THE INTERNATIONAL JOURNAL OF
SCIENCE & TECHNOLEDGE

Synthesis and Characterization of *cis*-dioxomolybdenum (VI) Schiff base Complexes Derived from S–methyldithiocarbazates, S–benzyldithiocarbazates, 2–aminoethanethiol and β–diketones

Niren Kathale
Assistant Professor, Department of Chemistry,
Sardar Patel Mahavidyalaya, Chandrapur, Maharashtra, India

Abstract:
The synthesis and characterization of some cis-dioxomolybdenum (VI) complexes with Schiff base ligands (H_2L) derived from β–diketones and amines such as S–methyldithiocarbazate, S–benzyldithiocarbazate and 2–aminoethanethiol are reported. These complexes were characterized by elemental analyses, molar conductance, IR, UV-Vis, ^1H NMR, AAS, and TGA. The spectroscopic and other analytical data reveal that these Schiff bases behave as dibasic tridentate O,N,S donor ligands and react with [$MoO_2(acac)_2$] in 1:1 ratio to give diamagnetic mononuclear complexes having the general formula [$MoO_2(L)(EtOH)$].

Keywords: *Schiff base, dioxomolybdenum (VI), b-diketone, complexes,*

1. Introduction

There is continuing interest in the study of molybdenum complexes of Schiff base ligands derived from S–alkyldithiocarbazates because of their potential for biological and physiological activity and industrial use. In enzymes such as nitrogenase, aldehyde oxidase, xanthine oxidase, sulphite oxidase, xanthine dehydrogenase and nitrate reductase, molybdenum cycles between the +4 and +6 oxidation states in their reactions with substrate and subsequent reactivation. The presence of the molybdenyl group has been reported in the oxidized form of xanthine oxidase and sulphite oxidase (Tullius et al., 1979; Cramer et al., 1979). The synthesis of mononuclear *cis*-dioxomolybdenum (VI) complexes with Schiff bases having one labile site that might allow binding and displacement of various substrates has been carried out in the recent years. These complexes serve as reactive intermediates in the catalytic oxidation of olefins and in hydrosulfurization (Gates et al., 1979; Green, 1979; Rao et al., 1999; Rao et al., 2000; Rao et al., 1999; Kathale et al., 2001; Kurapati et al., 2016; Ilhan et al., 2015).

In continuation of the work to synthesize, characterize and examine the oxotransfer activity of some *cis*-dioxomolybdenum (VI) complexes (Rao et al., 1999; Rao et al., 2000; Rao et al., 1999; Kathale et al., 2001;), we report here the synthesis and characterization of some *cis*-dioxomolybdenum (VI) complexes with Schiff ligands derived from *o*-acetoacetanisidide (ANS), *o*-acetoacetanilide (ANL) and amines such as S–methyldithiocarbazate (SMDTC), S–benzyldithiocarbazate (SBDTC), 2–aminoethanethiol (AmET). The structures of these Schiff bases along with their acronyms are shown in Fig. 1. These Schiff base ligands form mononuclear dioxomolybdenum (VI) complexes having the general formula [$MoO_2(L)(EtOH)$] (where H_2L = Schiff base represented as H_2L^1 (H_2ANS-SMDTC); H_2L^2 (H_2ANS-SBDTC); H_2L^3 (H_2ANS-AmET); H_2L^4 (H_2ANL-SMDTC); H_2L^5 (H_2ANL-SBDTC); and H_2L^6 (H_2ANL-AmET), with a labile site for binding and displacement of various substrates.

2. Experimental

2.1. Materials

Ammonium molybdate (VI) tetrahydrate was obtained from Sisco Research Laboratory Mumbai, India, *o*–acetoacetanisidide, *o*–acetoacetanilide and 2–aminoethanethiol were procured from Lancaster Synthesis Ltd. UK. S–Methyldithiocarbazate, S–benzyldithiocarbazate, were prepared by the reported procedures (Das et al., 1976; Ali et al., 1977). Ethanol used as solvent for the syntheses was of high purity. *cis*-$MoO_2(acac)_2$ was synthesized according to a reported method (Das et al., 1976).

