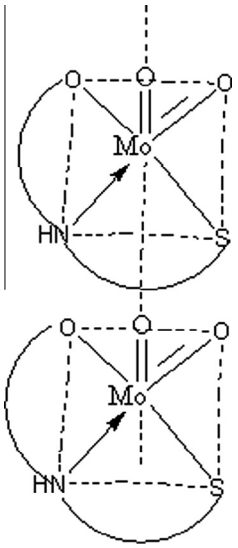
Fig. 1. ORTEP diagram of the compound [MoO_2 (dhsm)(EtOH)] **(1b)**, with 50% ellipsoidal probability. Hydrogen atoms are shown as smaller spheres of arbitrary radii.

Table 2
Selected bond lengths and angles for *cis*-[MoO_2(dhsm)(EtOH)] **(1b)**.

Bond lengths (Å)			
Mo1—O17	1.707(2)	C4—N5	1.293(4)
Mo1—O21	1.691(2)	Mo1—S3	2.458(8)
Mo1—O16	2.331(2)	S3—C4	1.722(3)
Mo1—O15	1.936(2)	S2—C4	1.758(3)
Mo1—N6	2.283(2)	S2—C18	1.787(4)
Bond angles (°)			
O16—Mo1—O21	169.65(9)	O16—Mo1—O17	84.34(9)
O17—Mo1—N6	157.93(9)	O15—Mo1—O21	97.91(11)
S3—Mo1—O15	153.96(7)	O16—Mo1—N6	76.15(7)
O17—Mo1—O21	105.90(11)	S3—Mo1—N6	75.57(6)
S3—Mo1—O17	91.73(7)	S3—Mo1—O21	95.97(9)
S3—Mo1—O16	81.98(6)	O15—Mo1—O16	80.42(8)
O15—Mo1—O17	105.41(9)	N6—Mo1—O21	93.50(9)
O15—Mo1—N6	81.67(8)		

ν(C—O) vibrations [25,33–36]. This confirms the participation of the azomethine nitrogen and the hydroxyl oxygen atom in coordination. The free ligand exhibits two strong distinct bands at 3109 and 1323 cm^{-1} due to ν(N—H) and ν(C=S) modes [1,3], both disappeared upon complex formation with the presence of a new medium band near 780 cm^{-1} arising from ν(C—S) vibration, suggesting deprotonation and coordination through thiolate sulfur [2,5,14].

Two strong bands near 935 and 900 cm^{-1} assigned to symmetric and asymmetric stretches of the *cis*-MoO_2 unit similar to those found for most of the *cis*-dioxomolybdenum(VI) complexes [25,33–36]. A strong broad band at 793 cm^{-1} was only observed in the complex [MoO_2(dhsm)] **(1a)**, which can be assigned to Mo=O···Mo grouping and suggesting a weak polymeric interaction [37,38] (Structure **1a**). In oxovanadium complexes, a strong band at 995 or 957 cm^{-1} was observed, due to ν(V=O) vibrations and the additional new medium band at 823 cm^{-1} found in complex (**2c**) is attributed to V—O···V bridging vibration of its dimeric nature [39]. The molybdenum and vanadium complexes exhibit also characteristic bands corresponding to the bound monodentate (ethanol, pyridine, imidazole), or bidentate donor (bipy, phen) [39] to complete six-coordination around molybdenum or vanadium atom. A new band near 500 cm^{-1} was observed for complexes, assigned to ν(M—N) [1,3,39].



