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SYNTHESIS, CHARACTERIZATION AND ANTIFUNGAL EVALUATION OF SOME NOVEL Mo(VI) COMPLEXES

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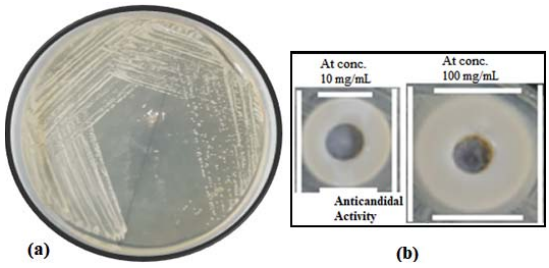
Interaction of tetrachlorooxomolybdenum with sodium salts of oximes HON=C(CH_3)Ar (Ar = C_4H_3S, C_4H_3O or C_5H_4N) and Schiff bases HOC(R)CHC(R')=NC_6H_5 (where, R = R' = CH_3 or C_6H_5; R = CH_3 and R' = C_6H_5) in 1:2 molar ratio in acetonitrile yielded dichlorooxomolybdenum(VI) complexes of the type [$MoOCl_2${ON=C(CH_3)Ar}$_2$] and [$MoOCl_2${OC(R)CHC(R')=NC_6H_5}$_2$]. All these newly synthesized complexes have been characterized by elemental analysis, IR, electronic, ^{1}H, ^{13}C - NMR and FAB mass spectral studies.

The anticandidal study carried out on complexes of the type [$MoOCl_2${ON=C(CH_3)Ar}$_2$] against *Candida albicans* showed that the complexes [$MoOCl_2${ON=C(CH_3)C_4H_3O}$_2$] and [$MoOCl_2${ON=C(CH_3)C_5H_4N}$_2$] are biologically active against this strain.



INTRODUCTION

Metal complexes have always been expected to exhibit better and greater activity than the corresponding ligands. Molybdenum(VI) complexes[1-4] have contributed significantly for promoting research interest on account of their versatile biological importance;[5-7] *i.e.*, anticancer,[8] antibacterial,[9] antioxidant,[10] antimicrobial,[11] biomedical[12] activities and their role as molybdoenzymes.[13-16] A number of metal oxime complexes have emerged out to be useful as antitubercular,[17] antimalarial,[18] antiviral,[19] antilepral[20] and active against certain kinds of tumors. In a similar fashion, Schiff's base complexes have proved themselves advantageous exhibiting varied biological activities.[21-28] The major reason for the use of such metal complexes is their feasible synthetic route and thermal stability.

In succession to our earlier reported work[29-32] and to further investigate oxomolybdenum complexes; we herein report the synthesis, characterization and anticandidal activity of novel complexes of the type [$MoOCl_2${ON=C(CH_3)Ar}$_2$] and [$MoOCl_2${OC(R)CHC(R')=NC_6H_5}$_2$].

MATERIALS AND METHODS

Reagents and solvents (from Sigma-Merck) were used as such. Precursor $MoOCl_4$[33] and ligands Oximes,[34] Schiff bases of β-diketones[35] were synthesized according to the literature methods. Molybdenum was estimated gravimetrically as oxinate.[36] C and H were analyzed on a Perkin-Elmer C, H, N and S II series 2400 analyzer. Sulphur[36] and nitrogen[36] were estimated by standard methods. FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer in the 4000–

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400 cm^{-1} range using KBr pellets. ^{1}H-NMR spectra were recorded in $CDC1_3$ and d_6-DMSO using TMS as an internal reference on a JEOL FX90Q spectrometer. UV spectra were measured using a copy- 50 Bio (Varian) UV-visible spectrophotometer. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/Data system using Ar/Xe (6kv, 10mA) as the FAB gas, *m*-nitrobenzyl alcohol was used as the matrix.

Synthesis of dichlorooxomolybdenum(VI) complexes

To a solution of $MoOCl_4$ (1.64 g, 6.47 mmol) in CH_3CN, a suspension of $NaON=C(CH_3)C_4H_3S$ (2.12g, 12.96 mmol) in CH_3CN was added. After 12 hrs of stirring, precipitated NaCl was filtered off (Scheme 1). Extra solvent was stripped from the filtrate and the product was dried under vacuum. The dark green product $[MoOCl_2\{ON=C(CH_3)C_4H_3S\}_2]$ so obtained was recrystallized by a mixture of CH_3CN and n – C_6H_{14} (10:1 v/v).