2.2. Physical Measurements

Microanalyses of the ligands and the complexes were performed on a Carlo-Erba 1106 elemental analyser. IR spectra were recorded on a Nicolet Magna IR 550 Series II spectrophotometer as KBr pellets. Electronic spectra were recorded in DMF on a Shimadzu UV 3101 PC spectrophotometer. The ^{1}H NMR spectra were recorded at 298 K in DMSO–d_6 on a Bruker DRX–300 instruments, using tetramethylsilane (TMS) as an internal standard. The solution electrical conductivity was measured at 298 K using a Toshniwal conductivity bridge. Thermo gravimetric analyses were done on a Mettler Toledo Star^e SDTA/TGA 851 instrument. Molybdenum was determined on a GBC Australia 932 double beam atomic absorption spectrometer.

2.3. Synthesis of Schiff Base Ligands (1a)–(4a)

A MeOH (10 mL) solution of *o*–acetoacetanisidide (1.0362 g, 5 mmol) or *o*–acetoacetanilide (0.886 g, 5 mmol) was added to a hot MeOH solution (10 mL) of S–methyldithiocarbazate (0.610 g, 5 mmol) or S–benzyldithiocarbazate, (0.990 g, 5 mmol). The mixture was heated under reflux on a water bath for 3 h and was then cooled in an ice bath. The white to cream yellow solid that separated out was filtered under reduced pressure, washed several times with hot ethanol and then dried in vacuum. The precipitate so obtained was recrystallized from MeOH.

2.4. Synthesis of Schiff Base Ligands (5a) and (6a)

The hydrochloride salt of 2–aminoethanethiol (0.587 g, 5mmol) was converted to the free amine by reaction with triethylamine (0.215 g, 5mmol) in methanol. The Schiff base ligands were prepared by reacting equimolar amounts of the *o*–acetoacetanisidide (1.0362 g, 5 mmol) or *o*–acetoacetanilide (0.886 g, 5mmol) and 2–aminoethanethiol (0.385 g, 5 mmol) in methanol at 0 °C in an ice bath under N_2 atmosphere. After stirring approximately for 2 h, the ligand (**5a**) was separated, washed several times with hot methanol and then dried in vacuum. The ligand (**5a**) was recrystallized in MeOH and obtained as pale yellow solid. Since the ligand (**6a**) was not isolated, the yellow colored solution was used as is for the synthesis of complex (**6b**).

2.5. Synthesis of Complexes (1b)–(5b)

The sample of the appropriate Schiff base ligand (2 mmol) was dissolved in 30 mL of absolute ethanol and to this was added a hot ethanolic solution of *cis*-$MoO_2(acac)_2$ (0.652 g, 2 mmol) with vigorous stirring. The reaction mixture was then refluxed on a water bath for 8 h and the precipitates, which separated out from their respective solutions, were filtered under reduced pressure, washed several times with hot EtOH and dried in vacuum.

2.6. Synthesis of Complex (6b)

A hot ethanolic solution of *cis*-$MoO_2\,(acac)_2$ (0.652 g, 2 mmol) was added to the ligand (**6a**) solution, with vigorous stirring, since the ligand (**6a**) was not isolated, the yellow colored solution was used as is for the synthesis of complex (**6b**). The reaction mixture was then refluxed on a water bath for 8 h and the precipitate which separated, out was filtered under reduced pressure, washed several times with hot EtOH and dried in vacuum..

3. Results & Discussion

Bis (acetylacetonato) dioxomolybdenum (VI), $MoO_2\,(acac)_2$, undergoes ligand exchange with the Schiff bases (**1a**)–(**6a**) in ethanol and complexes of the type $[MoO_2(L)(EtOH)]$ (where H_2L = Schiff base) are formed as follows:

$$\text{EtOH}$$

$$cis\text{-}MoO_2(acac)_2 \;+\; H_2L \xrightarrow[\text{Reflux}]{} cis\text{-}[MoO_2(L)(EtOH)] \;+\; 2\ acacH$$