(1a)

^{1}H NMR spectra

The ^{1}H NMR spectra for the diamagnetic molybdenum(VI) complexes recorded in $(CD_3)_2SO$ (Scheme 1, for atom numbering) showed absence of the ligand proton resonances for NH and hydrogen bonded 2-OH, while the proton of free hydroxyl group (3-OH), still appears as singlet but shifted up field by 0.11–0.20 ppm. The resonance arising from the azomethine nitrogen (CH=N) and aromatic protons (H4, H5 and H6) are shifted down field. This feature is indicative of a decrease in the electron density caused by electron withdrawal by the molybdenum ion [15]. These refer to complex formation and participation of hydroxyl oxygen (2-OH group), azomethine nitrogen and thiolate sulfur in coordination as confirmed by single crystal X-ray for *cis*-dioxomolybdenum(VI) complex **(1b)**. For the complexes *cis*-[MoO_2(dhsm)D] (D = EtOH, py,

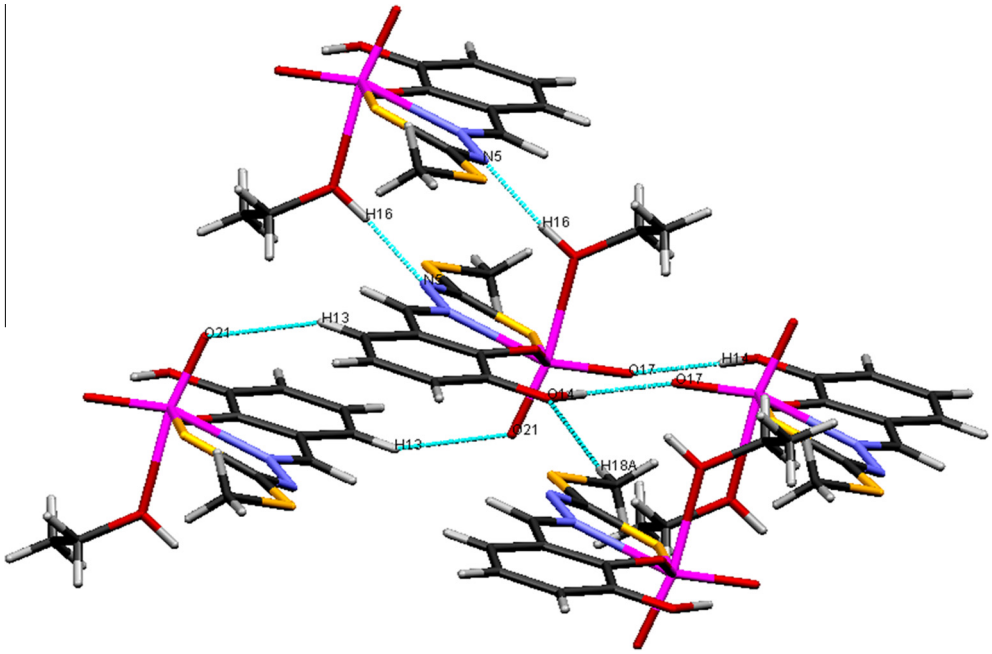


Fig. 2. The main intermolecular hydrogen bonding characterized in the lattice for the complex [MoO_2 (dhsm)(EtOH)] **(1b)**.

Table 3
Hydrogen bonding parameters (Å, °) for *cis*-[MoO_2 (dhsm) (EtOH)] **(1b)**.

D—H···A	Symmetry	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
O14—H14···O17	$1-x, -y, 1-z$	0.983(2)	1.971(2)	2.866(3)	150.2(2)
C13—H13···O21	$1-x, -y, -z$	0.960(3)	2.596(2)	3.478(4)	152.9(2)
C18—H18···O14	$1+x, y, 1+z$	0.960(3)	2.393(2)	3.291(4)	155.6(3)
O16—H16···N5	$-x, -y, -z$	0.936(2)	1.853(2)	2.779(3)	170.1(2)

imz), distinct resonances for the coordinated monodentate ligand D have been displayed.

