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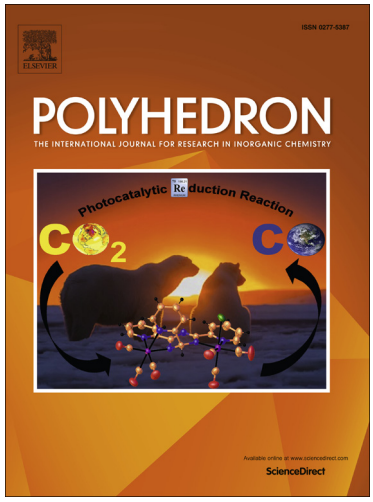

Synthesis, characterization and biomedical activities of molybdenum complexes of tridentate Schiff base ligands. Crystal and molecular structure of $[MoO_2(L^{10})(DMSO)]$ and $[MoO_2(L^{11})(DMSO)]$

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Synthesis, characterization and biomedical activities of molybdenum complexes of tridentate Schiff base ligands. Crystal and molecular structure of $[MoO_2(L^{10})(DMSO)]$ and $[MoO_2(L^{11})(DMSO)]$

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Abstract

The molybdenum complexes of different Schiff base ligands have drawn remarkable attention due to their different biological and analytical activities. Several molybdenum complexes of different Schiff base ligands, L^1 to L^{11} derived from dithiocarbazate, have been synthesized by the reaction of the ligands with molybdenum(VI)acetylacetonate. The complexes were characterized on the basis of IR, ^1H NMR and electronic spectral analyses, along with elemental, magnetochemical and conductometric data. All the complexes are diamagnetic and non-electrolytes in DMF solution. The molecular structures of two complexes were confirmed by X-ray crystallographic studies. Antibacterial and antifungal characteristics of the concerned compounds were investigated against different gram-positive and gram negative bacteria, and against fungi, respectively. Most of the complexes show good activity against fungi and bacteria; in some cases, the complexes were more active than the standard medications Nystatin and Ampicilin respectively.

Keywords: Antibacterial agent; Antifungal agent; Molybdenum; Spectral analysis; X-ray crystallography

1. Introduction

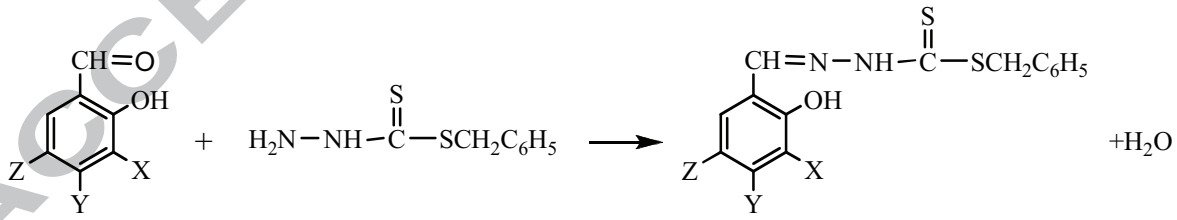
The coordination chemistry of molybdenum(VI) has assumed special importance due to its biochemical significance [1-3] as well as for the involvement of Mo(VI) compounds as catalysts in several industrial processes, such as epoxidation of olefins [4], olefin metathesis [5] and isomerisation of allylic alcohols [6]. The discovery of the presence of ONS donors in the coordination sphere the Mo(VI) centre of oxotransferase enzymes, such asxanthine oxidase, DMSO reductase [7,8] and others, led to the synthesis and exploration of the oxotransfer ability of a number of model complexes that mimic the oxotransferase activity of molybdoenzymes [9].

Oxotransferases catalyze oxidative and reductive oxygen (O^{2-}) transfer reactions and play an important role in the global metabolism of elements like nitrogen, carbon, sulfur and arsenic. These studies also led to the belief that the presence of the sulfur donor is essential for the oxotransfer activity of such systems.

Dithiocarbazate ($NH_2NHCS_2^-$) and its substituted derivatives have been investigated as ligands for a long time [10-13]. These compounds have received much attention for further studies because i) they provide an interesting series of ligands whose properties can be greatly modified by introducing different organic substituent, thereby causing a variation of the ultimate donor properties, ii) the interaction of these donors with metal ions gives rise to complexes of different geometries and properties, and iii) these complexes are potentially biologically active. The present study focuses on the synthesis, characterization and biological studies of molybdenum(VI) complexes of tridentate Schiff base ligands derived from dithiocarbazate.