The complexes $[MoOCl_2\{OC(CH_3)CHC(CH_3)=NC_6H_5\}_2]$, $[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NC_6H_5\}_2]$, $[MoOCl_2\{OC(C_6H_5)CHC(C_6H_5)=NC_6H_5\}_2]$, $[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$ and $[MoOCl_2\{ON=C(C_5H_4N)\}_2]$ were also synthesized using the similar procedure. The synthetic, physical and analytical data for these complexes are included in Table 1 and 2.

$$MoOCl_4 + 2NaON=C(CH_3)Ar \xrightarrow[RT,\ 12h]{CH_3CN} [MoOCl_2\{ON=C(CH_3)Ar\}_2] + 2NaCl$$

$$MoOCl_4 + 2NaOC(R)CHC(R')=NC_6H_5 \xrightarrow[RT,\ 12h]{CH_3CN} [MoOCl_2\{OC(R)CHC(R')=NC_6H_5\}_2] + 2NaCl$$

Scheme 1 – Synthesis of Dichlorooxomolybdenum(VI) complexes.

Table 1

Synthetic and Physical Data of the synthesized complexes

S. N.	Reactants, g (mmol)		Product (% yield)	State and Color
	$MoOCl_4$	NaL		
1	1.64 (6.47)	$NaON=C(CH_3)C_4H_3S$ 2.12 (12.96)	$[MoOCl_2\{ON=C(CH_3)C_4H_3S\}_2]$ (98)	Dark green solid
2	1.53 (6.03)	$NaON=C(CH_3)C_4H_3O$ 1.77 (12.10)	$[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$ (95)	Brown solid
3	1.19 (4.68)	$NaON=C(CH_3)C_5H_4N$ 1.49 (9.44)	$[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$ (83)	Brown solid
4	1.84 (7.25)	$NaOC(CH_3)CHC(CH_3)=NPh$ 2.86 (14.52)	$[MoOCl_2\{OC(CH_3)CHC(CH_3)=NC_6H_5\}_2]$ (86)	Brown solid
5	1.69 (6.66)	$NaOC(CH_3)CHC(C_6H_5)=NPh$ 3.46 (13.36)	$[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NC_6H_5\}_2]$ (88)	Brown solid
6	1.71 (6.74)	$NaOC(C_6H_5)CHC(C_6H_5)=NPh$ 4.33 (13.49)	$[MoOCl_2\{OC(C_6H_5)CHC(C_6H_5)=NC_6H_5\}_2]$ (90)	Brown solid

Table 2

Analytical Data for the complexes synthesized

S. N.	Complex	Temperature at which Decomposition starts	Elemental Analysis (%) Found (calcd.)				
			C	H	N	Cl	Mo
1	$[MoOCl_2\{ON=C(CH_3)C_4H_3S\}_2]$	167 ºC	30.91 (31.11)	2.10 (2.61)	5.87 (6.05)	14.83 (15.31)	21.52 (20.72)
2	$[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$	175 ºC	33.38 (33.43)	2.73 (2.81)	6.12 (6.50)	16.42 (16.45)	22.31 (22.26)
3	$[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$	178 ºC	37.41 (37.11)	3.05 (3.11)	12.14 (12.36)	15.71 (15.65)	21.04 (21.18)
4	$[MoOCl_2\{OC(CH_3)CHC(CH_3)=NPh\}_2]$	180 ºC	49.61 (49.73)	4.34 (4.55)	5.31 (5.27)	13.31 (13.35)	18.03 (18.06)
5	$[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NPh\}_2]$	190 ºC	58.69 (58.64)	4.25 (4.31)	4.57 (4.27)	10.85 (10.82)	14.63 (14.64)
6	$[MoOCl_2\{OC(C_6H_5)CHC(C_6H_5)=NPh\}_2]$	195 ºC	64.75 (64.71)	4.15 (4.14)	3.53 (3.59)	9.13 (9.10)	12.05 (12.31)

RESULTS AND DISCUSSION

Interaction of tetrachlorooxomolybdenum ($MoOCl_4$) with sodium salts of oximes $HON=C(CH_3)Ar$ (where, Ar = C_4H_3S, C_4H_3O or C_5H_4N) and Schiff's Bases $HOC(R)CHC(R')=NC_6H_5$ (where, R = R' = CH_3 or C_6H_5; R = CH_3 and R' = C_6H_5) in 1:2 molar ratio in CH_3CN yielded dichlorooxomolybdenum(VI) complexes of the type $[MoOCl_2\{ON=C(CH_3)Ar\}_2]$ and $[MoOCl_2\{OC(R)CHC(R')=NC_6H_5\}_2]$, respectively.