Electronic spectra

Electronic spectra of the complexes and the ligand (H_2dhsm) were recorded in CH_2Cl_2 and the results are summarized in Table 4. Dioxomolybdenum complexes **(1a–1d)** with $4d^0$ configuration showed the lowest energy absorption maxima located in the 390–402 nm range and may be assigned to S(pπ)-Mo(dπ) LMCT transitions [3,40]. Other LMCT bands are observed in the region 390–285 nm [3,41], which may be assigned to transitions from nitrogen or oxygen to molybdenum [3,40]. The oxomolybdenum(IV) **(1e)** in DMF gives brown solution and exhibits one low-energy charge transfer band at 660 nm ($\varepsilon = 350\ M^{-1}\ cm^{-1}$), similar to that found for related molybdenum complexes [3,37]. In the oxovanadium(IV) complexes **(2a–2c)** which are $3d^1$ system, medium to intense bands are found in the range 352–550 nm, attributed to LMCT arising from the ONS-donor ligand [14,42,43]. The weak broad bands ($\varepsilon = 310–540\ M^{-1}\ cm^{-1}$) lie in the region 660–780 nm, are as expected due to $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz}, d_{yz})$ and $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x2-y2})$ transitions while the other weak d–d transition of higher energy may be obscured by such LMCT bands [43]. The bands at or below 325 nm are of the intraligand transitions.

Oxo transfer reactivity of dioxomolybdenum(VI) complexes

The property of the complexes $Mo^{VI}O_2L$ **(1a–1d)** to transfer an oxygen atom to the substrate has been examined in CH_3CN containing PPh_3. The parent complex has a band near 400 nm due to a S(pπ) → Mo(dπ) LMCT transition. When the complex, e.g. *cis*-[MoO_2(dhsm)(EtOH)] **(1b)** is reacted with PPh_3, this band is found to be shifted to lower energy (476 nm) and a new band appears at 660 nm. The isolated complex [$Mo^{IV}O$(dhsm)] **(1e)** has the same spectral feature and the oxo-transfer reaction may be represented as:

$$Mo^{VI}O_2L + PPh_3 \rightarrow Mo^{IV}OL + OPPh_3$$

This oxo-transfer reaction may be visualized as a simple bimolecular reaction that involves the interaction between one MoO_2L and one PPh_3 molecule in the activated complex, leading to the transfer of an oxygen atom by the donation of the lone pair of electrons of the phosphorous atom into the antibonding Mo═O π^* orbital. This leads to the formation of the P—O bond and Mo(IV) – oxo complex with a $4d^2_{xy}$ configuration. We could isolate $OPPh_3$ which ascertained by identifying its characteristic peak at 1180 cm^{-1} in the IR spectrum. So, the reaction may be considered as a two-electron redox/oxygen atom transfer process.

The oxygen atom transfer from the substrate (Me_2SO) to [$Mo^{IV}O$(dhsm)] **(1e)** has been studied spectrophotometrically in DMF solution. When a drop of Me_2SO is added to the reddish brown solution of **(1e)**, the bands at 476 and 660 nm disappear within 15 min, and the band near 400 nm characteristic to Mo(VI) complex **(1a–1d)** makes its appearance with a predomination of an orange color solution. This observation clearly indicates the transfer of an oxygen atom from Me_2SO to the $Mo^{IV}O^{2+}$ core, leading to the formation of MoO_2^{2+} species and Me_2S [3,26,27]. The reaction may be shown as

Table 4
Electronic spectral and cyclic voltammetric data for complexes.

Compound[a]		λ_{max} nm (ε, M^{-1} cm^{-1})[a]	E_{pa}	E_{pc}
			V	
$[MoO_2(dhsm)]$	**(1a)**	290(35,025); 330(67,800); 402(19,150)	−0.67[b]	−1.12[b]
$[MoO_2(dhsm)(EtOH)]$	**(1b)**	285(33,600); 312(39,900); 395(14,700)	–	−0.65, −0.95
$[MoO_2(dhsm)(py)]$	**(1c)**	290(23,600); 330(47,270); 390(17,700)	–	−0.85, −1.25
$[MoO_2(dhsm)(imz)]$	**(1d)**	292(13,980); 340(44,550); 420(12,820)	–	−0.81, −1.23
[MoO (dhsm)]	**(1e)**	294(7510); 328(12,690); 398(5520); 476(1470); 660(350)[c]	+0.68[c]	–
[VO(dhsm)(bipy)]	**(2a)**	310(36,040); 360(31,330); 418(13,270); 675(360)[d], 780(300)[d]	+0.70	–
[VO(dhsm)(phen)]	**(2b)**	310(38,020); 352(39,350); 405(17,980); 660(310)[d], 760(200)[d]	+0.80	–
[VO(dhsm)]	**(2c)**	312(23,900); 325(24,170); 397(12,450); 550(5900); 740(540)	–	–