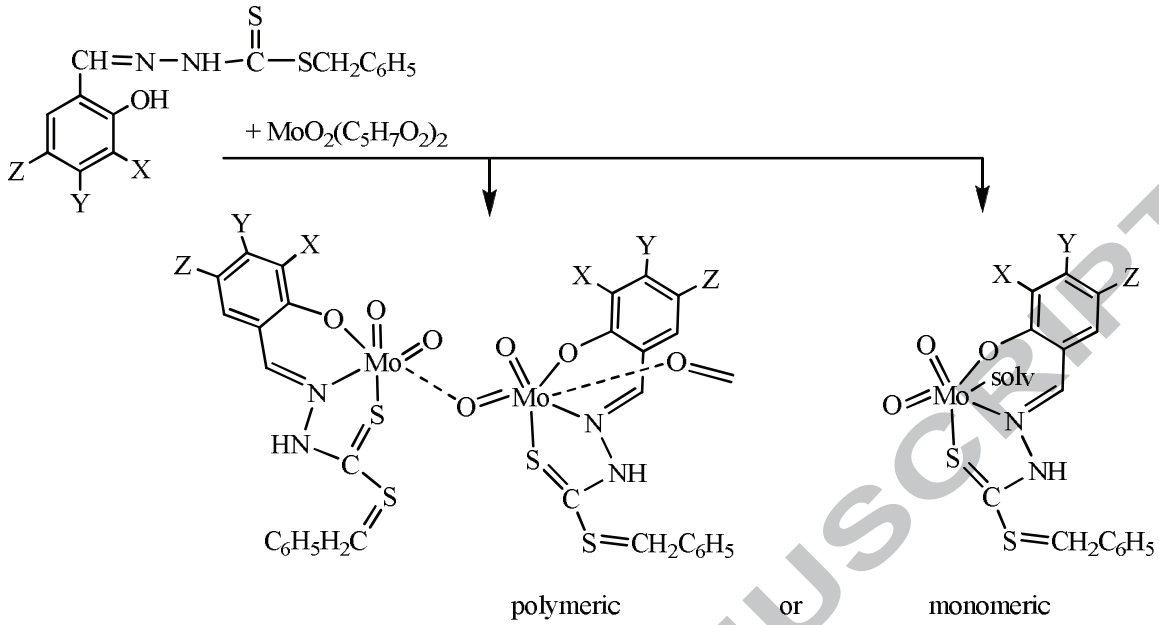
2. Results and Discussion

In model studies of molybdenum complexes, the selection of the ligand is of substantial importance. Earlier work [14-15], including rate and activation parameter data, indicated that at least one sulfur atom is essential for the resulting complex to be suitable for the kind of model studies described herein. Considering extended X-ray absorption fine structure (EXAFS) results, we thought that it is appropriate to concentrate on ONS ligands, also to avoid the formation of the biologically irrelevant μ-oxido-molybdenum(V) dimer in the course of the reaction. In this study, eleven Schiff base ligands (L^1- L^{11}) with ONS donor sets have been synthesized [10-13], the names and structures of which are provided in Table-S1. The general reaction Schemes 1 and 2 for the synthesis of the ligands and complexes can be represented as follows:



[X = H, Cl, Br, OMe, OEt; Y = $N(C_2H_5)_2$, H; Z = NO_2, Br, Cl, H]

Scheme 1



Scheme 2

Almost all of the molybdenum complexes prepared were orange in color, except for a few which were brown, golden-yellow or black (Table 1). The complexes showed a decomposition point ataround 200 °C (Table 1).

2.1. IR Spectra

The IR data (Table 2) of some of the complexes feature the presence of a broad band at about 3420 cm^{-1} due to the $\upsilon_{(OH)}$ stretch, indicative of the presence of water either in the coordinated or uncoordinated form. The Schiff bases exhibit a sharp strong band at 1620-1600 cm^{-1} due to the $\upsilon_{(C=N)}$ stretching frequency. In case of the molybdenum complexes, this band is shifted by 5-25 cm^{-1} to low frequency, indicating the coordination of the azomethine nitrogen atom to the molybdenum ion [16]. Medium to strong bands at about 1294-1250 cm^{-1} for the free ligands are assigned to $\upsilon_{(C-O)}$ (phenolic) which undergo a shift of 5-20 cm^{-1} to low frequency in the case of the molybdenum complexes [17]. In some cases, this band weakens in intensity for the complex. This suggests that the phenolic oxygen atom also coordinates to the molybdenum ion. No appreciable change is observed in the position of the band at about 1090-1030 cm^{-1}, which is assigned to the $\upsilon_{(N-N)}$ stretch in the case of the molybdenum complexes.

The IR spectra (Table 2) of the complexes exhibit two bands in the regions 980-950 and 850-900 cm^{-1} due to the $\upsilon(sym)_{(O=Mo=O)}$ and $\upsilon(asym)_{(O=Mo=O)}$ stretches, respectively, the reported range being $\upsilon(sym)$ = 892-964 cm^{-1} and $\upsilon(asym)$ = 840-925 cm^{-1} for the majority of dioxidomolybdenum(VI) complexes [18]. These bands are absent in the free ligand, thus proving the formation of the dioxidomolybdenum complexes. These IR data are also indicative of the presence of a *cis*-MoO_2^{2+} moiety, as the *trans*-MoO_2^{2+} moiety would show only one IR-active $\upsilon_{(O=Mo=O)}$ band due to the asymmetric stretch. The MoO_2^{2+} moiety prefers to form *cis*-dioxido groups due to optimal utilization of the d-orbitals for chemical bonding. A medium strong band at about 520-560 cm^{-1} for the molybdenum complexes is assigned to the $\upsilon_{(Mo-N)}$ stretching mode [19]. This band is absent in the free ligands. A weak band in the range 420-440 cm^{-1} is due to the molybdenum-sulfur stretching frequency [20]. Thus, from the above discussion, it is clear that the ligands are attached to the molybdenum atom of the MoO_2^{2+} moiety via the azomethine nitrogen, phenolic oxygen and thiolato sulfur atoms; the ligands are thus acting as tridentate dinegative ligands.

2.2. ^{1}H NMR Spectra

The NMR spectra of the complexes (Table 3) account for all the protons of the ligands in the complexes except for the phenolic proton and the thiol sulfur proton, which are lost during complex formation, thus evidencing coordination via the phenolic oxygen and thiolato sulfur atoms of the ligand. Multiplet peaks in the range δ 7-9 ppm are due to the phenyl protons of the salicylaldehyde and benzyl moieties. The range is large because different substituents are attached to the phenyl group. A singlet in the range δ 8-9 ppm is due to the azomethine proton of the ligand [21]. The peak of the $–SCH_2$ proton appears in the range δ 3.3-4.2 ppm. These peaks are common for all of the complexes. The complexes $[MoO_2(L^2)(H_2O)]$ and $[Mo(O_2)(L^5)]$, where a methoxy group is present in the ligand moiety, show a separate peak in the NMR spectra at δ 3.3 ppm [21]. The complex $[MoO_2(L^3)(CH_3CH_2OH)]\cdot H_2O$ shows two separate peaks at δ 3.1 ppm (for the $–CH_2$ protons) [22] and δ 1.3 ppm (for the $–CH_3$ protons) [23]. This type of separate peaks for $–CH_3$ and $–CH_2$ protons is found in all complexes where the CH_3CH_2OH molecule is attached to the complex, and in fact proves coordination of CH_3CH_2OH (stemming from the solvent) to the molybdenum ion. Many molybdenum complexes found in the literature are comparable, i.e. associated with the solvent molecule. The other peaks found in some spectra are due to H_2O present in the complex and/or to a contaminant in DMSO-d_6 [24].