All these colored complexes are soluble in coordinating solvents and are characterized by elemental analysis and spectral studies.

IR Spectra

The signals in the range 3600-3200 cm^{-1} due to ν (O–H), were found absent in spectra of the synthesized complexes; which corresponds that the ligands are bonded with Mo atom via deprotonation.[37] The bands observed in the spectra of the complexes $[MoOCl_2\{ON=C(CH_3)Ar\}_2]$ around 1625–1590 cm^{-1} have been assigned to azomethine group (>C=N); and they are lower in values as compared to that of free oximes observed in the range 1690-1640 cm^{-1} (Table 3). Shifting of these bands to lower frequencies suggest bonding of ligand moieties to Mo atom. Similarly; the bands at 935-900 cm^{-1} assigned to ν (N-O) of the oxime moiety in complexes; are at lower frequencies in comparison to that of free oximes, observed around 945 cm^{-1}. Moreover ν (C-X) where X = O, S or N in aromatic ring of oximato complexes, were observed around 1465–1375 cm^{-1} in spectra. These values are lower as compared to that of free oximes (1490-1405 cm^{-1});[38, 39] which suggests the bidentate behavior of oximes.

The bands observed in the region 1595–1565 cm^{-1} in the spectra of the complexes $[MoOCl_2\{OC(R)CHC(R')=NC_6H_5\}_2]$ due to ν (C=N) are lower in values as that of free schiff bases, observed in the range 1630-1620 cm^{-1};[40] it suggests the coordinate bond formation to Mo atom via Nitrogen atom of the ligand moiety. Bidentate behavior of Schiff bases is also supported by C=C bands of β-diketone observed around 1390-1365 cm^{-1} in the spectra of respective complexes; which are at lower values as compared to that of free Schiff bases (1460-1405 cm^{-1}). The ν (C-O) band of Schiff bases make their appearance in the region 1350–1310 cm^{-1}. All these complexes also exhibit a strong band in the region 980–905 cm^{-1} due to (Mo=O) stretching modes.

^{1}H-NMR Spectra

The values of proton chemical shifts have been summarized in Table 4. The signals due to OH group were absent in spectra of the synthesized complexes; which corresponds that the ligands are bonded with Mo atom via deprotonation. Aromatic protons of oximes in the spectra of the complexes $[MoOCl_2\{ON=C(CH_3)Ar\}_2]$ and phenyl protons in the spectra of the complexes $[MoOCl_2\{OC(R)CHC(R')=NC_6H_5\}_2]$**,** show slight highfield shifting as compared to that of free ligands.[37-40] This indicates the bidentate behavior of ligands to Molybdenum atom.

^{13}C{^{1}H}NMR Spectra

$^{13}C\{^1H\}$NMR Spectra of all these complexes show all the desired signals that correspond well with the structure proposed for these complexes (Table 5). Shifting of C=N, C-2 and C-5 aryl carbon signals of oxime group downwards, as well as C=N and pheny1 carbon signals of Schiff base[38, 39] suggests the bidentate behavior of these ligands.

Table 3

Some relevant IR spectral data (in cm^{-1}) of the complexes

S. N.	Complex	ν (N-O) or ν (C-O)	ν (C=N)	ν (C-X; aromatic ring) or ν (C=C; β-diketone)	ν (Mo=O)
1	$[MoOCl_2\{ON=C(CH_3)C_4H_3S\}_2]$	905	1625	1375	905
2	$[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$	900	1615	1390	950
3	$[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$	935	1590	1465	940
4	$[MoOCl_2\{OC(CH_3)CHC(CH_3)=NC_6H_5\}_2]$	1310	1595	1390	950
5	$[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NC_6H_5\}_2]$	1325	1570	1370	970
6	$[MoOCl_2\{OC(C_6H_5)CHC(C_6H_5)=NC_6H_5\}_2]$	1350	1565	1365	980