[a] UV/Vis data of the ligand (H_2dhsm): 295(24,800), 320(57,100), 334(65,800).
[b] C.V. data obtained in CH_3CN.
[c] UV/Vis and C.V. data recorded in DMF.
[d] d–d transition bands used for calculated g-values.

$$MoOL + Me_2SO \rightarrow MoO_2L + Me_2S$$

It is worthwhile to note that the reaction of $Mo^{IV}O$ complexes with Me_2SO in DMF solvent has a high reaction velocity of more than 13-fold times than that in the absence of DMF [26c], and the identity of Me_2S formed was confirmed by GC/MS-head space analysis for similar molybdenum reactions to oxidize PPh_3 catalytically [26d].

Magnetic and EPR spectra

Magnetic susceptibility of the solid complexes were measured at 298 K. Oxovanadium complexes **(2a)** and **(2b)** are paramagnetic corresponding to one unpaired electron, with μ_{eff} values of 1.70 and 1.75 BM close to the spin only value (1.73 BM), as expected for a simple S = 1/2 with d_{xy} based ground state mononuclear complexes [43]. EPR spectra at 298 K in CH_2Cl_2 exhibit a set of eight hyperfine lines arising from interaction of the unpaired electron of the oxovanadium(IV) center with the single vanadium nucleus (^{51}V, I = 7/2). A typical spectrum (Fig. 3) for [VO(dhsm)(bipy)] **(2a)** shows an eight line pattern: g_{av}, 1.976 and A_{av}, 82.6×10^{-4} cm^{-1}. Using both energies of our corresponding electronic spectral data (Table 4.) for the d–d transitions of complexes **(2a)** and **(2b)** and the Eqs. (1) and (2) [44], we have got values (g_{av}) in a good agreement with the experimental results.

$$g\perp = 2[1 - (c_1^*)^2\lambda/E(^2B_2 \rightarrow {}^2E)] \quad (1)$$

$$g_{//} = 2[1 - (c_1^*)^2 4\lambda/E(^2B_2 \rightarrow {}^2B_1)] \quad (2)$$

where the c_1^* are 0.907 and 0.946 for the first and second excited states, respectively; λ is the spin–orbit coupling parameter, taken to be 135 cm^{-1}. The g_{av}-value, corrupted from $g\perp$ and $g_{//}$ components above is given by: $g_{av} = 1/3(g_{//} + 2g\perp)$. It is worthwhile to note that calculated $g\perp > g_{//}$ as expected and $g\perp$ has a relatively larger values when compared with those for related oxovanadium(IV) complexes in N/O donor environments [45]. This indicates moderate π-interaction of sulfur in the present ONS ligand system, leading to increased delocalization of the vanadium unpaired electron [43]. For the oxovanadium complex **(2c)**, the μ_{eff} (at 298 K) has a lower value of 1.10 BM, as similarly found for oxovanadium(IV) complexes with tridentate Schiff base ligands having subnormal magnetic moments [46], and arise from the antiferromagnetic spin–spin interaction between neighboring oxovanadium(IV) centers [47]. The EPR spectra at room temperature for complex **(2c)** in both CH_2Cl_2 and powdered sample shows a 15-line spectrum which is characteristic of a tentative dimeric structure **(2c)** [39,47] and confirmed by IR data before, with a proposed square-pyramidal geometry [47]. This is due to spin–spin coupling between the two adjacent vanadium atoms, as the case for similar related vanadium(IV) complexes [47,48].