Elemental analyses, molar conductance, and spectroscopic studies (IR, UV-vis and ^1H NMR) data are given for all the ligands and complexes (Tables I, II, and III). The analytical data shows that the Schiff bases are tridentate ligands, hence, complete replacement of the bidentate acetylacetone occurs under the reaction conditions and ethanol occupies the sixth coordination site. The analytical data further support the formulation of the complexes as $[MoO_2(L)(EtOH)]$ (see structures I and II for the ligands and III and IV for the complexes in Fig. 1 and 2). The thermo gravimetric analyses also support the above structures of the complexes. The weight loses registered at T > 160° C corresponded to coordinated ethanol. The presence of ethanol is further supplemented through IR and NMR spectral data. These complexes are found to be insoluble in methanol, ethanol, acetone, dichloromethane, diethyl ether and acetonitrile. However, they are soluble in dimethylformamide and dimethyl sulfoxide. The conductance of the complexes in DMF shows that they are all non-electrolytes (λ_M = 2.2–4.8 $ohm^{-1}\ cm^2\ mol^{-1}$). The complexes are diamagnetic as expected for $4d^0$ system.

4. IR Spectra

The IR spectra of the complexes (Table 2) exhibit two bands in the region 940–950 and 905–915 cm^{-1} regions due to the ν_{sys}(O=Mo=O) and ν_{asy}(O=Mo=O) stretches, respectively; (Kathale et al., 2001; Chen et al., 1976; Rao et al., 1993; Syamal et al., 1989; Kurapati et al., 2016) indicating O=Mo=O in the *cis* form. The MoO_2^{+2}moiety prefers to form *cis*–dioxo grouping due to the maximum utilization of the d–orbitals for chemical bonding (Rao et al., 1993; Syamal et al., 1989; Pickett et al., 1982; Kathale et al., 2001).

The absence of an IR band at *ca*. 2500 cm^{-1} due to the ν(SH) stretch in the ligands **(1a)**–**(4a)** indicates the thione (C=S) nature of the ligands. These Schiff bases **(1a), (2a), (3a)** and **(4a)** exhibit a strong band in the range 1062–1066 cm^{-1} due to the ν(C=S) stretching vibration[14]. The presence of this band in the ligands supports the thione nature of the above Schiff bases. In the dioxomolybdenum (VI) complexes this band disappears and a new band at 677–832 cm^{-1} appears due to the ν(C–S) stretching vibration (Pickett et al., 1982), which suggests thio-enolization of the >C=S group and coordination of the S atom to the metal center. The IR spectra of the ligands and complexes (Table 2) exhibit a broad band in the region 2990–3269 cm^{-1} due to the ν(N–H) stretching vibration, present in the β–diketone moiety. A strong band in all of the Schiff bases in the region 1540–1600 cm^{-1} (Table 2) is assigned to ν(C=N) (Dave et al., 1981; Kathale et al. 2001). This band disappears on complex formation and a new band is observed in the range 1588–1627 cm^{-}

^{1} due to the >C=N–C=N< framework in the complexes indicating the participation of the azomethine nitrogen in coordination (Kathale et al. 2001). The Schiff bases exhibit the ν(O–H) stretching vibration at 3405–3440 cm^{-1} which is due to enolic OH. The complexes exhibit a broad band in the 3411–3451 cm^{-1} region due to the ν(O–H) stretching vibration, which shows coordination of a solvent molecule to the labile binding site (Kathale et al. 2001). The Schiff bases exhibit the ν(C–O) stretching vibration at 1114–1173 cm^{-1} which shifts by 10–35 cm^{-1} to lower wavenumber in the complexes indicating the coordination of the enolic oxygen atom to molybdenum (Rao et al., 1999). Thus the IR data indicate that the Schiff bases behave as tridentate ligands coordinating through the azomethine nitrogen, enolic oxygen and thioenolic sulfur atoms.