Table 4

^{1}H-NMR Spectral Data (in δ p.p.m.) of the complexes

S. N.	Complex	^{1}H Chemical Shift
1	$[MoOCl_2\{ON=C(CH_3)C_4H_3S\}_2]$	2.22 (s, 6H, CH_3); 7.13 (dd, 2H, H-4); 7.45 (d, 2H, H-3); 7.93 (d, 2H, H-5)
2	$[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$	2.28 (s, 6H, CH_3); 6.38 (dd, 2H, H-4); 6.43 (d, 2H, H-3); 7.51 (d, 2H, H-5)
3	$[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$	2.54 (s, 6H, CH_3); 7.32 (dd, 2H, H-4); 7.48 (dd, 2H, H-5); 7.64 (d, 2H, H-3); 7.93 (d, 2H, H-6)
4	$[MoOCl_2\{OC(CH_3)CHC(CH_3)=NC_6H_5\}_2]$	2.03 (s, 6H, CH_3CN); 2.16 (s, 6H, CH_3CO); 5.56 (s, 2H, CH); 6.51-7.45 (m, 10H, C_6H_5)
5	$[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NC_6H_5\}_2]$	2.68 (s, 6H, CH_3CO); 3.88 (s, 2H, CH); 7.11-8.17 (m, 20H, C_6H_5)
6	$[MoOCl_2\{OC(C_6H_5)CHC(C_6H_5)=NC_6H_5\}_2]$	3.49 (s, 2H, CH); 7.15-8.11 (m, 30H, C_6H_5)

Table 5

$^{13}C\{^{1}H\}$ Spectral Data (δ p.p.m.) of the complexes

S. N.	Complex	$^{13}C\{^{1}H\}$ Chemical Shift
1	$[MoOCl_2\{ON=C(CH_3)C_4H_3S\}_2]$	11.5 (CH_3); 123.5 (C-4); 123.9 (C-3); 126.8 (C-5); 141.9 (C-2); 152.2 (C=N)
2	$[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$	10.5 (CH_3); 103.5 (C-4); 111.1 (C-3); 143.5 (C-5); 145.9 (C-2); 155.4 (C=N)
3	$[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$	10.9 (CH_3); 118.5 (C-5); 120.3 (C-3); 135.6 (C-4); 147.9 (C-6); 153.6 (C-2); 156.8 (C=N)
4	$[MoOCl_2\{OC(CH_3)CHC(CH_3)=NC_6H_5\}_2]$	18.71 (CH_3CN); 27.86 (CH_3CO); 39.50 (CH); 121.97-137.02(C_6H_5); 158.60 (CN); 193.75 (CO)
5	$[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NC_6H_5\}_2]$	18.89 (CH_3CN); 96.03 (CH); 120.15-130.01 (C_6H_5); 155.59 (CN); 194.05 (CO)
6	$[MoOCl_2\{OC(C_6H_5)CHC(C_6H_5)=NC_6H_5\}_2]$	92.79 (CH); 126.89-134.77 (C_6H_5); 167.63 (CN); 185.22 (CO)

FAB Mass Spectrum

FAB mass spectral ion peaks of a representative complex, $[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NC_6H_5\}_2]$ have been summarized in Table 6. The molecular ion peak (M-18) at m/z = 638, indicate the monomeric nature of the complex.

Table 6

FAB Mass Spectral data of $[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NC_6H_5\}_2]$