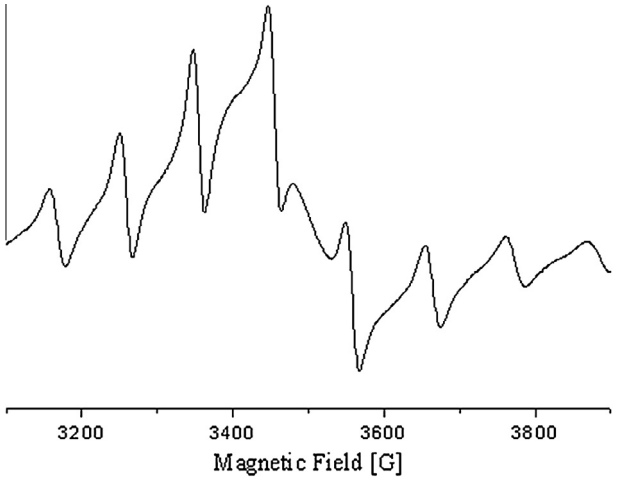
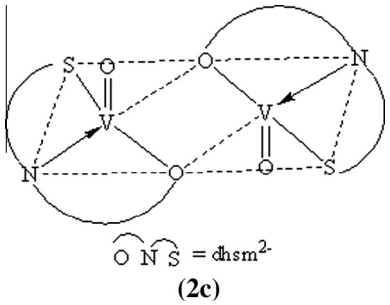


Fig. 3. X-band EPR spectra of [VO (dhsm)(bipy)] **(2a)** at 298 K in 5×10^{-3} M CH_2Cl_2 solution.



(2c)

Electrochemical properties

Cyclic voltammograms of the complexes at Pt-electrode were recorded in dry degassed CH_2Cl_2 containing 0.1 M (n-Bu_4N)PF_6 as supporting electrolyte. Voltammetric data *versus* a silver electrode are shown in Fig. 4a and c and Table 4. The $E_{1/2}$ for ferrocene/ferrocenium couple under the experimental conditions was 0.4 V (ΔE = 65 mV) [49]. The complex $[Mo^{VI}O_2(dhsm)]$ **(1a)** showed an irreversible reductive peak (E_{pc} = −1.12 V) and another one for oxidative response (E_{pa} = −0.67 V), each peak of current height twice that observed in the other complexes **(1b–1d)**. This is assigned to a metal center $2e^-$ process [3,5,29], Mo^{VI}/Mo^{IV} reduction and Mo^{IV}/Mo^{VI} oxidation. Two irreversible one electron reductive responses are found in molybdenum(VI) complexes **(1b–1d)** due to Mo^{VI}/Mo^{V} and Mo^{V}/Mo^{IV} reductions. The complex $[Mo^{IV}O(dhsm)]$ **(1e)**

showed a high current anodic peak (E_{pa} = +0.68 V), arising from Mo^{IV}/Mo^{VI} oxidation [3]. For oxovanadium(IV) complexes **(2a)** and **(2b)** an anodic oxidation peak has been observed which is attributed to V^{IV}/V^{V} oxidation, while the complex **(2c)** shows electro inactive behavior.

Catalytic oxidation

Many oxoperoxo-molybdenum(VI) complexes are commonly known to catalyze the oxidation of alcohols to aldehyde/ketones [50], but dioxomolybdenum(VI) complexes are scarce for such