5. Electronic Spectra

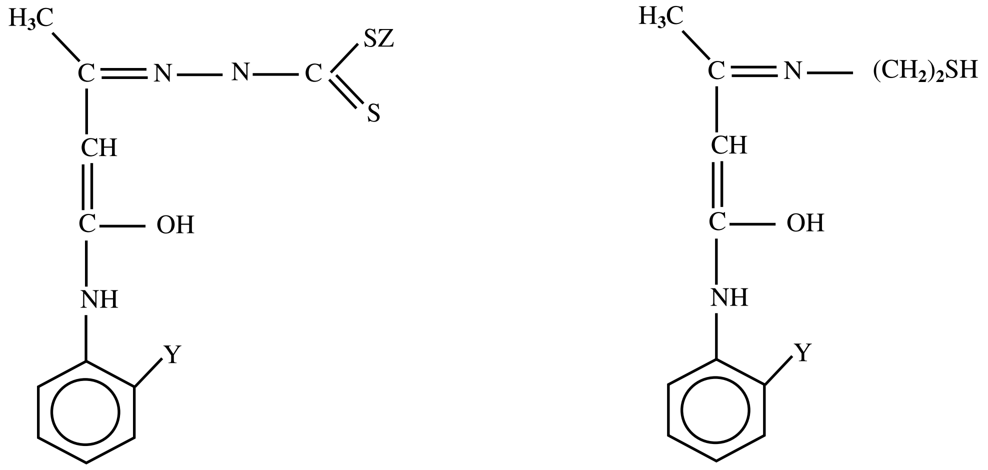
The electronic spectra of the ligands (1a)–(5a) and complexes (1b)–(6b) were studied in the concentration of 1 x 10^{-4} m in dmf. In addition to the ligand based peaks in the range 345–370 nm, a broad band was observed in the region 350–385 nm in the complexes which may be due to the ligand to metal charge transfer transitions (lmct) between the lowest empty d–orbital (dπ) of molybdenum and the highest occupied ligand molecular orbital (pπ). As expected for a $4d^0$ system, no d–d transitions were observed. (see table 3).

6. Proton NMR Spectra

The ^{1}H NMR spectral data (Table 3) of the ligands exhibits two signals in the range 10.07 – 12.72 ppm (singlets, 1H each) due to the NH and enolic OH protons. The presence of NH protons and absence of the SH protons in the spectra of the ligands **(1a)–(4a)** indicate the thione nature of the Schiff bases which is also supported by the IR spectra. The absence of the signals due to enolic OH and NH protons in the spectra of the complexes indicate coordination through the enolic oxygen, thio-enolization and consequent deprotonation of NH. The Schiff bases display a multiplet at 6.94–7.96 ppm due to the aromatic protons and this band did not show any appreciable change upon complexation. The EtOH coordination to molybdenum is supported by the presence of OH (singlet, 2.48–2.52 ppm), CH_3 (triplet, 1.45 ppm, J = 6.3 Hz) and CH_2 (quartet, 3.26 ppm, J = 7.2 Hz).

On the basis of the IR, NMR and electronic spectra, the structures III and IV in Fig. 2 with tridentate ONS donor ligand occupying the meridonial position are suggested for the complexes.

As is evident from the above data, the Schiff base ligands behave as dibasic tridentate ligands and coordinate to the MoO_2 moiety through the azomethine nitrogen, enolic oxygen and enolic sulfur. The sixth site in the complexes is occupied by an EtOH molecule, which allows the binding and displacement of several substrate molecules during their use as catalysts in the oxidation reactions.

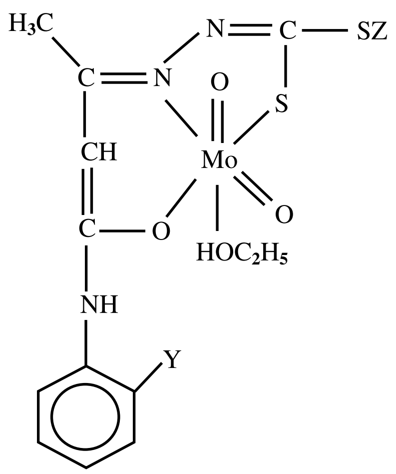


I **II**

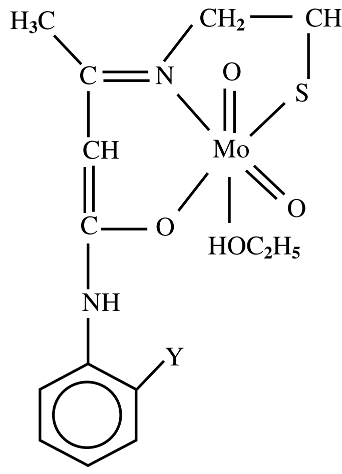
	Z	Y	Abbreviations
(1a)	$-CH_2C_6H_5$	$-OCH_3$	H_2ANS – SBDTC
(2a)	$-CH_2C_6H_5$	----	H_2ANL – SBDTC
(3a)	$-CH_3$	$-OCH_3$	H_2ANS – SMDTC
(4a)	$-CH_3$		H_2ANL – SMDTC

	Y	Abbreviations
(5a)	$-OCH_3$	H_2ANS – AmET
(6a)	---	H_2ANL – AmET

Figure 1: Chemical structures of tridentate Schiff base ligands.