2.3. Molar Conductance and Magnetochemical Data

The molar conductance data indicate that all the compounds are non-electrolytes in DMF, while the magnetic susceptibility data reveal that all compounds are diamagnetic (Table 1).

2.4. Electronic Spectra

The spectra were taken in dimethylsulfoxide (DMSO) and show only one peak at 320-330 nm (Table 3). A band in this region may be attributed to a ligand-to-metal charge transfer or to an intraligand transition. The absence of bands due to d-d transitions in the range 650-420 nm in the spectra of these complexes supports the presence of the molybdenum(VI) ion [25].

From all of the data, we can deduce two different types of structures for the above complexes, viz. a polymeric and a monomeric one. In either case, Mo is in an octahedral coordination sphere; Figs. 1 (a) and 1(b).

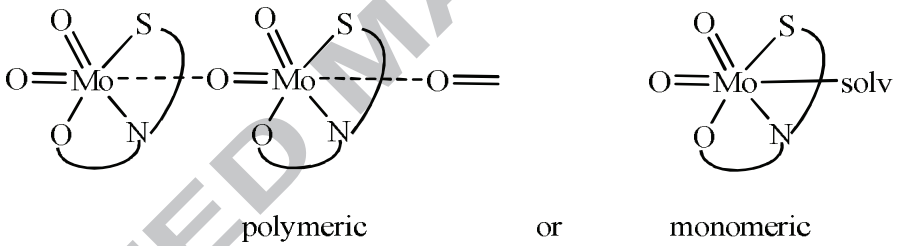


Fig. 1 **1(a)** **1(b)**

From the above structure it is clear that some complexes have a polymeric structure without a solvent molecule, while other complexes have a solvent molecule (ethanol) attached, within the normal octahedral structure of the molybdenum complex. This statement is supported by the crystal structure of the complexes. A derivative of $[MoO_2(L^1)(H_2O)]$ crystallized as [(*cis*-MoO_2L^1)(μ-O)(*cis*-$MoOL^1(OH_2)$)·$CHCl_3$ from chloroform, and had been studied by X-ray crystallography [26]. The detailed crystallographic analyses of $[MoO_2(L^{10})(C_2H_5OH)]$ and $[MoO_2(L^{11})(C_2H_5OH)]$, recrystallized as $[MoO_2(L^{10})(DMSO)]$ and $[MoO_2(L^{11})(DMSO)]$ from DMSO, are discussed in sections 2.5 and 2.6.

2.5. Crystal structure and relevant data of the complex [$MoO_2(L^{10})$(DMSO)]

The molecular structure and atom numbering scheme for [$MoO_2(L^{10})$(DMSO)] are shown in Fig 2 and selected atomic distances and angles are provided in Table 5. The Mo1 atom features in a *cis* $[MoO_2]^{2+}$ core, to which is also bonded a dinegative tridentate S-benzyl-3-(2-hydroxy-3,5-dichlorophenyl)-methylene-dithiocarbazate ligand via sulfur, oxygen and nitrogen donors, and a DMSO molecule to complete the octahedral coordination geometry. In the structure of the complex, the molybdenum atom is octahedrally surrounded by two terminal oxido ligands (the oxygen atoms O1 and O2), by the phenolic oxygen O3, imine nitrogen N2 and sulfur S2 atoms belonging to the ligand, and finally by the oxygen atom O4 from the coordinated DMSO. The values of the Mo=O bonds, 1.7075(9) and 1.7082(9) Å, are common for *cis*-MoO_2 complexes. The ligand forms one six- and one five-membered chelate ring with the central Mo ion. The Mo-O3, Mo-N2 and Mo-S2 bond lengths are 1.9283(8), 2.3189(10) and 2.4528(3) Å, respectively. The Mo-O4 bond length is 2.2431(9) Å.

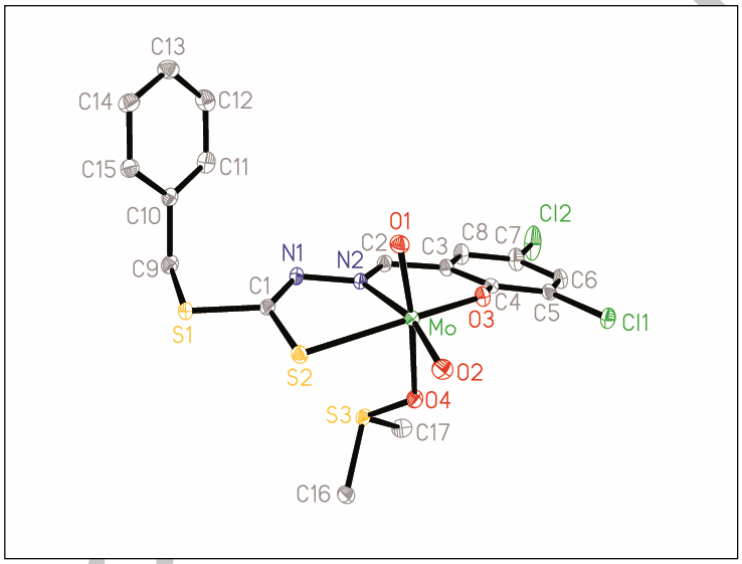


Fig.-2: **Structure of [MoO_2L^{10}DMSO]**

2.6. Crystal structure and the relevant data of the complex [$MoO_2(L^{11})$(DMSO)]

The molecular structure and atom numbering scheme for [MoO_2 (L^{11})(DMSO)] are shown in Fig. 3 and selected atomic distances and angles are provided in Table 6. In the ORTEP plot of the complex, the molybdenum atom is octahedrally surrounded by two terminal oxido-ligands, O1 and O2, the phenolic oxygen O4, imine nitrogen N2 and sulfur S2 atoms belonging to the ligand, and finally by the oxygen O3 atom from the coordinated DMSO molecule. The values of the