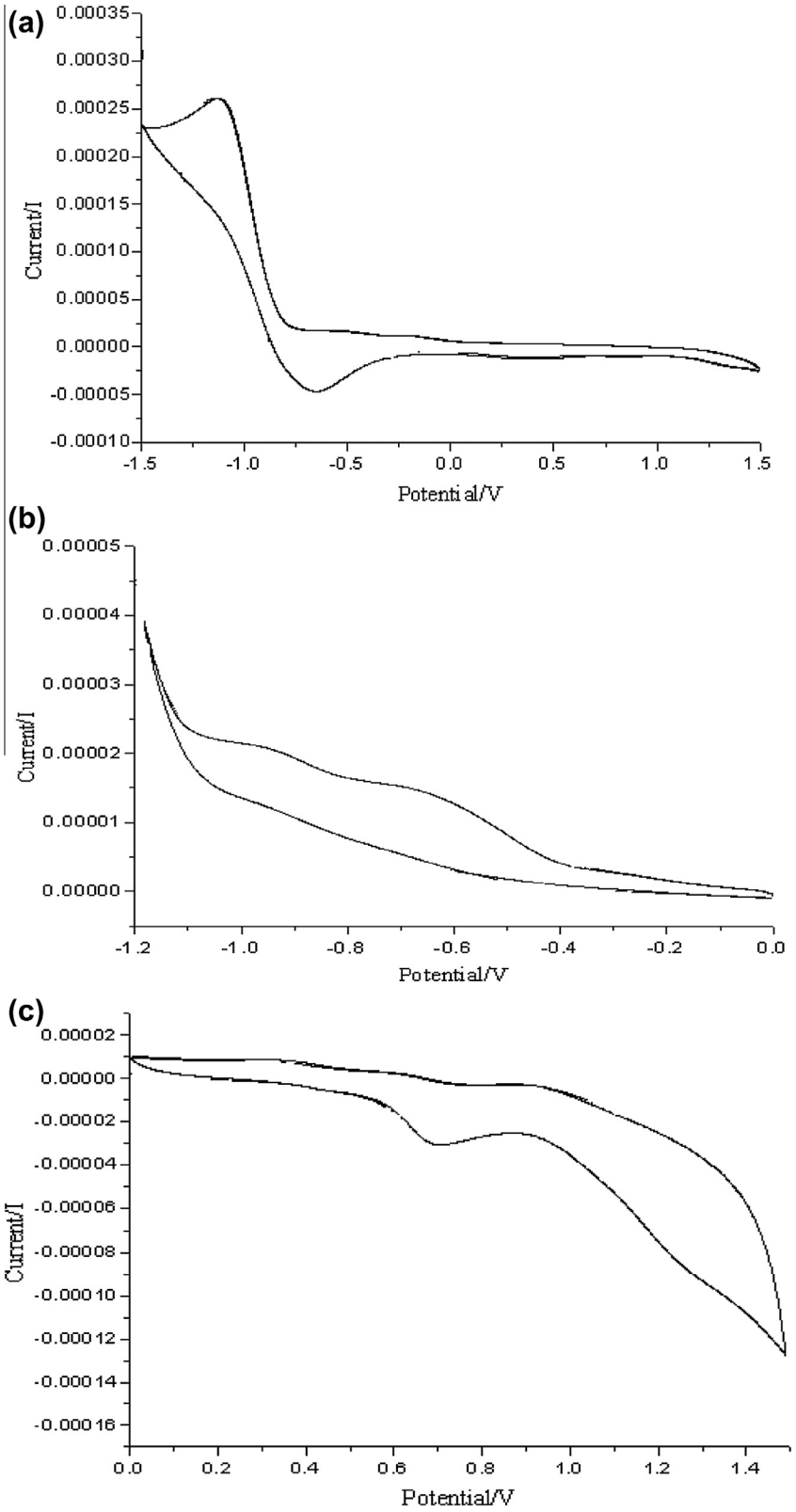


Fig. 4. Cyclic voltammogram with scan rate 50 mV s^{-1} for 10^{-3} M of: (a) $[MoO_2(dhsm)]$ **(1a)** in CH_3CN (b) $[MoO_2(dhsm)(EtOH)]$ **(1b)** in CH_2Cl_2 (c) [VO(dhsm)(bipy)] **(2a)** in CH_2Cl_2.

Table 5
Catalytic oxidation by molybdenum(VI)/(IV) and vanadium(IV) complexes.