III



IV

	Z	Y	Abbreviations
(1a)	$-CH_2C_6H_5$	$-OCH_3$	H_2ANS – SBDTC
(2a)	$-CH_2C_6H_5$	----	H_2ANL – SBDTC
(3a)	$-CH_3$	$-OCH_3$	H_2ANS – SMDTC
(4a)	$-CH_3$		H_2ANL – SMDTC

	Y	Abbreviations
(5a)	$-OCH_3$	H_2ANS – AmET
(6a)	---	H_2ANL – AmET

Figure 2: Suggested structures of molybdenum dioxo Schiff base complexes.

Sr. No.	**Ligands/Complexes**	**Color**	**F. W.^{a}**	**Yield (%)**	**M.p.^{b} (^{O}C)**	**Elemental Analysis (%) Found (Calculated)**				
						C	**H**	**N**	**S**	**Mo**
(**1a**)	H_2ANS–SBDTC $C_{19}H_{21}N_3O_2S_2$	White	387	70	135	58.34 (58.91)	5.78 (5.42)	10.23 (10.85)	16.84 (16.53)	---
(**1b**)	[MoO_2(ANS–SBDTC)(X)] $MoC_{21}H_{25}N_3O_5S_2$	Pale Green	559.4	65	> 250	45.12 (45.1)	4.49 (4.5)	7.48 (7.5)	11.96 (11.46)	17.52 (17.15)
(**2a**)	H_2ANL–SBDTC $C_{18}H_{19}N_3OS_2$	Pale yellow	357	75	150	60.58 (60.50)	5.41 (5.32)	11.04 (11.76)	17.10 (17.92)	---
(**2b**)	[MoO_2(ANL–SBDTC)(X)] $MoC_{20}H_{22}N_3O_4S_2$	Olive Green	528.5	55	> 250	45.53 (45.5)	4.12 (4.1)	7.88 (7.9)	12.69 (12.13)	18.42 (18.15)
(**3a**)	H_2ANS–SMDTC $C_{13}H_{17}N_3O_2S_2$	White	311.4	80	136	50.62 (50.14)	5.57 (5.50)	13.53 (13.49)	20.64 (20.59)	---
(**3b**)	[MoO_2(ANS–SMDTC)(X)] $MoC_{15}H_{23}N_3O_5S_2$	Grey	485.4	60	> 250	37.25 (37.1)	4.61 (4.77)	8.36 (8.66)	13.82 (13.21)	19.42 (19.76)
(**4a**)	H_2ANL–SMDTC $C_{12}H_{14}N_3O_2S_2$	Pale yellow	296.39	75	160	48.71 (48.62)	4.72 (4.76)	14.22 (14.17)	21.73 (21.64)	---
(**4b**)	[MoO_2(ANL–SMDTC)(X)] $MoC_{14}H_{18}N_2O_4S_2$	Algae	437.94	65	> 250	38.37 (38.36)	4.15 (4.11)	6.29 (6.3)	14.21 (14.61)	21.97 (21.90)
(**5a**)	H_2ANS–AmET $C_{13}H_{18}N_3O_2S$	Pale yellow	266.36	80	120	58.91 (58.62)	6.13 (6.8)	10.62 (10.51)	11.79 (12.0)	---
(**5b**)	[MoO_2(ANS–AmET)(X)] $MoC_{15}H_{22}N_2O_5S$	Olive Green	437.94	55	> 250	41.11 (41.10)	5.10 (5.02)	6.33 (6.3)	7.66 (7.3)	21.95 (21.90)
(**6a**)	H_2ANL–AmET $C_{12}H_{15}N_2OS$		c	c	c	c	c	c	c	c
(**6b**)	[MoO_2(ANL–AmET)(X)] $MoC_{14}H_{19}N_2O_4S$	Brown	407	60	> 250	41.27 (41.2)	4.61 (4.67)	6.82 (6.88)	7.14 (7.86)	23.48 (23.57)

Table 1: Analytical Physical Data for the Ligands and Complexes
X = EtOH, ^{a}Empirical Formula Weight, ^{b}Complexes decompose at > 250^{0}C, ^{c}could not be isolated.