Mo=O bonds, ranging from 1.672(13) and 1.689(14) Å, are usual for *cis*-MoO_2 complexes. The ligand forms one six- and one five-membered chelate ring with the Mo atom. The Mo-O4 and Mo-N2 bond lengths are 1.946(13) and 2.293(13) Å respectively. The Mo-O3 bond length is 2.241(15) Å.

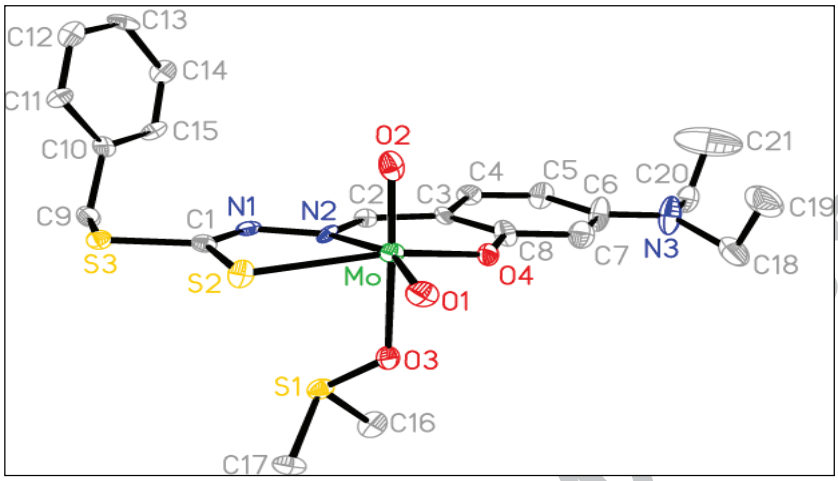


Fig.-3: **Structure of [$MoO_2(L^{11})$(DMSO)**

3. Biomedical Studies

3.1. Antifungal Studies

From Table 7, it is clear that all the five fungi under investigation were very sensitive towards all of the test compounds. Among these, *Fusarium equiseti* and *Colletotrichum corchori* were the most sensitive ones. These growths were 100% inhibited by application of almost all the test compounds, but with time, the parent inhibition of the mycelial growth decreased for some compounds, while for other compounds it remained constant. As a general trend for almost all of the compounds, the sensitivity of the fungi decreased with time. The test compounds exhibited moderate effectiveness against the other fungi. Table 4 shows that *Curvularia lunata* was less sensitive in comparison to the other fungi for most of the compounds. The data (Tables S4 and S3) reveal that the ligands are more potent antifungal agents than the corresponding complexes. This observation corresponds to that seen for some other cases [27]. However, the observation is in contrast with other transition metal complexes of different Schiff base ligands. Comparing the

activity of the complexes with the standard fungicide Nystatin revealed that almost all of the compounds showed a more pronounced activity than Nystatin.

3.2. Antibacterial Studies

All of the synthesized molybdenum complexes have been screened for their antibacterial activity against selected Gram positive and Gram negative bacteria. The results are summarized in Tables 8 and 9. During the study of the zone of inhibition of Gram positive bacteria (Table 8), it was found that most of the metal complexes show some activity against the bacteria under investigation, although other compounds are inactive. Among the complexes, $[MoO_2(L^5)]$ (23 mm) and $[MoO_2(L^6)]$ (20 mm) showed a remarkable zone of inhibition against *Bacillus megaterium,* clearly more extended than in the case of the antibiotic Ampicillin (15mm). Nearly all of the molybdenum complexes in fact showed very good inhibition zones against all of the Gram positive bacteria, and are thus comparable with Ampicillin. The results for the antibacterial activity of the metal complexes against Gram negative bacteria (Table 9) are almost the same as in the case of Gram positive bacteria, except for two of the bacterial strains (*Vibrio cholerae* and *Escherichia coli)*. In accordance with the data for Gram positive bacteria, the ligand H_2L^1 (Table S4) was found to be very effective against all the Gram negative bacteria except *Escherichia coli*. Individually, $[MoO_2(L^4)]$ showed the most extended zone of inhibition against *Salmonella typhi* (20 mm, Ampicillin 25 mm), while $[MoO_2(L^6)]$ was particularly effective in the inhibition against *Salmonella paratyphi* (21 mm, Ampicillin 12 mm) and *Pseudomonas species* (20 mm, Ampicillin 19 mm). One interesting observation from Table 9 is that, in some cases, the zone of inhibition increases with time, which is not found in case of gram positive bacteria.

It is observed that the molybdenum complexes are more effective against Gram positive than Gram negative bacteria when comparing the data of the zones of inhibition for the Gram positive and Gram negative bacteria. In many cases, more extended zones of inhibition than in the case of Ampicillin have been observed, and in almost all cases, our compounds were comparable to Ampicillin. However, the data (Tables 5, 6, S4 and S5) reveal that the antibacterial activity of most of the complexes is almost the same as that of the ligands. In some cases, the ligands are even more potent, while in other cases the complexes are more potent. So no definite trend could be deduced, and further studies are thus warranted with analogous series.