m/e	Assignment
683	$[MoOCl_2\{OC(CH_3)CHC(C_6H_5)NC_6H_5\}_2.C_2H_3]$
656	$[MoOCl_2\{OC(CH_3)CHC(C_6H_5)NC_6H_5\}_2]$
638	$[MoOCl_2\{C(CH_3)CHC(C_6H_5)NC_6H_3\}\{OC(CH_3)CHC(C_6H_5)NC_6H_5\}]$
615	$[MoOCl_2\{CH_2CH(C_6H_5)NC_6H_5\}\{OC(CH_3)CHC(C_6H_5)NC_6H_5\}]$
575	$[MoOCl_2\{CH_2CH(C_6H_5)C_4H_3\}\{OC(CH_3)CHC(C_6H_5)NC_6H_5\}]$
555	$[MoOCl_2\{C_5H_5NC_6H_5\}\{OC(CH_3)CHC(C_6H_5)NC_6H_5\}]$
546	$[MoOCl_2\{CH_2CH(C_6H_5)C_4H_3\}\{OC(CH_3)CHC(C_6H_5)=C_5H_3\}]$
511	$[MoOCl\{CH_2CH(C_6H_5)C_4H_3\}\{OC(CH_3)CHC(C_6H_5)=C_5H_3\}]$
488	$[MoOCl\{OC(CH_3)CHC(C_6H_5.C_3H_4)\}.2C_6H_5]$
436	$[MoOCl(C_4H_8.3C_6H_5)]$
374	$[MoO(C_2H_5.3C_6H_5)]$
313	$[MoO(C_3H_3.2C_6H_5)]$ or $[MoOCl(C_6H_{12})_2]$
251	$[MoO(C_9H_{10})]$
197	$[MoO(C_6H_{11})]$
118	$[Mo(H_2O.H_2)]$

Electronic Absorption Spectra

Electronic absorption spectra of these complexes are recorded in CH_3CN (Table 7). The complexes $[MoOCl_2\{ON=C(CH_3)Ar\}_2]$ exhibits the bands at 349-371 and 210-214 nm, which may be assigned to intraligand transitions $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$; respectively.[41] Whereas, in complexes $[MoOCl_2\{OC(R)CHC(R')=NC_6H_5\}_2]$, such transitions occur in the 369-370 nm and 215–218 nm ranges.[42] Both types of complexes show $O_t \rightarrow Mo^{VI}$ charge transfer transitions at 310–321 nm.[29]

Antifungal Activity

The *in vitro* evaluation was carried out in Dr. B. Lal Clinical Laboratory Pvt. Ltd. - CIRD, Jaipur. The anticandidal activity of complexes of the type $[MoOCl_2\{ON=C(CH_3)Ar\}_2]$ was carried out against *Candida albicans* (ATCC 14053) cultured on Sabouraud's Dextrose Agar using Kirby-Bauer well diffusion method.[43] Compounds were dissolved in DMSO at concentrations C1 = 10 mg/mL and C2 = 100 mg/mL; Itraconazole was used as PC- positive control at 5 mg/mL concentration and DMSO was used as NC- negative control (Table 8).

The observed results reveal that the complexes $[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$ and $[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$ are biologically active against this strain (Figure 1).

Table 7

Some Relevant Electronic Absorption Spectral Data [λ_{max} in nm (Å)] of complexes

S. N.	Complex	$n\rightarrow\pi^*$	$\pi\rightarrow\pi^*$	$O^t \rightarrow Mo^{VI}$
1	$[MoOCl_2\{ON=C(CH_3)C_4H_3S\}_2]$	369 (1.39)	214 (-0.36)	310 (1.57)
2	$[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$	349 (1.51)	212 (0.59)	321 (1.63)
3	$[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$	371 (1.41)	210 (-0.37)	312 (1.58)
4	$[MoOCl_2\{OC(CH_3)CHC(CH_3)=NC_6H_5\}_2]$	369 (1.34)	218 (-0.64)	314 (0.66)
5	$[MoOCl_2\{OC(CH_3)CHC(C_6H_5)=NC_6H_5\}_2]$	370 (1.42)	215 (-0.36)	313 (1.61)
6	$[MoOCl_2\{OC(C_6H_5)CHC(C_6H_5)=NC_6H_5\}_2]$	370 (1.33)	215 (-0.67)	311 (0.64)

Table 8

Anticandidal activity of complexes $[MoOCl_2\{ON=C(CH_3)Ar\}_2]$

S. N.	Complex	Organism	PC	NC	At conc. 10 mg/mL	At conc. 100 mg/mL
1	$[MoOCl_2\{ON=C(CH_3)C_4H_3S\}_2]$	Candida			NZI	NZI
2	$[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$	albicans	18	NZI*	22 mm	28 mm
3	$[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$		mm		15 mm	22 mm