Catalyst	Substrate	Product[a]	Time	t-BuOOH	H_2O_2
				Turnover	
(**1b**)	Benzyl alcohol	A	3	40	10
	Cinnamyl alcohol	A	3	15	35
	Cyclohexanol	K	4	20	0
(**1e**)	Benzyl alcohol	A	3	22	12
	Cinnamyl alcohol	A	3	10	20
	Cyclohexanol	K	4	20	7
(**2b**)	Benzyl alcohol	A	3	80	50
	Cinnamyl alcohol	A	3	10	17
	Cyclohexanol	K	4	30	0

[a] A = corresponding aldehyde, K = corresponding ketone.

catalytic oxidation [17]. Oxovanadium(IV) complexes catalyzed oxidations of several alcohols have been reported with high selectivity but low turnovers [51,52]. We have investigated the use of t-butyl hydroperoxide (t-BuOOH) and H_2O_2 as co-oxidants with the present metal complexes (**1b**, **1e** and **2b**) as typical examples in the catalytic oxidations of alcohols. Table 5 summarizes the results of these experiments. Using t-BuOOH under solvent-free conditions at 70 °C for 3–4 h, benzyl alcohol and cyclohexanol were oxidized. Selectivity to benzaldehyde and cyclohexanone (turnovers, 80–10). Unsaturated alcohol, e.g. cinnamyl alcohol is oxidized without competing double bond attack. Under similar reaction conditions with H_2O_2 as co-oxidant, the complexes were ineffective towards cyclohexanol oxidation and lower turnovers (*ca.* 50–7) achieved in oxidation of other alcohols. This reflects better catalytic oxidations obtained with t-BuOOH than H_2O_2, due to more solubility of alcohols and catalysts in the former co-oxidant. The oxovanadium(IV) complex (**2b**) shows higher turnovers compared to those for molybdenum complexes (**1b** and **1e**). Oxidation products obtained under similar reaction conditions and in the absence of these metal complexes. Oxidations of benzyl alcohol to the corresponding benzoic acid with the systems of dioxomolybdenum(VI) Schiff base complexes/H_2O_2 in THF at 90 °C for 24 h have achieved modest turnovers (40–26) [17], while oxovanadium(IV) complexes/t-BuOOH in dry toluene at RT (24–48 h) have oxidized allylic alcohols to their corresponding aldehydes or ketones with 20 turnovers [18].

In the presence of excess peroxide, either molybdenum trioxide with different donor ligands or oxovanadium(IV) are readily converted to their corresponding oxoperoxo-molybdenum(VI) or vanadium(V) species [50,53]. So, we suggest that oxidation by molybdenum and vanadium catalysts in the presence of excess H_2O_2 or t-BuOOH as co-oxidants proceeds *via* oxoperoxo molybdenum or vanadium intermediates. Vanadium monoperoxo complexes can function as a "catalytic pump" for generation of hydroxyl radicals [54], which are very reactive and strong oxidants and promote other radical chains, e.g. by abstracting H from an organic substrate [55].

Conclusion

The Schiff base ligand derived from S-methyl dithiocarbazate and 2,3-dihydroxybenzaldhyde has been used to prepare the new *cis*-dioxomolybdenum(VI) and oxovanadium(IV) complexes in high yields. The oxomolybdenum(IV) has been obtained from dioxomolybdenium(VI) species by oxo abstraction with PPh_3. The redox properties have been studied by cyclic voltammetry. Analytical and spectroscopic data together with the X-ray crystal structure for one of the dioxomolybdenum(VI) complexes showed that the Schiff base behaves as a dianionic ONS tridentate ligand in its thiolate form. The complexes showed catalytic reactivity towards selective oxidation of primary alcohol into the corresponding aldehyde under solvent free conditions.

Supplementary data

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 873349 for [MoO2(dhsm)(EtOH)]. Copy of information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccd.com.ac.uk https://www.ccdc.cam.ac.uk.

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