4. Experimental

4.1. Materials and method

All chemicals were of analytical grade (Sigma Aldrich) or equivalent grades and were used without further purification. The solvents were of reagent grade and dried according to literature procedures. Dioxido-bis(acetylacetonato)molybdenum(VI) ($MoO_2(acac)_2$) was obtained from commercial sources. UV-visible spectra were recorded on a Shimadzu UV-visible spectrophotometer in pure DMSO. Conductance measurements were carried out on a conductivity bridge Hanna instrument HI-8820 in pure DMF. Magnetic measurements were performed on a Gouy Balance which was calibrated using $Hg[Co(NCS)_4]$. IR spectra were recorded on a Shimadzu IR 20 spectrophotometer as KBr disks. Microanalyses of the complexes were carried out on a C, N, H analyser at the Institute of Inorganic and Applied Chemistry, University of Hamburg, Germany. ^{1}H NMR spectra were recorded in DMSO with a 400 MHz Bruker DPX-400 spectrometer using TMS as internal standard at the BCSIR Laboratory, Dhaka, Bangladesh.

4.2. Synthesis of the tridentate ligands and their molybdenum complexes derived from S-benzyldithiocarbazate

4.2.1. Synthesis of the ligands of S-benzyldithiocarbazate (H_2L)

The ligands were prepared by condensation of hydrazine with carbondisulfide in alkaline medium to form the S-alkylmercaptocarbonylhydrazines, followed by condensation with the aldehyde or ketone to the hydrazonate.

4.2.2. Preparation of the molybdenum complexes of the ligands derived from *S-benzyldithiocarbazate*

Dioxido-*bis*(acetylacetonato)molybdenum(VI) [$MoO_2(acac)_2$] (3.27 g, 10 mmol) was dissolved in hot ethanol and then added to a hot ethanolic solution (20 mL) of the respective ligands in a ratio of 1:1. The solution was then refluxed for 8 to 12 hours on a water bath. After reducing the volume of the refluxed solution, a dark coloured crystalline product appeared from the solution. The crystalline product was then filtered and washed with ethanol several times. The product was then recrystallized from chloroform and dried in a vacuum desiccator over silica gel.

For, $[MoO_2(L_1)(H_2O)]$ Calcd (%) for $C_{15}H_{14}N_2O_4S_2Mo$: C 40.36, H 3.16, N 6.28; found: C 40.32, H 3.10, N 6.25.

For, $[MoO_2(L^2)(H_2O)]$ Calcd (%) for $C_{16}H_{16}N_2O_5S_2Mo$: C 40.34, H 3.39, N 5.88; found: C 40.30, H 3.34, N 5.85.

For, $[MoO_2\,(L^3)(C_2H_5OH)].\,H_2O$, Calcd (%) for $C_{17}H_{24}N_2O_6S_2MoN_2$: C 39.85, H 4.72, N 5.47; found: C 39.82, H 4.70, N 5.44.

For, $[MoO_2(L^4)]$ Calcd (%) for $C_{15}H_{13}N_2O_3S_2MoBr$: C 35.38, H 2.57, N 5.50; found: C 35.35, H 2.55, N 5.48.

$[MoO_2(L^5)]$ Calcd (%) for $C_{15}H_{15}N_3O_6S_2Mo$: C 36.52, H 3.06, N 8.52; found: C 36.48, H 3.04, N 8.50.

For, $[MoO_2(L^6)]$ Calcd (%) for $C_{15}H_{13}N_2O_3S_2MoCl$: C 38.76, H 2.82, N 6.03; found: C 38.74, H 2.80, N 6.01.

For, $[MoO_2(L^7)(C_2H_5OH)].\,H_2O$, Calcd (%) for $C_{17}H_{18}N_2O_5S_2MoBr$: C 35.80, H 3.18, N 4.91; found: C 35.78, H 3.15, N 4.88.

For, $[MoO2(L^8)(C_2H_5OH)].H_2O$, Calcd. (%) for $C_{17}H_{19}N_3O_7S_2Mo$: C 33.08, H 3.10, N 6.81; Found: C 33.05, H 6.78, N 6.79.

For, $[MoO_2(L^9)(C_2H_5OH)]$, Calcd (%) for $C_{17}H_{16}N_2O_4S_2MoBrCl$: C 34.74, H 2.74, N 4.77; found: C 34.72, H 2.70, N 4.75.

For, $[MoO_2(L^{10})(C_2H_5OH)]$Calcd (%) for $C_{17}H_{16}N_2O_4S_2MoCl_2$: C 32.76, H 2.59, N 4.50; Found: C 32.72, H 2.55, N 4.48.

For, $[MoO_2(L^{11})(C_2H_5OH)]$, Calcd (%) for $C_{21}H_{27}N_3O_4S_2Mo$: C 46.24, H 4.99, N 7.70; found: C 46.20, H 4.95, N 7.65.

4.4. X-ray Single Crystal Structure Analysis

During recrystallization from DMSO, the complexes $[MoO_2(L^{10})(C_2H_5OH)]$ and $[MoO_2(L^{11})(C_2H_5OH)]$ crystallized as orange $[Mo(O_2)L^{10}DMSO]$ and brown $[MoO_2(L^{11})(DMSO)]$, by replacement of the C_2H_5OH molecule by DMSO.The datasets for the

compounds were collected with Mo-$K_\alpha$radiation, using a graphite monochromator, and ω-scans at 100 K. An empirical absorption correction was carried out with the program SADABS [28]. All structures were solved with direct methods (SHELXS-97) [29] and refined with full-matrix least-squares on F_o^2, using the program SHELXL-2013 [30]. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were calculated in idealized positions using a riding model with isotropic temperature factors. For the molecular graphics and publication materials, the program package SHELXTL-PLUS (PC v5.03) [31] was used.