Sr. No.	Ligands/Complexes	ν(C=N)/ ν(C=N–C=N)	ν(C–S)	ν(C=S)	ν(OH)	ν(NH)	ν(Mo=O)		ν(C– O)
							sym	asym	
(**1a**)	H_2ANS–SBDTC	1599 m		1064 s	3416 w	3252 w			1117 m
(**1b**)	[MoO_2(ANS–SBDTC)(X)^a]	1607 m	729 m		3430 w	3206 w	946 s	914 s	1087 m
(**2a**)	H_2ANL–SBDTC	1598 m		1065 s	3440 w	3269 w			1229 m
(**2b**)	[MoO_2(ANL–SBDTC)(X)]	1610 m	677 m		3430 w	3198 w	945 s	913 s	1263 m
(**3a**)	H_2ANS–SMDTC	1540 m		1062 s	3440 w	3258 w			1117 m
(**3b**)	[MoO_2(ANS–SMDTC)(X)]	1599 m	750 m		3411 w	3219 w	945 s	913 s	1089 m
(**4a**)	H_2ANL–SMDTC	1598 m		1066 s	3439 w	3257 w			1173 m
(**4b**)	[MoO_2(ANL–SMDTC)(X)]	1621 m	832 m		3433 w	3199 w	945 s	913 s	1089 m
(**5a**)	H_2ANS–AmET	1595 m		1060 s	3405 w	2990 w			1114 m
(**5b**)	[MoO_2(ANS– AmET)(X)]	1588 m	721 m		3451 w	3065 w	949 s	906 s	1123 m
(**6a**)	H_2ANL–AmET	b	b	b	b	b	b	b	b
(**6b**)	[MoO_2(ANL–AmET)(X)]	1627 m	707 m		3431 w	3060 w	941 s	910 s	1157 m

Table 2: Infrared Spectral Data (cm^{-1}) of the Ligands and Complexes

^{a}X = EtOH, ^{b}could not be isolated.