*NZI – No zone of Inhibition

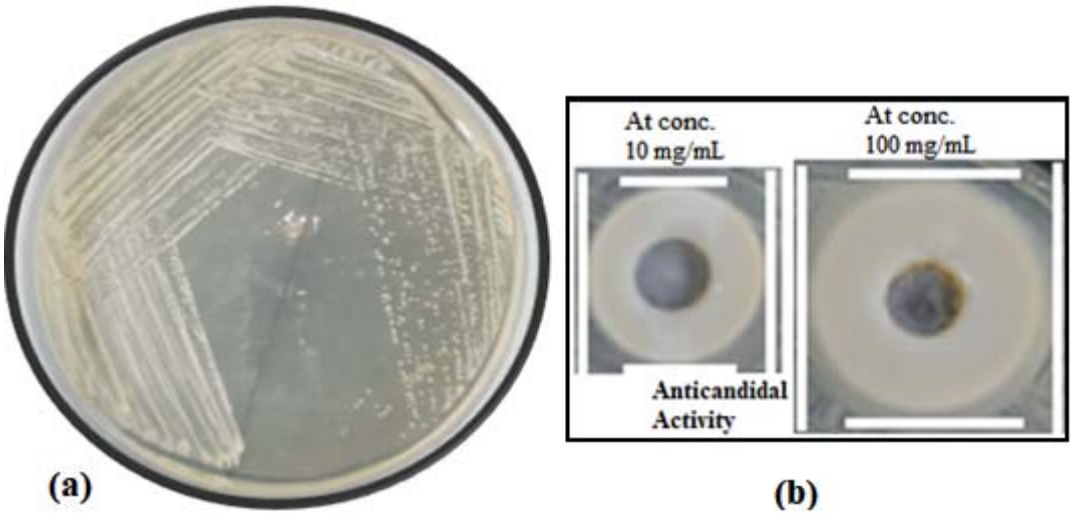

Fig. 1 – (a) 24hours grown culture of *C. albicans* on MH agar plate, (b) Anticandidal activity of $[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$.

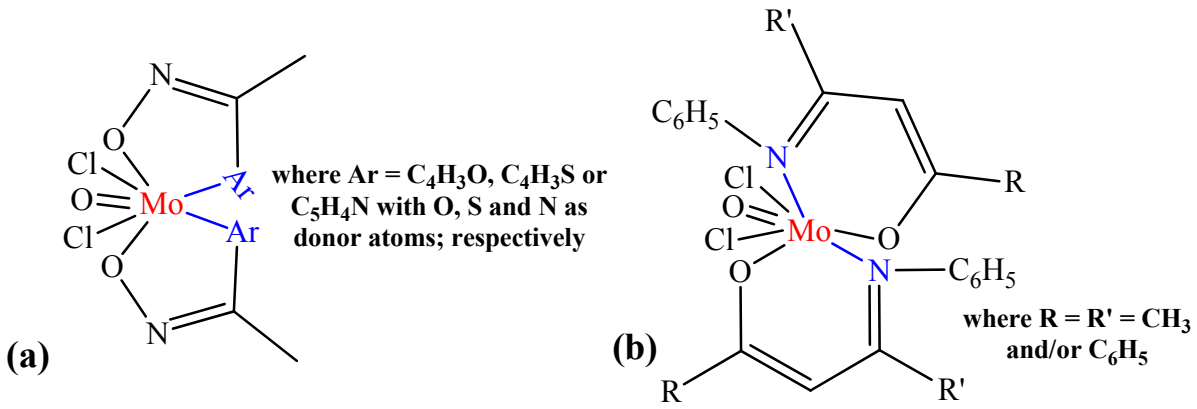

Fig. 2 – Proposed coordination for (a) $[MoOCl_2\{ON=C(CH_3)Ar\}_2]$ and (b) $[MoOCl_2\{OC(R)CHC(R')=NC_6H_5\}_2]$.

CONCLUSIONS

In view of the elemental and spectral studies, the following coordination may be proposed for both types of dichlorooxomolybdenum(VI) complexes (Figure 2). The anticandidal study carried out on complexes of the type $[MoOCl_2\{ON=C(CH_3)Ar\}_2]$ against *Candida albicans* showed that the complexes $[MoOCl_2\{ON=C(CH_3)C_4H_3O\}_2]$ and $[MoOCl_2\{ON=C(CH_3)C_5H_4N\}_2]$ are appreciably active against this strain.

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