4.5. Biological Studies

4.5.1. Antibacterial activities

Antibacterial activities of the ligands and their complexes against selected gram-positive and gram-negative bacteria were investigated by the disc diffusion method. Paper discs (6 mm in diameter) and Petri plates (70 mm in diameter) were used throughout the experiment. Pour plates were made with sterilized melted nutrient agar NA (45 °C) and after solidification of the pour plates, the test organisms (suspension in DMSO) were separately spread uniformly over the plates with sterilized glass rods. The paper discs, after soaking with test chemicals (1% in DMSO), were placed at the centre of the inoculated pour plate. A control plate was also maintained in each case with DMSO. The plates were first kept for four hours at low temperature (4 °C) and the test chemicals diffused from the disc to the surrounding medium in this time. The plates were then incubated at (35±2) °C for growth of test organisms and were observed at 24 and 48 hour intervals. The activity was expressed in terms of the zone of inhibition in mm. The test was repeated three times at a 24 hour interval for statistical analysis

4.5.2. Antifungal activities

The *in vitro* antifungal activities of the complexes against selected phytopathogenic fungi were assessed by the poisoned food technique. Potato Dextrose Agar (PDA) was used as a growth medium. Dimethylsulfoxide (DMSO) was used as the solvent to prepare solutions of the molybdenum complexes. The solutions were then mixed with the sterilized PDA so as to maintain the concentrations of the compounds at 0.01 % (ca. 3 μM). 20 ml of these solutions were each poured into a Petri dish. After the medium had solidified, a 5 mm mycelial disc of each fungus was placed in the centre of each assay plate, along with a control. The linear growth of the fungus was measured in mm after five days of incubation at 25 ± 2 °C.

Table 1. Some physical and analytical data of molybdenum complexes

Complex	Colour	Melting point (°C)	Conductance in DMF ($ohm^{-1}\ cm^2\ mol^{-1}$)	μ_{eff}
$[MoO_2(L^1)(H_2O)]$	Orange	214	00	Diamagnetic
$[MoO_2(L^2)(H_2O)]$	Black	210	00	Diamagnetic
$[MoO_2(L^3)(C_2H_5OH)].\ H_2O$	Orange	110	00	Diamagnetic
$[MoO_2(L^4)]$	Orange	218	00	Diamagnetic
$[MoO_2(L^5)]$	Orange	216	00	Diamagnetic
$[MoO_2(L^6)]$	Orange	210	00	Diamagnetic
$[MoO_2(L^7)(C_2H_5OH)].\ H_2O$	Orange	220	00	Diamagnetic
$[MoO_2(L^8)(C_2H_5OH)].\ H_2O$	Orange	198	00	Diamagnetic
$[MoO_2(L^9)(C_2H_5OH)]$	Golden yellow	220	00	Diamagnetic
$[MoO_2(L^{10})(C_2H_5OH)]$	Brown	184	00	Diamagnetic
$[MoO_2(L^{11})(C_2H_5OH)]$	Brown	200	00	Diamagnetic

Table 2.Selected IR absorption bands (cm^{-1}) of the molybdenum complexes

Ligand/Complex	$\nu_{(OH)}$	$\nu_{(C=N)}$	$\nu_{(C-O)}$	$\nu_{(N-N)}$	$\nu_{(O=Mo=O)}$ (Sym)	$\nu_{(O=Mo=O)}$ (Asym)	$\nu_{(Mo-N)}$	$\nu_{(Mo-S)}$
$[MoO_2(L^1)(H_2O)]$		1598st	1253s	1018s	977s	875ms	540ms	414w
$[MoO_2(L^2)(H_2O)]$	3420 br	1596st	1222s	1029s	906s	873ms	563ms	426w
$[MoO_2(L^3)(C_2H_5OH)].H_2O$	3404 br	1589st	1261st	1083s	975s	856sm	565ms	453w
$[MoO_2(L^4)]$		1596st	1253ms	1022s	981s	842s	540ms	447w
$[MoO_2(L^5)]$		1568s	1267s	1022s	968st	906st	522ms	439w
$[MoO_2(L^6)]$		1598st	1207s	1068sm	952s	833st	547ms	420w
$[MoO_2(L^7)(C_2H_5OH)].H_2O$	3422 br	1583st	1213s	1024s	983s	893ms	543ms	418w
$[MoO_2(L^8)(C_2H_5OH)].H_2O$	3420 br	1598st	1294s	1099st	964s	852ms	509ms	420w
$[MoO_2(L^9)(C_2H_5OH)]$		1589st	1213s	1085s	983s	867ms	545ms	414w
$[MoO_2(L^{10})(C_2H_5OH)]$		1591st	1211s	1085s	987s	896s	549ms	428w
$[MoO_2(L^{11})(C_2H_5OH)]$		1608s	1271sm	1076s	981s	862sm	563ms	428w

Table 3. ^{1}H NMR (δ, ppm) and electronic spectral (nm) data of the molybdenum complexes