Sr. No.	Ligands/Complexes	^{1}H NMR^{a}δ, ppm	UV^b λ(ε M^{-1}cm^{-1})
(**1a**)	H_2ANS–SBDTC	1.28 (s, –CH_3, 3H); 3.90 (s, –OCH_3, 3H); 3.47 (s, –CH_2, 2H); 7.40 – 7.32 (m, ArH, 9H); 12.72 (s, –OH, 1H); 10.07 (s, –NH, 1H).	345
(**1b**)	[MoO_2(ANS–SBDTC)(X)]^c	1.123 (s, –CH_3, 3H); 3.90 (s, –OCH_3, 3H); 1.95 (t, –CH_3, 3H, J = 6.2 Hz); 3.36 (q, –CH_2, 2H, J = 7.2 Hz); 3.41(s, –CH_2, 2H); 7.24 – 6.92 (m, ArH, 9H); 2.48 (s, –OH, 1H); 10.15 (s, –NH, 1H).	350 (3200)
(**2a**)	H_2ANL–SBDTC	1.27 (s, –CH_3, 3H); 3.48 (s, –CH_2, 2H); 7.39 – 7.31(m, ArH, 10H); 12.72 (s, –OH, 1H); 10.07 (s, –NH, 1H).	370
(**2b**)	[MoO_2(ANL–SBDTC)(X)]	1.22 (s, –CH_3, 3H); 1.96 (t, –CH_3, 3H, J = 6.2 Hz); 3.33 (q, –CH_2, 2H, J = 7.2 Hz); 3.47(s, –CH_2, 2H); 7.51 – 7.06 (m, ArH, 10H); 2.48 (s, –OH, 1H); 10.16 (s, –NH, 1H).	385 (2800)
(**3a**)	H_2ANS–SMDTC	1.25 (s, –CH_3, 3H); 3.90 (s, –OCH_3, 3H); 7.40 – 7.32 (m, ArH, 4H); 12.72 (s, –OH, 1H); 10.07 (s, –NH, 1H).	370
(**3b**)	[MoO_2(ANS–SMDTC)(X)]	1.22 (s, –CH_3, 3H); 3.90 (s, –OCH_3, 3H); 1.94 (t, –CH_3, 3H, J = 6.3 Hz); 3.35 (q, –CH_2, 2H, J = 7.1 Hz); 7.53 – 7.07 (m, ArH, 4H); 2.50 (s, –OH, 1H); 10.15 (s, –NH, 1H).	380 (2000)
(**4a**)	H_2ANL–SMDTC	1.26 (s, –CH_3, 3H); 7.41 – 7.32 (m, ArH, 4H); 12.70 (s, –OH, 1H); 10.07 (s, –NH, 1H).	370
(**4b**)	[MoO_2(ANL–SMDTC)(X)]	1.24 (s, –CH_3, 3H); 1.94 (t, –CH_3, 3H, J = 6.3 Hz); 3.33 (q, –CH_2, 2H, J = 7.1 Hz); 7.51 – 7.05 (m, ArH, 5H); 2.50 (s, –OH, 1H); 10.16 (s, –NH, 1H).	380 (2000)
(**5a**)	H_2ANS–AmET	1.27 (s, –CH_3, 3H); 3.91 (s, –OCH_3, 3H); 2.52 (t, –CH_2, 2H, J = 6.2 Hz); 2.78 (t, –CH_2, 2H, J = 6.2 Hz); 7.51 – 7.05 (m, ArH, 5H); 12.71 (s, –OH, 1H); 10.07 (s, –NH, 1H).	370
(**5b**)	[MoO_2(ANS–AmET)(X)]	1.25 (s, –CH_3, 3H); 3.91 (s, –OCH_3, 3H); 1.03 (t, –CH_3, 3H, J = 6.2 Hz); 3.27 (q, –CH_2, 2H, J = 7.3 Hz); 2.43 (t, –CH_2, 2H, J = 6.3 Hz); 2.76 (t, –CH_2, 2H, J = 6.2 Hz); 6.9 – 8.25 (m, ArH, 5H); 2.51 (s, –OH, 1H); 10.15 (s, –NH, 1H).	380 (1600)
(**6a**)	H_2ANL–AmET	d	d
(**6b**)	[MoO_2(ANL–AmET)(X)]	1.222 (s, –CH_3, 3H); 1.177 (t, –CH_3, 3H, J = 6.3 Hz); 3.27 (q, –CH_2, 2H, J = 7.3 Hz); 2.99 (t, –CH_2, 2H, J = 6.1 Hz); 3.12 (t, –CH_2, 2H, J = 6.2 Hz); 7.8 – 8.7 (m, ArH, 5H); 2.51 (s, –OH, 1H); 10.15 (s, –NH, 1H).	370 (2800)

Table 3: ^{1}H NMR and UV-Vis Spectral Data of Ligands and Complexes

^{a}In DMSO d_6, ^{b}In DMF, ^{c}X = EtOH, ^{d}could not be isolated.

7. References

i. Ali, M.A.; Trafdar, M.T.H., (1977)**,** Metal Chelates of Schiff Bases Formed by Condensation of 2-Methoxybenzaldehyde and 2-Hydroxybenzaldehyde with S-Benzyldithiocarbazte, J. Inorg. Nucl. Chem.**,** 39, 1785.
ii. Chen, G.J.J.; Mc Donald J.W.; Newton, W.E., (1976), Synthesis of Molybdenum (VI) and Molybdenum (V) Complexes Using Oxo Abstraction by Phosphines. Mechanistic Implications, Inorg. Chem.**,** 15, 2612.
iii. Cramer, S.P.; Gray, H.B.; Rajagopalan, K.V., (1979), The Molybdenum Site of Sulfite Oxidase. Structural Information from X-ray Absorption Spectroscopy, J. Am. Chem. Soc., 101, 2772.
iv. Dave L.D.; Thampy, S.K., (1981), Pyridine Adduct of Nickel (II) Thiosemicarbazones, J. Indian. Chem. Soc.**,** 58, 538.