Complex	Phenyl proton	Azomethine proton	-SCH_2- proton	Other peaks	λ_{max}
$[MoO_2(L^1)(H_2O)]$	7.2-7.5	7.7	4.2		320
$[MoO_2(L^2)(H_2O)]$	7.0-7.4	8.9	3.8	3.3(-OCH_3)	326
$[MoO_2(L^3)(C_2H_5OH)]. H_2O$	6.9-7.4	8.9	4.0	3.1(-CH_2-) 1.3(-CH_3-)	326
$[MoO_2(L^4)]$	6.9-8.0	8.9	3.3		
$[MoO_2(L^5)]$	7.2-8.5	9.2.	3.9	3.3(-OCH_3)	337
$[MoO_2(L^6)]$	6.9-7.9	8.9	3.3		323
$[MoO_2(L^7)(C_2H_5OH)]. H_2O$	7.2-8.0	9.0	3.4	3.1(-CH_2-) 1.2(-CH_3-)	329
$[MoO_2(L^8)(C_2H_5OH)]. H_2O$	7.0-8.8	9.2	3.4	3.1(-CH_2-) 1.0(-CH_3-)	322
$[MoO_2(L^9)(C_2H_5OH)]$	7.2-7.8	8.7	3.7	3.6(-CH_2-) 1.2(-CH_3-)	328
$[MoO_2(L^{10})(C_2H_5OH)]$	7.2-7.9	9.0	3.4	3.3(-CH_2-) 1.0(-CH_3-)	325
$[MoO_2(L^{11})(C_2H_5OH)]$	6.1-7.4	8.6	4.3	3.1(-CH_2-) 1.1(-CH_3-)	

Table 4. Crystal data of $[MoO_2(L^{10})(DMSO)]$and $[Mo(O_2)(L^{11})DMSO]$

	$[MoO_2(L^{10})(DMSO)]$	$[Mo(O_2)(L^{11})(DMSO)]$
empirical formula	$C_{17}H_{16}Cl_2MoN_2O_4S_3$	$C_{21}H_{27}MoN_3O_4S_3$
formula weight	575.34	577.57
crystal habit, color	block, orange	plate, brown
crystal system	Triclinic	Monoclinic
space group	P-1	$P2_1$
a (Å)	7.6964(4)	8.054(4)
b (Å)	8.1821(4)	6.903(3)
c (Å)	17.3440(8)	21.508(9)
α (°)	96.654(1)	90
β (°)	98.015(1)	93.945(5)
γ (°)	91.684(1)	90
volume ($Å^3$)	1073.09(9)	1192.9(9)
Z	2	2
density, calc. (Mg/m^3)	1.781	1.608
absorption coefficient (mm^{-1})	1.179	0.846
F(000)	576	592
crystal size (mm^3)	0.50×0.36 × 0.29	0.24 x 0.05 x 0.02
reflections collected	24386	10278
independent reflections	6149	5158
index ranges	-10<=h<=10, -11<=k<=11, - 24<=l<=24	-10<=h<=10, -8<=k<=8, -27<=l<=26
number of parameters	281	295
goodness-of-fit on F^2	0.999	1.091
final R indices [$I \geq 2\sigma(I)$]	R1= 0.0172, wR2=0.0460	R1 = 0.0843, wR2 = 0.1981
R indices [all data]	R1= 0.0176, wR2=0.0463	R1 = 0.1148, wR2 = 0.2178
largest difference peak and hole (e $Å^{-3}$)	0.512 and -0.494	1.540 and -1.152

Table :5 Selected Bond lengths [Å] and angles [°] for [$MoO_2(L^{10})$DMSO]

Bond Length		Bond Angle	
Mo-O1	1.7082(9)	O2-Mo-O1	104.22(4)
Mo-O2	1.7075(9)	O1-Mo-O3	99.20(4)
Mo-O3	1.9283(8)	O1-Mo-N2	88.95(3)
Mo-O4	2.2431(9)	O1-Mo-S2	93.75(3)
Mo-N2	2.3189(10)	O2-Mo-O4	88.84(4)
Mo-S2	2.4528(3)	O3-Mo-O4	79.20(3)

Table -6: Selected bond lengths [Å] and angles [°] for [$MoO_2(L^{11})$DMSO]

Bond Length		**Bond Angle**	
Mo-O1	1.688(14)	O1-Mo-O2	104.5(7)
Mo-O2	1.696(16)	O2-Mo-O4	98.40(7)
Mo-O3	2.241(15)	O2-Mo-N2	91.50(6)
Mo-O4	1.946(13)	O2-Mo-S2	96.50(5)
Mo-N2	2.293(15)	O1-Mo-O3	84.70(7)
Mo-S2	2.446(5)	O1-Mo-S2	91.20(5)

Table 7: Antifungal activity of the molybdenum complexes

Complexes (100 µgdw/mL PDA)	% Inhibition of mycelial growth after 48 and 72 hours of incubation									
	Macrophomina phaseolina		*Alternaria alternata*		*Fusarium equiseti*		*Colletotrichum corchori*		*Curvularia lunata*	
	48h	72h	48h	72h	48h	72h	48h	72h	48h	72h
$[MoO_2(L^1)(H_2O)]$	70	60	100	100	100	100	71	42	81	68
$[MoO_2(L^2)(H_2O)]$	44	64	57	57	100	100	100	71	62	21
$[MoO_2(L^3)(C_2H_5OH)].\ H_2O$	70	60	100	65	100	77	71	42	53	37
$[MoO_2(L^4)]$	84	70	85	71	100	100	100	100	81	68
$[MoO_2(L^5)]$	90	80	85	42	100	66	100	71	100	100
$[MoO_2(L^6)]$	90	80	85	42	88	66	100	100	81	53
$[MoO_2(L^7)(C_2H_5OH)].\ H_2O$	80	60	85	71	100	88	100	85	62	06
$[MoO_2(L^8)(C_2H_5OH)].\ H_2O$	70	60	85	57	100	88	85	71	81	37
$[MoO_2(L^9)(C_2H_5OH)]$	84	70	100	85	100	88	100	71	68	21
$[MoO_2(L^{10})(C_2H_5OH)]$	70	50	94	47	100	88	100	100	37	0
$[MoO_2(L^{11})(C_2H_5OH)]$	70	50	77	42	100	88	71	28	81	37
Nystatin	76		51		45		41		70	

PDA= Potato dextrose agar medium used for the culture medium for antifungal tests.[dw = dry weight]