v. Das M.; Livingstone, S.E., (1976), Metal Chelates of Dithiocarbazic Acid and its Derivatives. IX. Metal Chelates of Ten New Schiff Bases Derived From S-Methyldithiocarbazate, Inorg. Chim. Acta19, 5.

vi. Gates, B.C.; Katzer, J.R.; Schuit, G.C.A., (1979), Chemistry of Catalytic Processes; McGraw Hill: New York, 390.

vii. Green. M.L.H. (1979), In Proceedings of Third International Conference on the Chemistry and Uses of Molybdenum; Barry, H.F.; Mitchell, P.C.H.; Eds.; Climax Molybdenum Company: Ann Arbor, MI,; 34.

viii. Ilhan Celylan B.; Deniz N.G.; Kahraman S. and Ulkuseven B., (2015), cis – Dioxomolybdenum(VI) complexes of a new ONN chelating thiosemicarbazidato ligand; synthesis, characterization, crystal, molecular structures and antioxidant activities, Spectrochim Acta A Mol Biomol Spectrosc., 141, Apr. 272 – 7.

ix. Kathale, N.; Rao, S.N.; Rao, N.N.; Munshi, K.N., (2001), Synthesis and Characterization of Some Dioxomolybdenum(VI) Complexes with O, N, S Donor Schiff Bases Derived From S-Methyldithiocarbazate, S-Benzyldithiocarbazate, 2-aminoethanethiol and Substituted Salicylaldehydes. Synth. React. Inorg. Met.-Org. Chem. 31(5), 859.

x. Pickett, C.; Kumar, S.; Vella, P.A.; Zubieta, J., (1982), Investigation of Coordination Chemistry of Molybdenum with Facultative Tetradentate Ligands Possessing N_2S_2 Donor Sets. 2. Preparation, Chemical Characterization and Electrochemical Study of Molybdenum (VI), (V) and (IV) Oxo Complexes. Inorg. Chem.**,** 21, 908.

xi. Rao, S. N.; Munshi, K.N.; Rao, N.N., (1999), Catalytic Air Oxidation of Cyclooctene Using [cis–MoO_2(Sal–SH)(DMF)] (Sal–SH = Salicylidene Salicyloyl Hydrazinato–) and its Zeolite–Y Encapsulated Composite. J. Mol. Catal. A: Chem., 145, 203.

xii. Rao, S. N.; Munshi, K.N.; Rao, N.N.; (2000), Catalytic Oxidation of Styrene Using cis–MoO_2(L)(solv) [L = Salicylidene Salicyloyl Hydrazine)] and its Zeolite Composite as Catalyst in Presence of Molecular Oxygen. J. Mol. Catal. A: Chem., 156, 205.

xiii. Rao, S. N.; Munshi, K.N.; Rao, N.N.; Bhadbhade, M.M.; Suresh, E., (1999), Synthesis Spectral and X–ray Structural Characterization of cis–MoO_2(L)(solv)(Salicyloyl Salicylidene Hydrazine) and its Use as Catalytic Oxidant. Polyhedron,18, 2491.

xiv. Rao, S.N.; Jaiswal, M.N.; Mishra, D.D.; Maurya R.C.; Rao, N.N., (1993), Synthesis and Characterization of cis–Dioxomolybdenum(VI) Schiff Base Complexes Derived from 1-Phenyl-3-methyl-4-benzoyl-5-pyrazalone. Polyhedron**,** 12, 2045.

xv. Syamal A.; Maurya, M.R., (1989), Coordination Chemistry of Schiff Base Complexes of Molybdenum. Coord. Chem. Rev.**,** 95, 183.

xvi. Satish Kumar Kurapati; Samudrnil Pal, (2016), cis – Dioxomolybdenum (VI) complexes with unsymmetric linear tetradentate ligands: syntheses, structures and bromoperoxidase activities, Applied organometallic Chemistry, 30 (3), March, 116 – 124.

xvii. Tullius, T.D.; Kurtz, D.M. Jr.; Conradson, S.D.; Hodgson, K.O., (1979), The Molybdenum Site of Xanthine Oxidase. Structural Evidence from X-ray Absorption Spectroscopy. J. Am. Chem. Soc., 101, 2776.