Table 8: Antibacterial activity of molybdenum complexes against Gram positive bacteria

Complexes (100µgdw/disc)	Zone of inhibition in mm after 24 and 48 hours of incubation							
	Bacillus cereus		*Bacillus subtilis*		*Staphylococcus aureus*		*Bacillus megaterium*	
	24h	48h	24h	48h	24h	48h	24h	48h
$[MoO_2(L^1)(H_2O)]$	15	15	18	18	15	15	8	8
$[MoO_2(L^2)(H_2O)]$	15	15	15	15	15	15	15	15
$[MoO_2(L^3)(C_2H_5OH)].\ H_2O$	15	15	15	15	15	15	15	15
$[MoO_2(L^4)]$	12	12	0	0	8	8	2	8
$[MoO2\ (L^5)]$	15	15	0	0	13	13	23	23
$[MoO_2(L^6)]$	10	10	15	15	0	0	20	20
$[MoO_2(L^7)(C_2H_5OH)].\ H_2O$	8	8	5	5	0	0	0	0
$[MoO_2(L^8)(C_2H_5OH)].\ H_2O$	5	5	5	5	0	0	0	0
$[MoO2(L^9)(C_2H_5OH)]$	8	8	15	15	0	0	10	10
$[MoO_2(L^{10})(C_2H_5OH)]$	0	0	0	0	0	0	13	13
$[MoO_2\ (L^{11})(C_2H_5OH)]$	10	10	0	0	0	0	10	10
Ampicillin	16	16	16	17	20	22	15	15

Table 9: Antibacterial activity of molybdenum complexes against Gram negative bacteria

Complexes (100µg dw/disc)	Zone of inhibition in mm after 24 and 48 hours of incubation													
	Escherichia coli		*Vibrio cholerae*		*Salmonella typhi*		*Salmonella paratyphi*		*Pseudomona species*		*Shigella sonnei*		*Shigella dysenteriae*	
	24h	48h	24h	48h	24h	48h	24h	48h	24h	48h	24h	48h	24h	48h
$[MoO_2L^1 H_2O]$	0	0	0	0	15	16	15	15	15	15	18	19	15	15
$[MoO_2L^2 H_2O]$	8	8	0	0	15	16	15	15	15	17	15	15	15	16
$[MoO_2L^3C_2H_5OH]. H_2O$	0	0	0	0	15	16	15	15	15	15	15	15	15	15
$[MoO_2L^4]$	0	0	0	0	20	20	12	13	15	15	0	0	10	10
$[MoO_2L^5]$	0	0	0	0	13	14	8	8	20	20	0	0	5	5
$[MoO_2L^6]$	0	0	0	0	15	15	20	21	20	20	0	0	0	0
$[MoO_2L^7C_2H_5OH]. H_2O$	0	0	0	0	0	0	10	11	15	15	0	0	5	5
$[MoO_2L^8C_2H_5OH]. H_2O$	0	0	0	0	15	15	10	10	5	6	0	0	13	13
$[MoO_2L^9C_2H_5OH]$	0	0	0	0	0	0	5	5	10	11	0	0	0	0
$[MoO_2L^{10}C_2H_5OH]$	0	0	0	0	8	8	12	12	8	9	8	8	0	0
$[MoO_2L^{11}C_2H_5OH]$	0	0	0	0	5	6	10	10	10	10	0	0	0	0
Ampicillin	28	28	24	24	25	25	12	13	19	20	24	24	13	14

'dw' means dry weight

Appendix A. Supplementary data

CCDC 745141 and 1453808 contain the supplementary crystallographic data for $[MoO(L^{10})(DMSO)]$ and $[Mo(O_2)(L^{11})DMSO]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Scheme-1

Synthesis of the ligands from S-benzyldithiocarbazate

Scheme-2

Preparation of the molybdenum complexes of the ligands

Figure-1

1(a)Polymeric structure of molybdenum complexes 1(b) Monomeric structure of the molybdenum complexes

Figure-2

Structure of $[MoO_2(L^{10})(DMSO)]$

Figure-3

Structure of $[MoO_2(L^{11})(DMSO)$

Synthesis, characterization and biomedical activities of molybdenum complexes of tridentate Schiff base ligands. Crystal and molecular structure of $[MoO_2(L^{10})(DMSO)]$ and $[MoO_2(L^{11})(DMSO)]$

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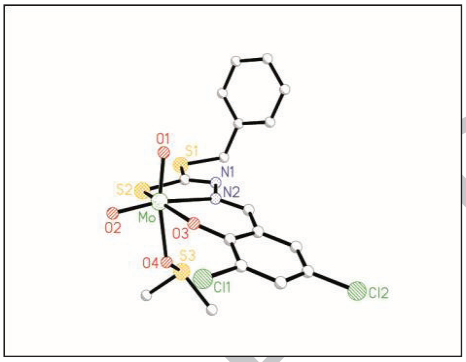
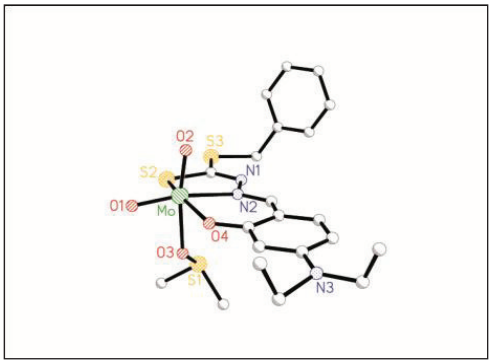
Different Schiff base ligands and their molybdenum complexes have been prepared. The complexes were characterized by using a multitude of analytical methods. Biomedical activities of the compounds were also studied. The structures of two compounds were confirmed by X-ray crystallography.



$[MoO_2(L^{10})(DMSO)]$



$[MoO_2(L^{11})(DMSO)]$